Axens
IFP Group Technologies

AXENS' IRAN SEMINAR

PAVING THE WAY TO A HIGHLY COMPETITIVE IRANIAN REFINING INDUSTRY

TEHRAN - 29/30 TIR 1395 (19/20 JULY 2016)

Sulfur Recovery Catalysts

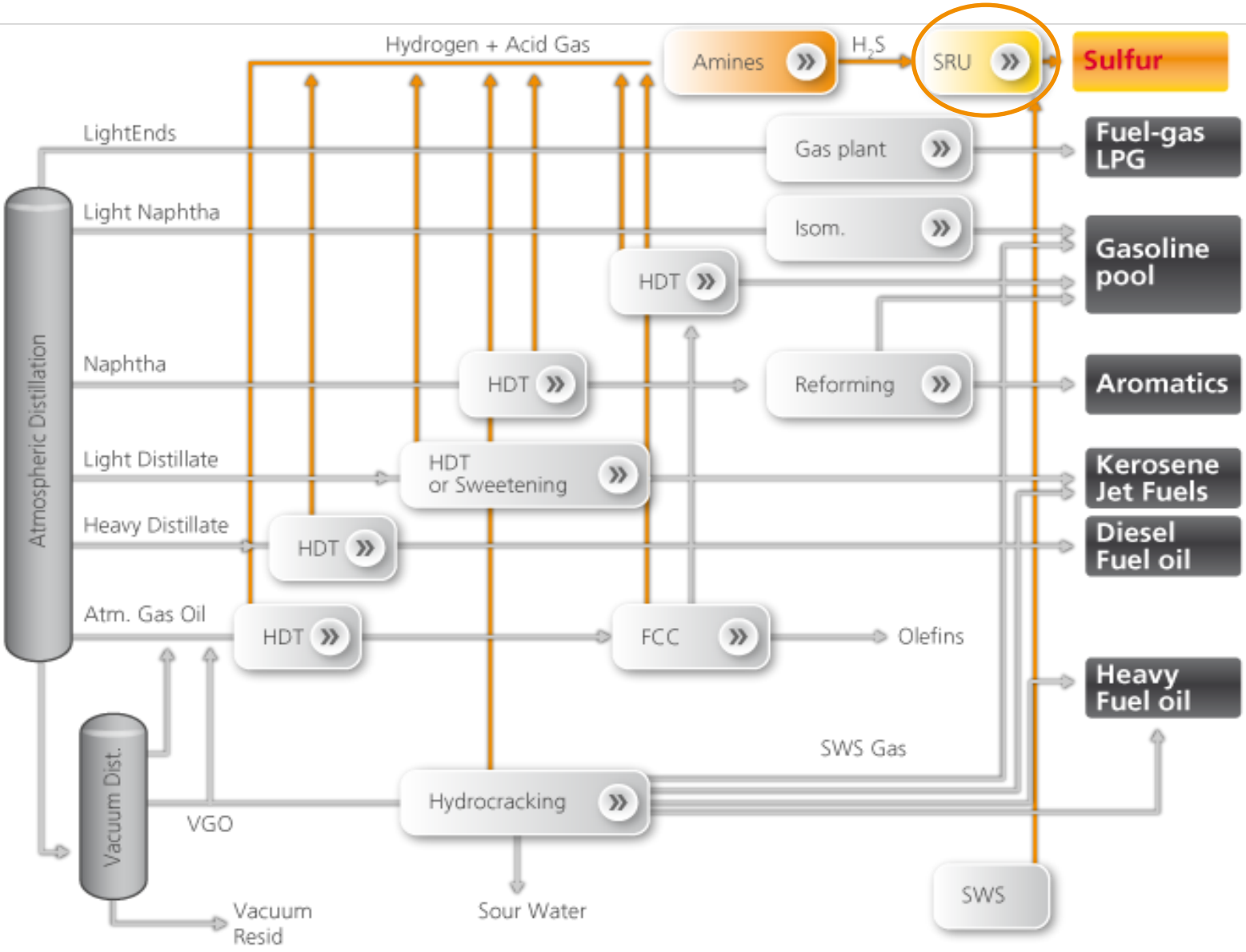
Driving Sulfur Recovery towards Excellence

