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Overcoming operational issues in a Claus tail gas hydrogenation unit

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Haldor Topsoe

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What is the typical reason for shutting down a Claus tail gas unit?
A or B?

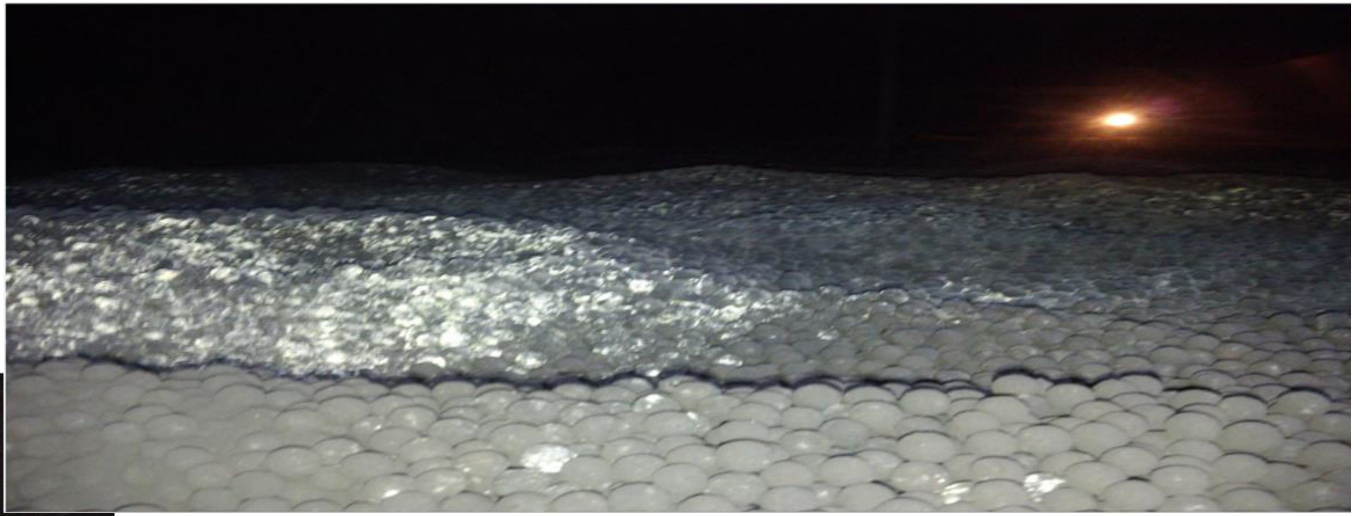
A:

Shut down because of catalyst deactivation?