Dr. Fabien Porcheron

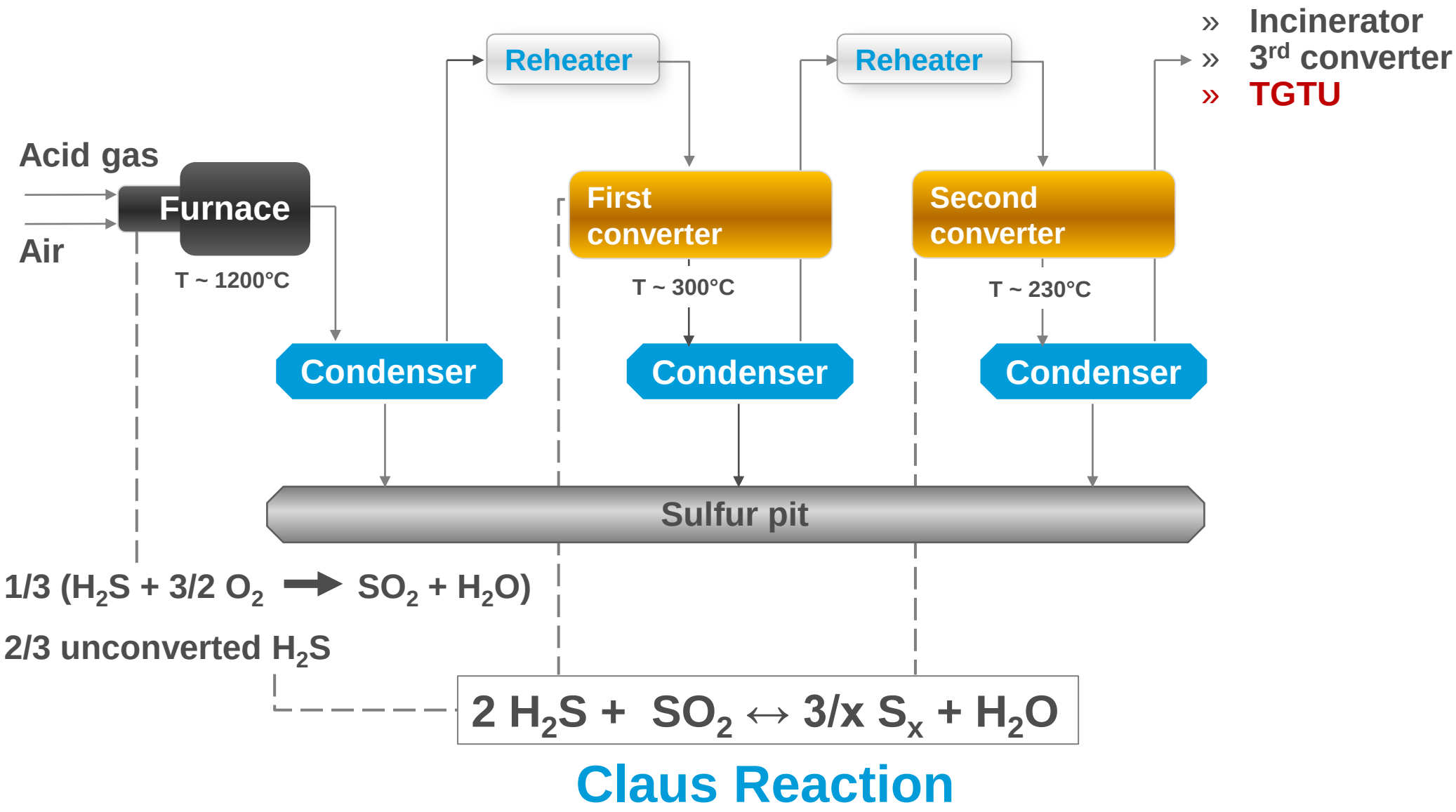
Agenda

- Introduction
- Sulfur Recovery Unit Catalysts
- Hydrogenation Based Tail Gas Treating Unit Catalysts
- Conclusions

Global Refining Scheme



Claus Process



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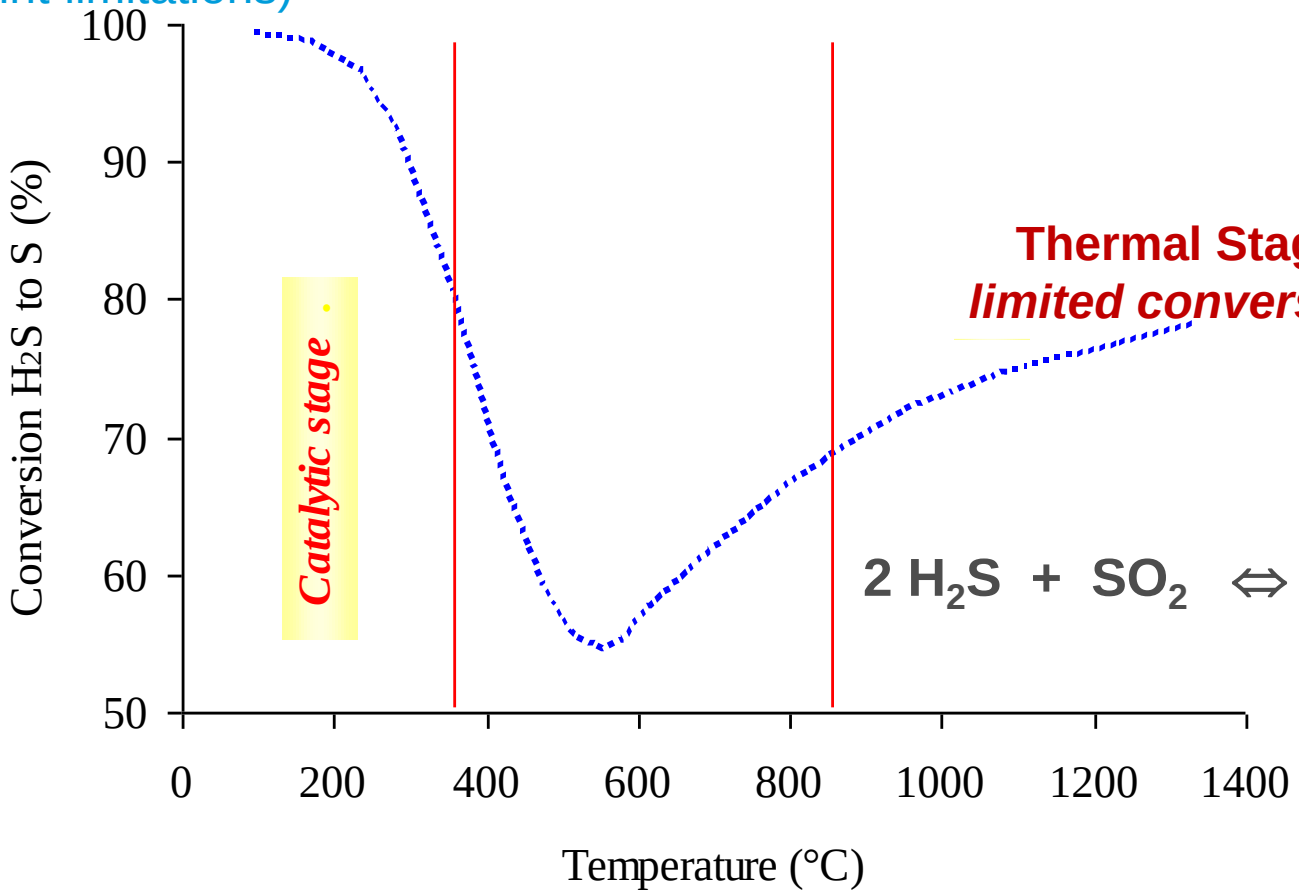
Claus Catalysts Portfolio

Type	Name	Shape
Alumina (Al_2O_3)	**CR 3-7** Standard Claus catalyst 300+ references **CR-3S** Optimized Claus catalyst 300+ references	
Titania (TiO_2)	**CRS 31** Used for very high sulfur recovery Recommended for high COS & CS_2 hydrolysis yield 300+ references	

Thermodynamics of the Claus Reaction

The colder the better

(but Sulfur dewpoint limitations)



$$2\ H_2S + SO_2 \Leftrightarrow 3/x\ S_X + 2\ H_2O$$

Claus catalysts shall be designed to prevent condensation of sulfur

Macroporosity is the key factor.

Claus Alumina CR 3-7

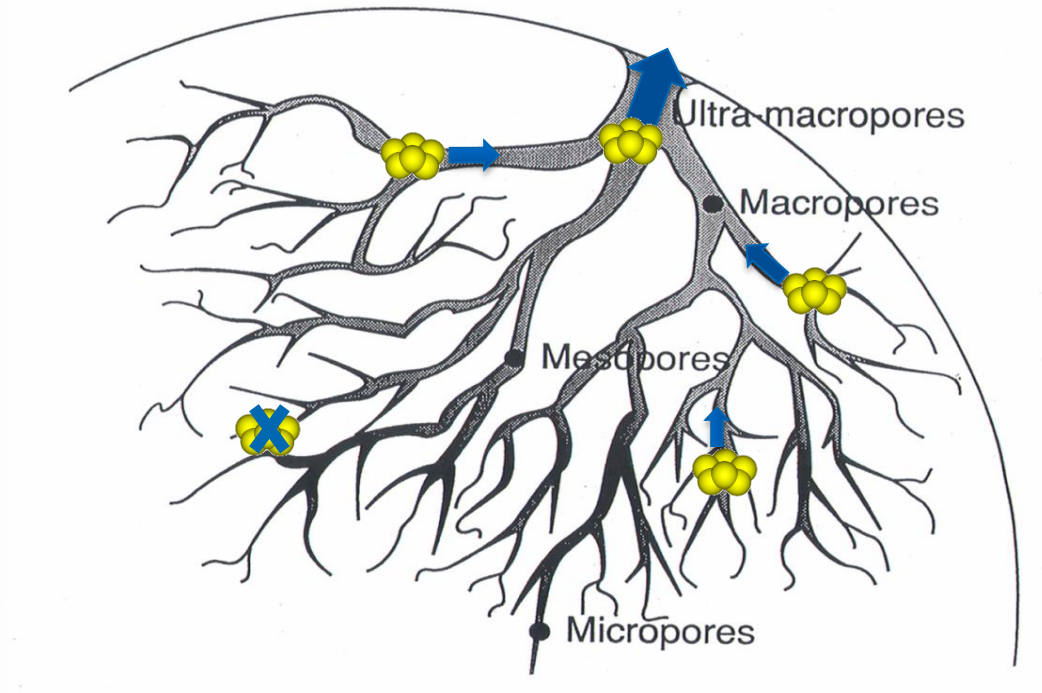
- **Al_2O_3 is a well-known Claus active component**
- **CR 3-7**
  - Standard Alumina Catalyst
  - Beads shape

  - **Macroporosity (>750 Å) of CR 3-7 is one of the highest on the market**
  - Suited for basic priorities: simple conversion & low pressure drop requirements are imposed
  - This low-cost catalyst is attractive when there are no specific processing constraints

Can we further optimize the catalyst structural & chemical properties to reach higher yields?

Of the Importance of Macroporosity

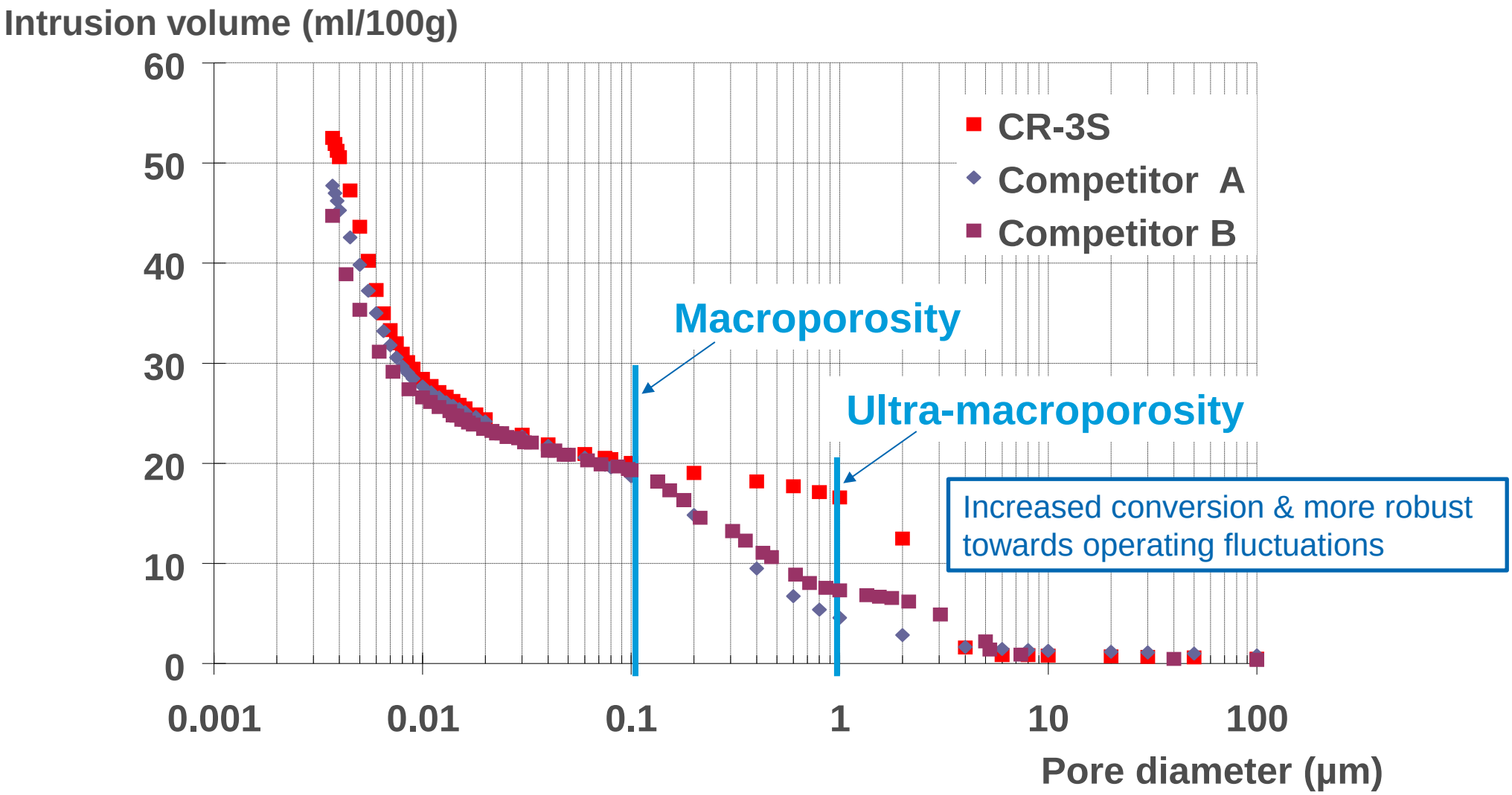
- **Large S_8 molecules have to get out of the catalyst porosity**