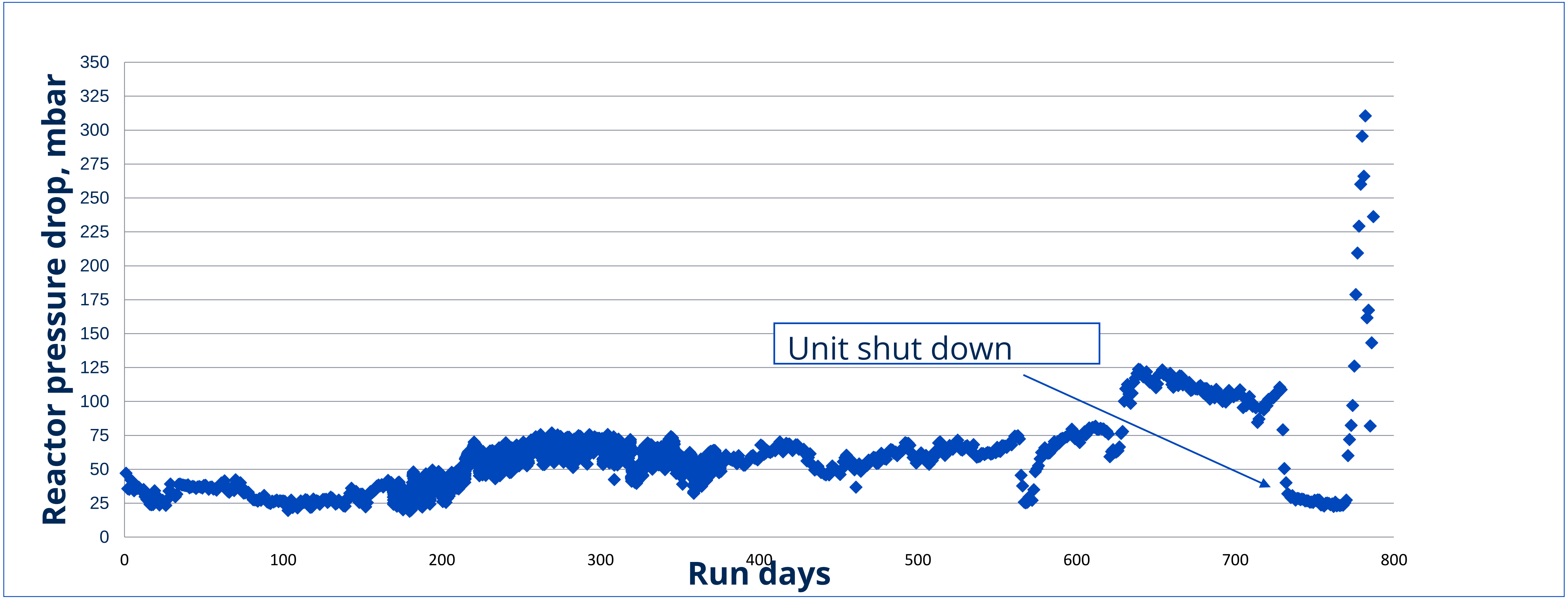
B

Shut down because of operational upset?

The cause of the problems



European refinery suffering from pressure drop problems



Reactions in a tail gas unit

The purpose of the tail gas catalyst is to convert all sulfur species to H_2S. The following reactions take place:

1) $S_2 + 2H_2 \Leftrightarrow 2H_2S$

2) $SO_2 + 3H_2 \Leftrightarrow H_2S + 2H_2O$

3) $COS + H_2O \Leftrightarrow CO_2 + H_2S$

4) $CS_2 + 2H_2O \Leftrightarrow CO_2 + 2H_2S$

5) $CO + H_2O \Leftrightarrow CO_2 + H_2$

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The problems in tail gas treatment

Problems

Soot, CO and O_2

Corrosion

Milling

=

Contaminant pressure drop issues

=

Premature shutdown

Potential operational problems

Soot, CO and O_2

- Carbon formation on the catalyst leading to **accelerated deactivation**
- Soot formation from the burner leading to **pressure drop build-up**
- Temperature excursions as a result of excess air (over-stoichiometric) leading to **loss of catalyst activity/surface area**
- Thermal sintering of the active sites due to temperature and age leading to **accelerated deactivation**
- Sulfidation of the alumina, $Al_2(SO_4)_3$ leading to **catalyst decomposition**

Problems caused by CO and O_2

Soot, CO and O_2

The following reactions may occur in the tail gas catalyst when the air/fuel ratio is too low and CO and soot is formed:

1. **$SO_2 + 3CO \Leftrightarrow COS + 2CO_2$**
2. **$S_2 + 2CO \Leftrightarrow 2COS$**
3. **$H_2S + CO \Leftrightarrow COS + H_2$**

COS is more difficult to hydrotreat

The following reactions may occur if excess oxygen from the burner reaches the tail gas catalyst:

1. **$O_2 + 2H_2 \Leftrightarrow 2H_2O$**
2. **$O_2 + 2SO_2 \Leftrightarrow 2SO_3$**
3. **$3SO_3 + Al_2O_3 \rightarrow Al_2(SO_4)_3$ (sulfidation)**
4. **$2FeS + 9/2\ O_2 \rightarrow Fe_2O_3 + 2SO_3$**

$Al_2(SO_4)_3$ leading to catalyst decomposition, and Fe_2O_3 giving pressure drop problems