- **Micropores (<30 Å)**
  quickly plugged by liquid sulfur
  - inactive -
- **Mesopores (30-100 Å)**
  difficult diffusion
- **Macropores (>750 Å)**
  easy diffusion
- **Ultra-macropores (>10 000 Å)**
  even better

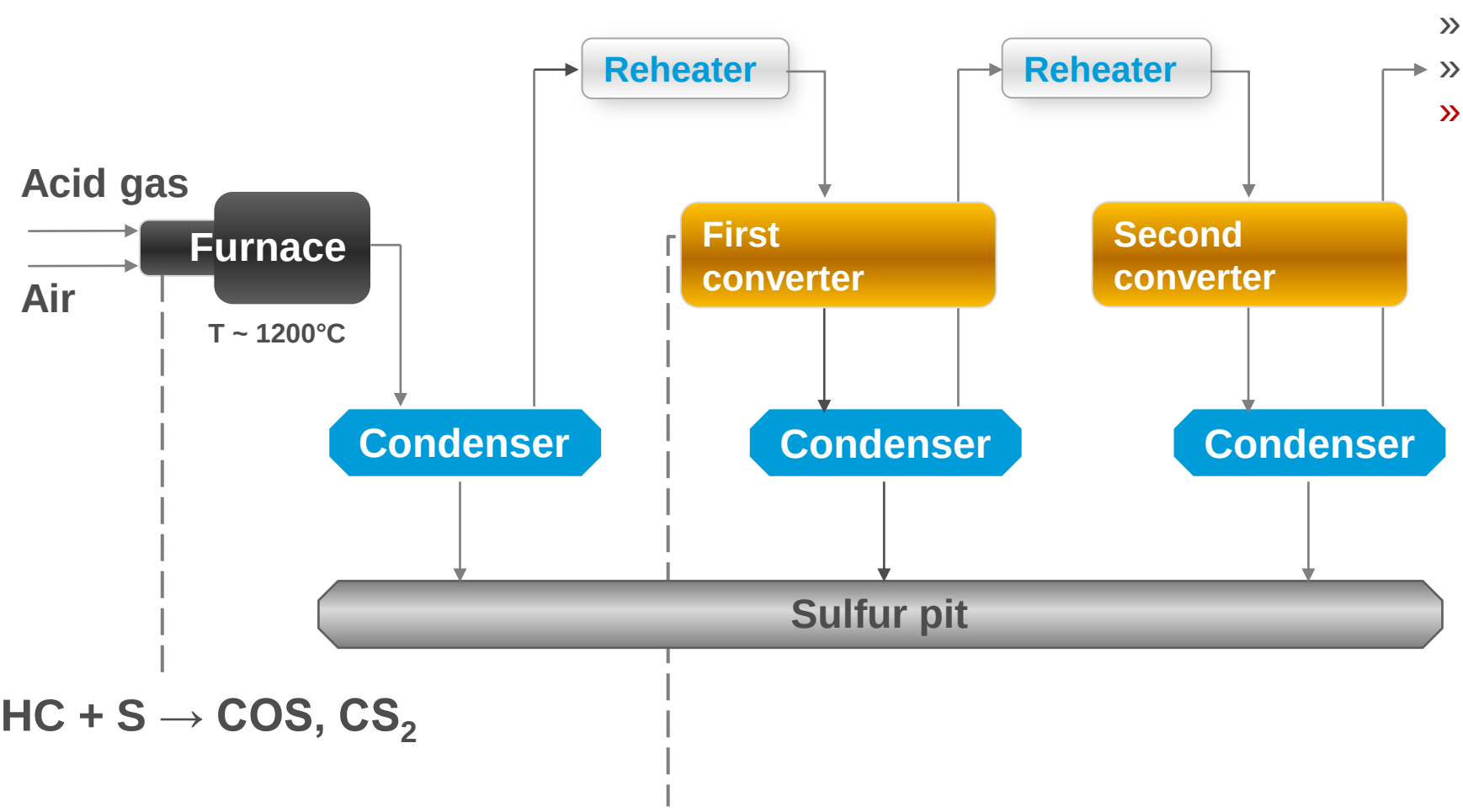
Macroporosity has to be tuned in order to minimize the diffusion constraints

Claus Alumina CR-3S Pore Size Distribution



The pores of CR-3S are the largest on the market

Claus Process

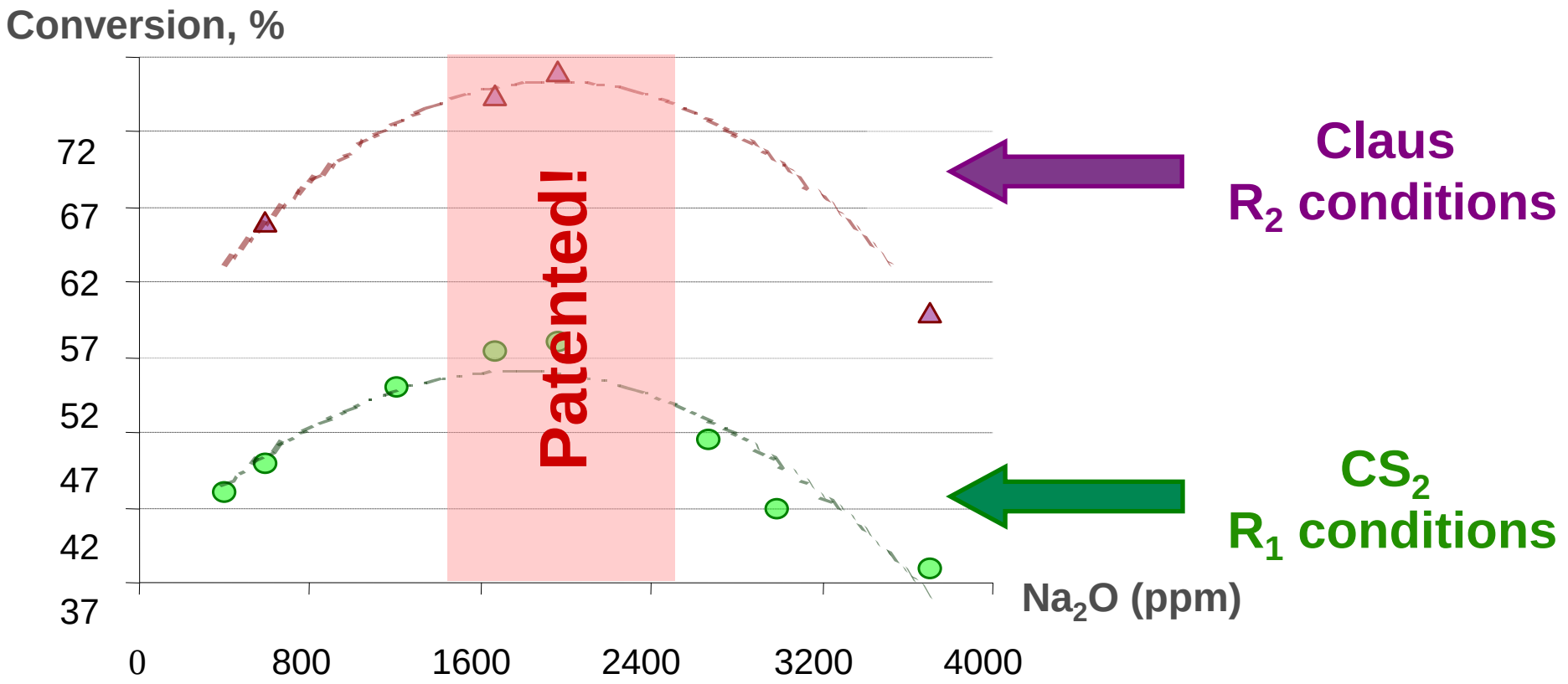


CO_2, HC + S → COS, CS_2

$$COS + H_2O \leftrightarrow CO_2 + H_2S$$

$$CS_2 + 2\,H_2O \leftrightarrow CO_2 + 2\,H_2S$$ **Most difficult reaction**

Claus Alumina CR-3S Soda Content



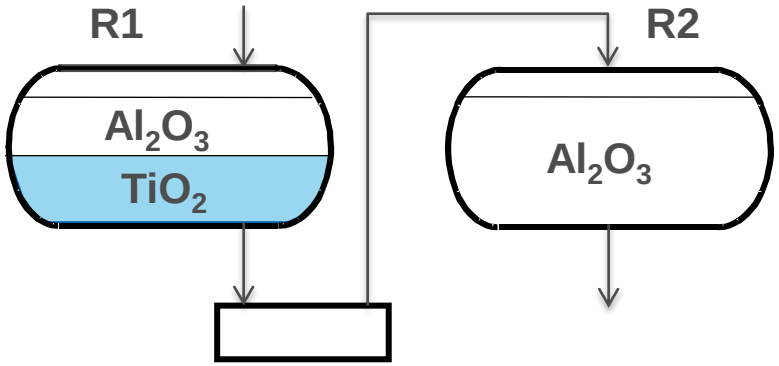
Na_2O content has to be in between 1500 and 2500 ppm
Competition products contain 3500 ppm Na2O
Additional step required to manufacture CR-3S

Claus TiO_2 Catalyst

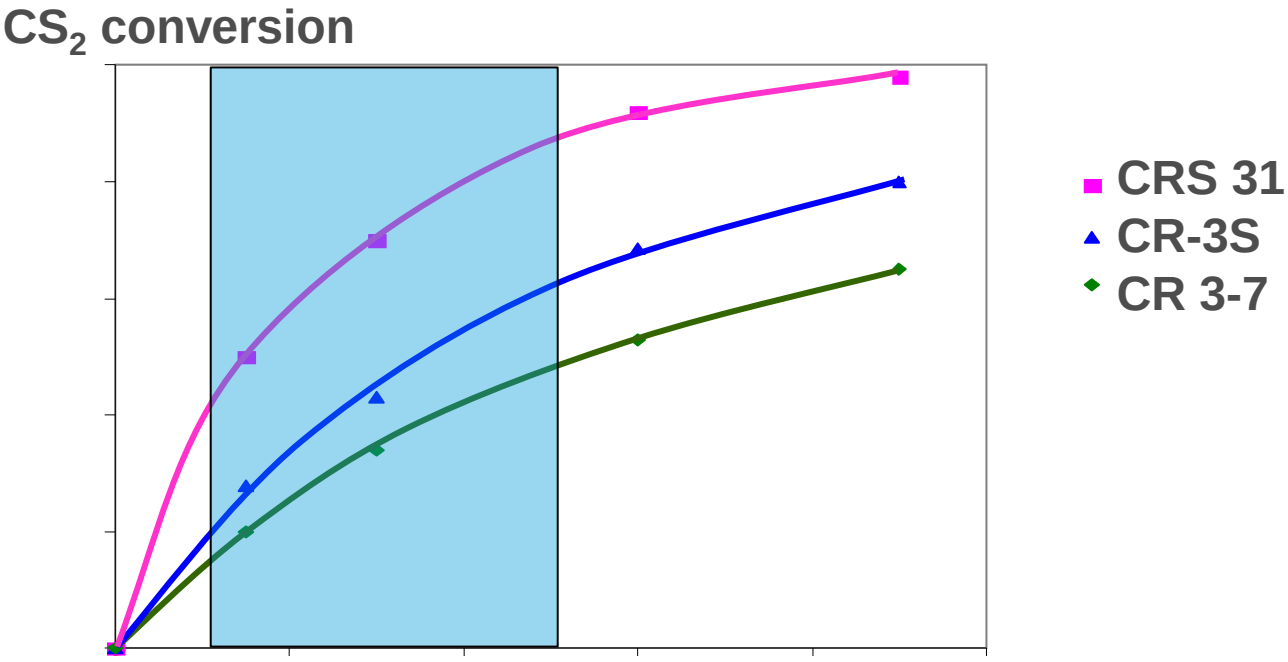
- **TiO_2 is the ultimate Claus active component**
  - Reaches Claus reaction thermodynamics equilibrium
  - **Total COS and CS_2 hydrolysis**
  - Allows debottlenecking
  - Very long life time & resistant to sulfation