Solution: Burner operation

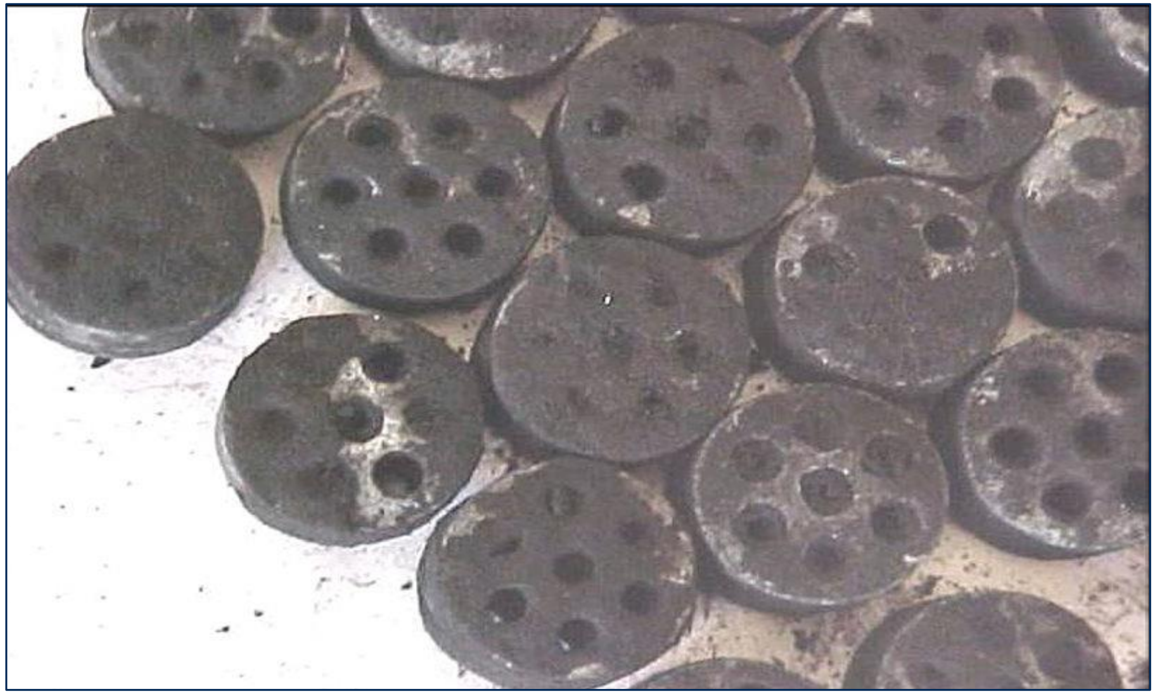
Soot, CO and O_2

- Burner control and operation are key to the unit operation
- The preferred operating range is between 70% and 90% of the required stoichiometric oxygen concentration
- If the air/fuel ratio is too high (> 90%), oxygen will reach the tail gas catalyst
- If the air/fuel ratio is too low (< 70%), soot and CO can be formed. Soot will plug the catalyst pores.
- The optimum air/fuel ratio is dependent on the burner design

Potential operating problems
Corrosion

Corrosion

- Iron scales and particles from corrosion leading to **pressure drop build-up**

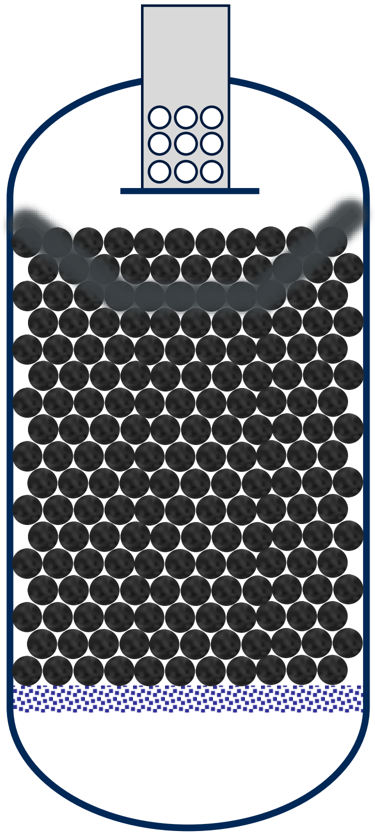


Milling
Top layer

Milling

- Milling is catalyst particles being caught by the vortexes of the inlet stream and then being “tossed” around in the reactor
  - Results in a crust of catalyst dust

- Milling of catalyst can occur if:
  - Catalyst is loaded too close to the inlet distributer
  - Too high inlet flow or poor inlet distributor



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Grading is the solution

Solution: Grading
Concept of grading

The principles:

- Shape-optimized
- Void
- Particle size
- Catalyst activity

Background:

- Grading products are used for all hydrotreating purposes
- We have more than 40 years experience in developing grading
- So far, we have sold more than 4000 charges for 600 different unit
- We know it works!

Contaminant Pressure drop issues

Catalyst activity

Particle size

Solution
Corrosion

Corrosion

- TK-26 TopTrap™ is inert macro porous material designed to pick up iron scale, coke fines, and other inorganic particulates
- TK-26 TopTrap™ is produced in 1/2" QL with three center holes
- TK-26 TopTrap™ should be loaded below TK-10 or TK-15 high void topping material