- **CRS 31**
  - Titanium dioxide based Catalyst
  - Cylindrical extrudates shape in 3.5 mm

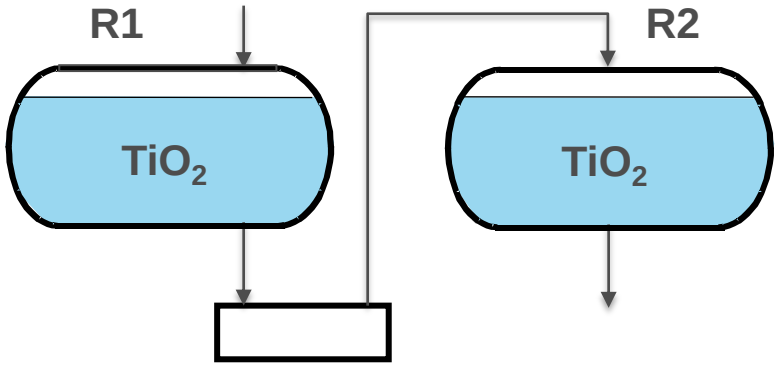
Best Strategy for TiO_2 – Option 1



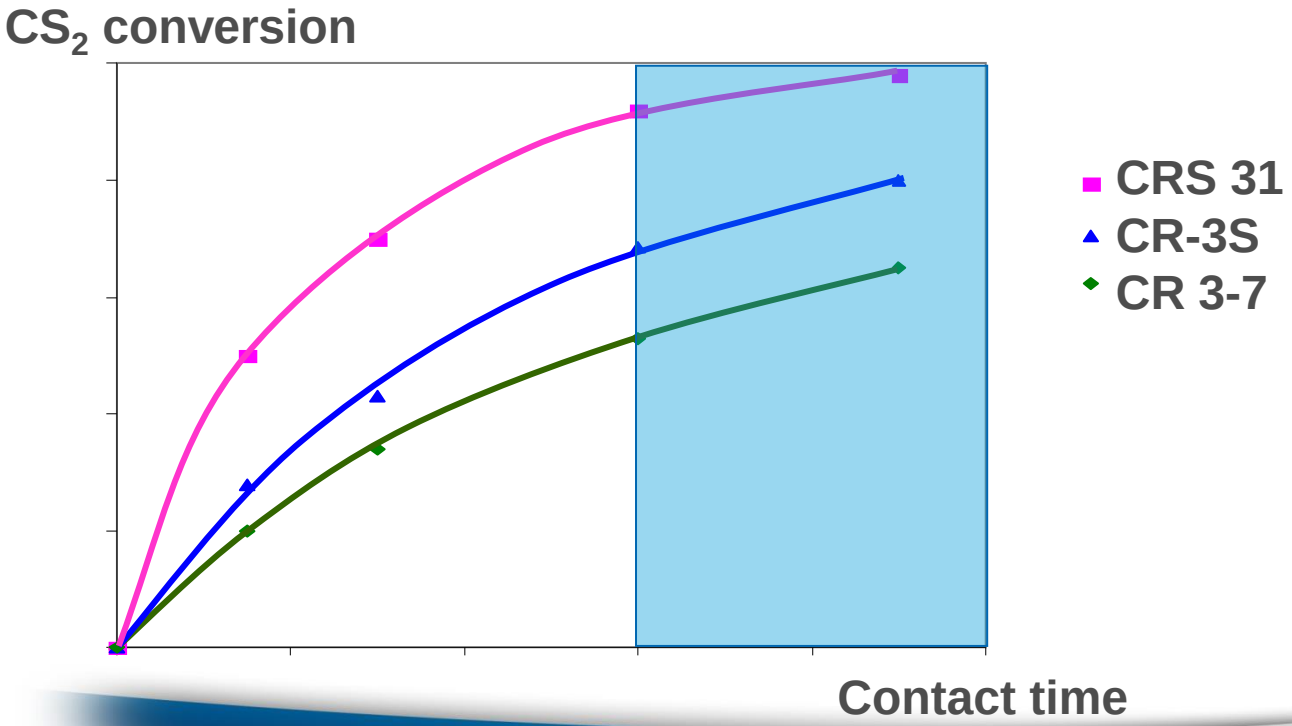
- **CRS 31 layer in R_1**
  - Full COS-CS_2 hydrolysis
  - Higher overall recovery
  - Similar life time than alumina loading



Best Strategy for TiO_2 – Option 2



- **Full CRS 31 loading**
  - Outstanding sulfur recovery (thermodynamic limitation)
  - Extended life time (> 10 years)
  - Possible throughput increase



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- **Hydrogenation Based Tail Gas Treating Unit Catalysts**
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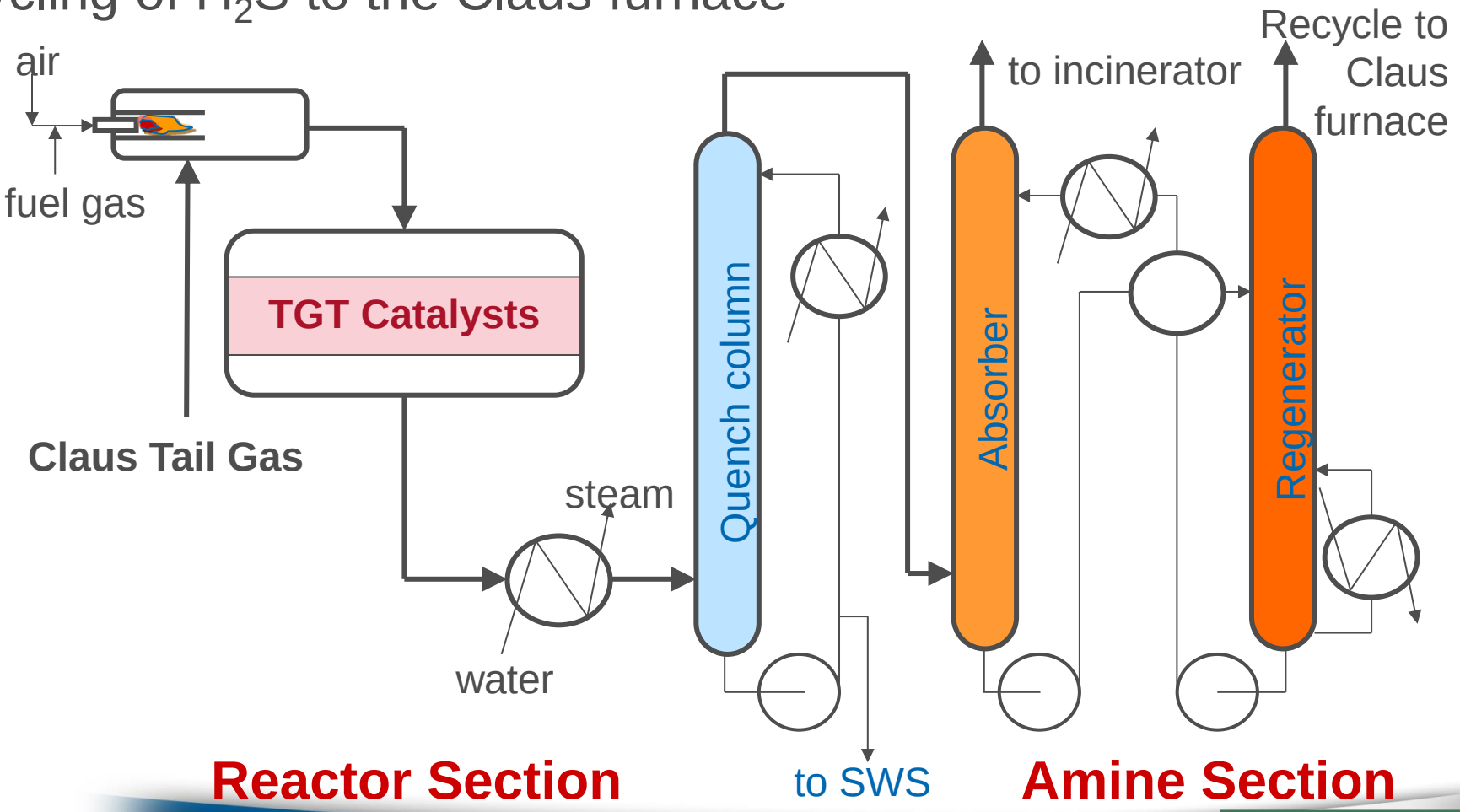
Hydrogenation Based Tail Gas Treating Units

- **Principle = A small HDT unit**
  - Transformation of Sulfur species into H_2S
  - Recycling of H_2S to the Claus furnace