Solution: Grading

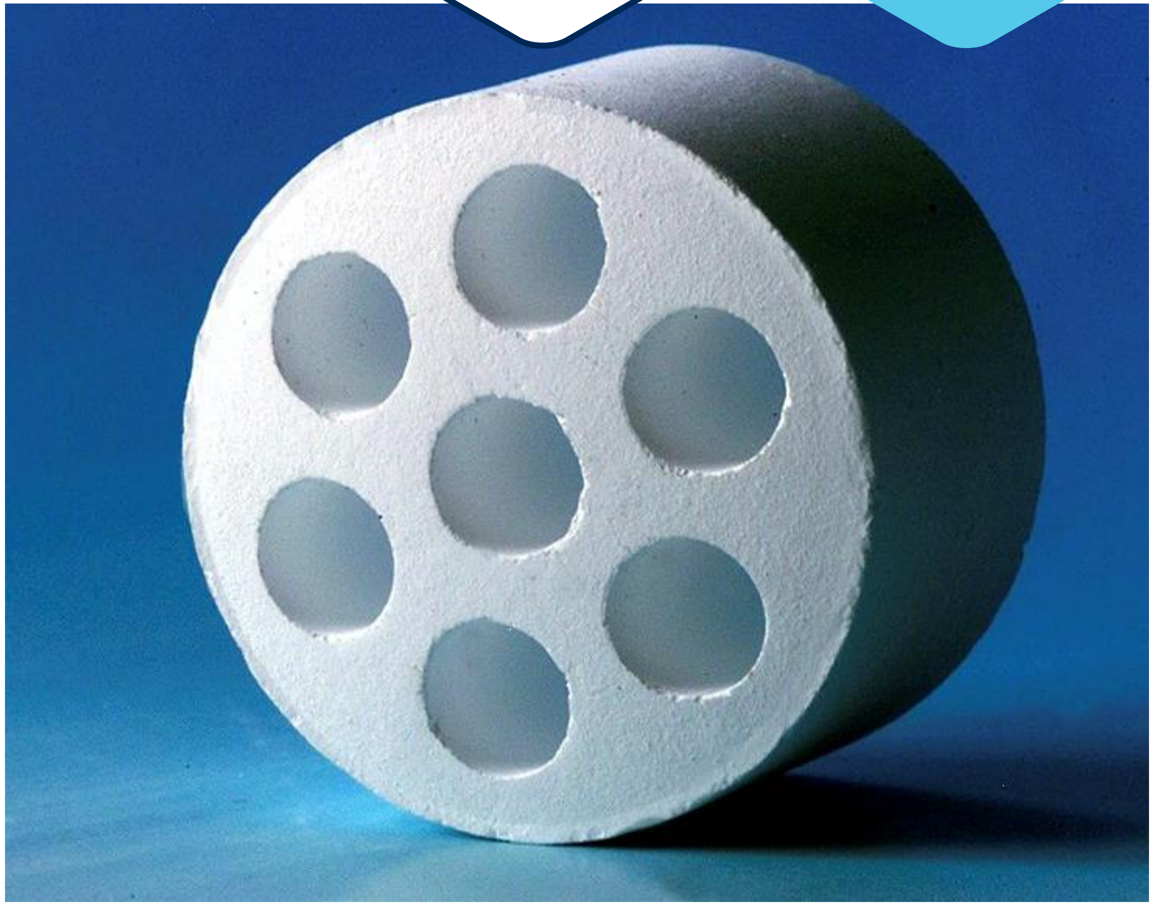
TK-10 High void topping

Corrosion

Soot, CO and O_2

Traps impurities leading to pressure drop problems

- Size: 16x11 mm
- Void fraction: ~55
- Bulk density: 800 kg/m³



Solution: Grading
High void topping

Milling

Our TK-15 is specifically developed as a grading product with a hold down function and should replace ceramic balls

- Size: 1.5”
- Void fraction: ~65
- Bulk density: 1190 kg/m^3

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Selection of the right catalyst

The Claus tail gas catalysts
Optimal performance with TK-220, TK-222, and TK-224

High activity + Low pressure drop + High physical strength + Good thermal stability = Optimal performance

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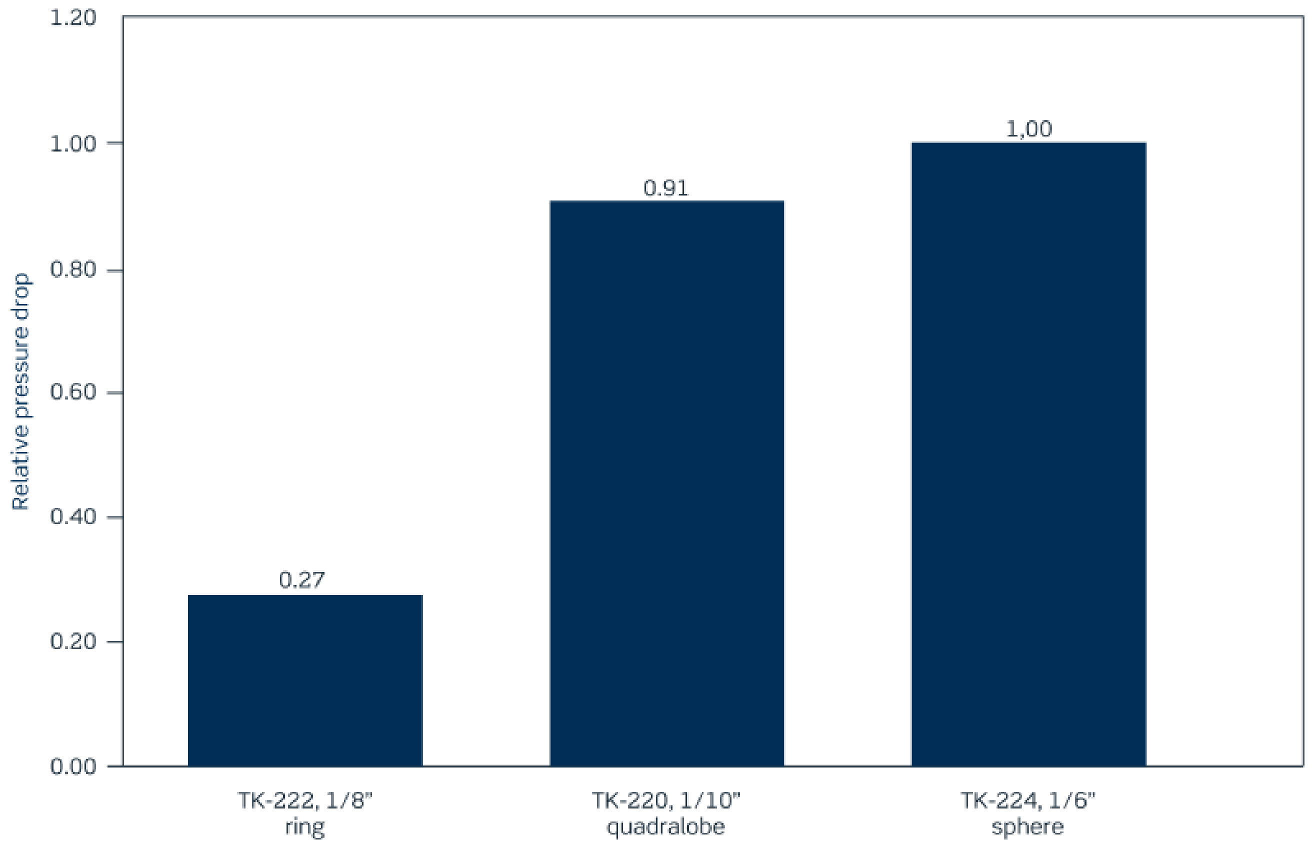
Relative pressure drops
Claus tail gas catalysts

Low pressure drop



Catalyst pressure drop and capacity

Low pressure drop

- Clean pressure drop in the tail gas unit is determined solely by the catalyst's **size and shape**
- TK-222 1/8" ring has the highest void fraction of any tail gas catalyst in the market today and will provide the refiner with the **lowest possible SOR pressure drop**
- Lower pressure drop means:
  - Possible higher feed rate
  - Increased crude capacity and consequently increased profitability
  - Debottlenecking of sulfur recovery unit

Benefits of low pressure drop
Calculation example

Low pressure drop


	TK-220	TK-222
Size	1/10'' Quadralobe	1/8'' Ring
Relative ΔP	100	100
Relative gas flow	100	180

80% higher capacity at same pressure drop

Physical strength

Claus tail gas catalysts

High physical strength

High physical strength prevent breakage of particles and creation of fines during catalyst handling and unit upsets.

	TK-220	TK-222	TK-224
Size	1/10'' Quadralobe	1/8'' Ring	1/6'' Spheres
Side crush strength, kp/mm	>1.5	>0.7	13.6 kp

Thermal stability

Claus tail gas catalysts

Good thermal stability

A sample of TK-220 was heated in an oven to the below listed temperatures, and the Side Crush Strength (SCS) and surface area were measured after the heat treatment.

Temperature, °C	SCS, kp/mm	Surface area, m^2/g*
400	1.85	297
540	1.94	300
650	2.12	281

Haldor Topsoe’s tail gas catalyst exhibits a temperature stability.

Conclusion: Overcoming operational issues

Pressure drop

- Follow the guidelines for burner operation
- Installing a grading solution

Increasing capacity

- We recommend taking advantage of the very low pressure drop of TK-222 by combining it with TK-220 or TK-224 to increase capacity