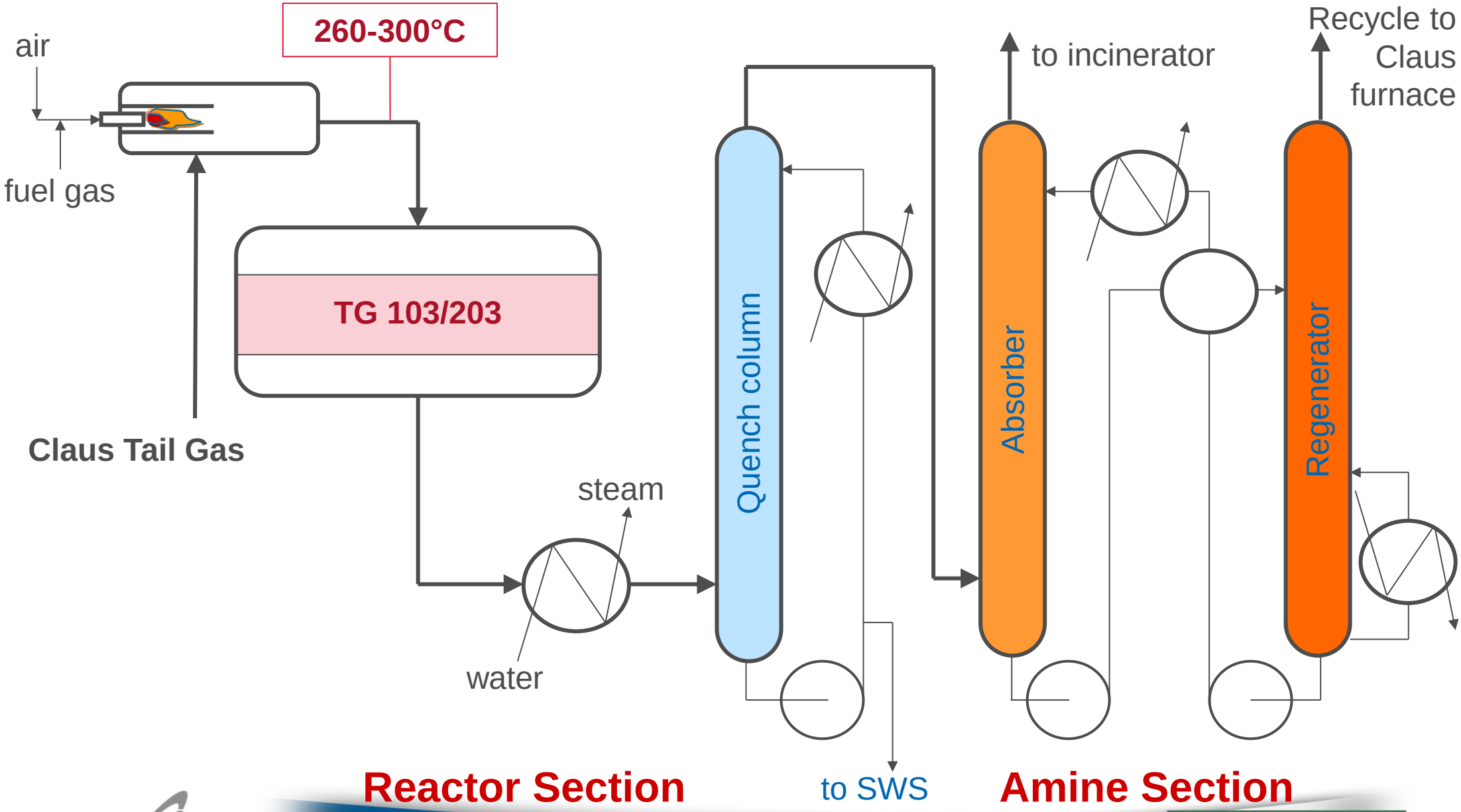


Hydrogenation Catalysts Portfolio

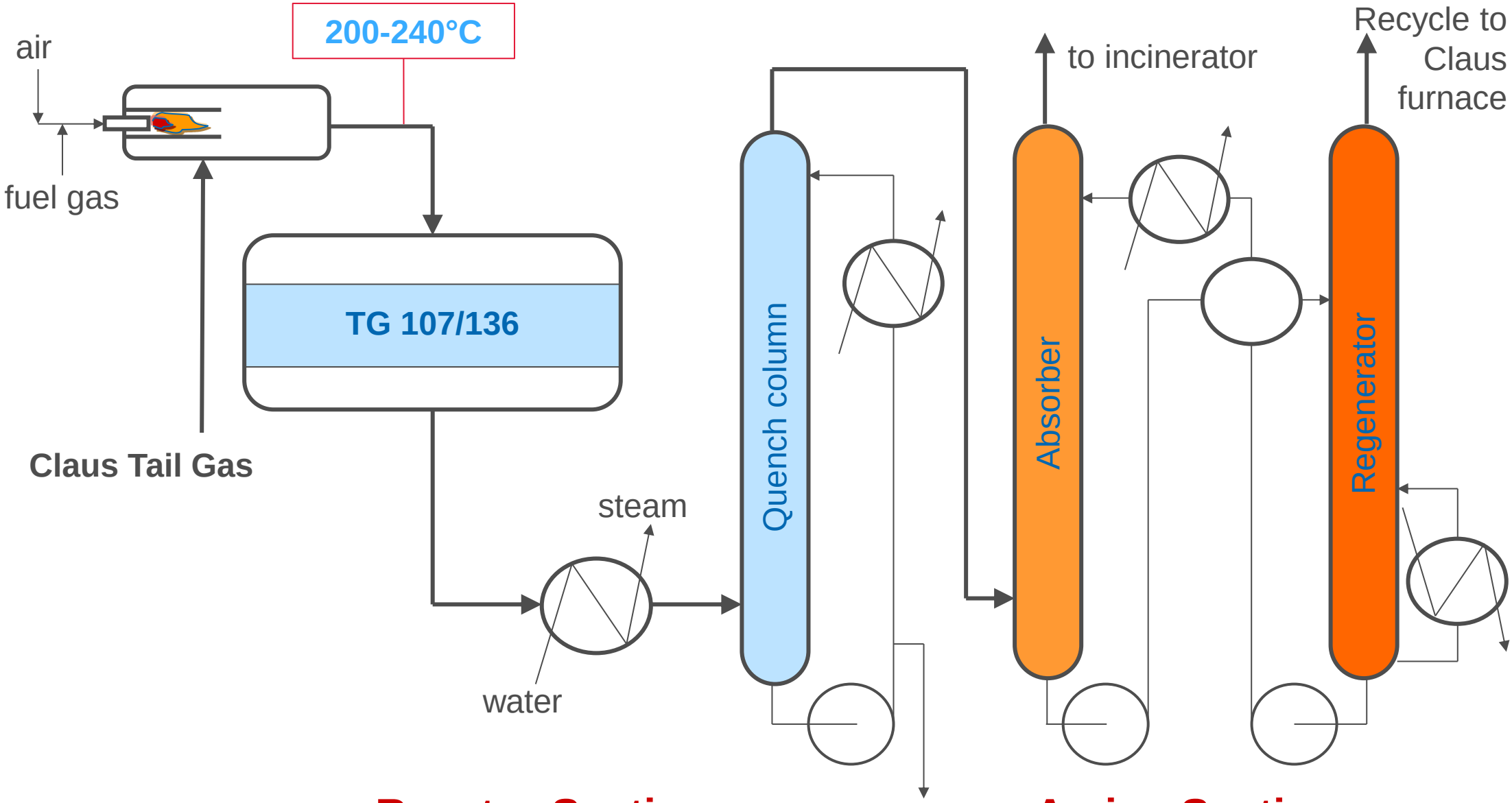
- **CoMo catalysts**

Shape	Beads 2-4 mm 	Trilobes 2.5mm 
Conventional Temperature	**TG 103** - High density, high activity **TG 203** low density, low cost Released in 2015	
Low Temperature	TG 107 - High density, high activity, the original LT catalyst	TG 136 - Lower density, lower deltaP

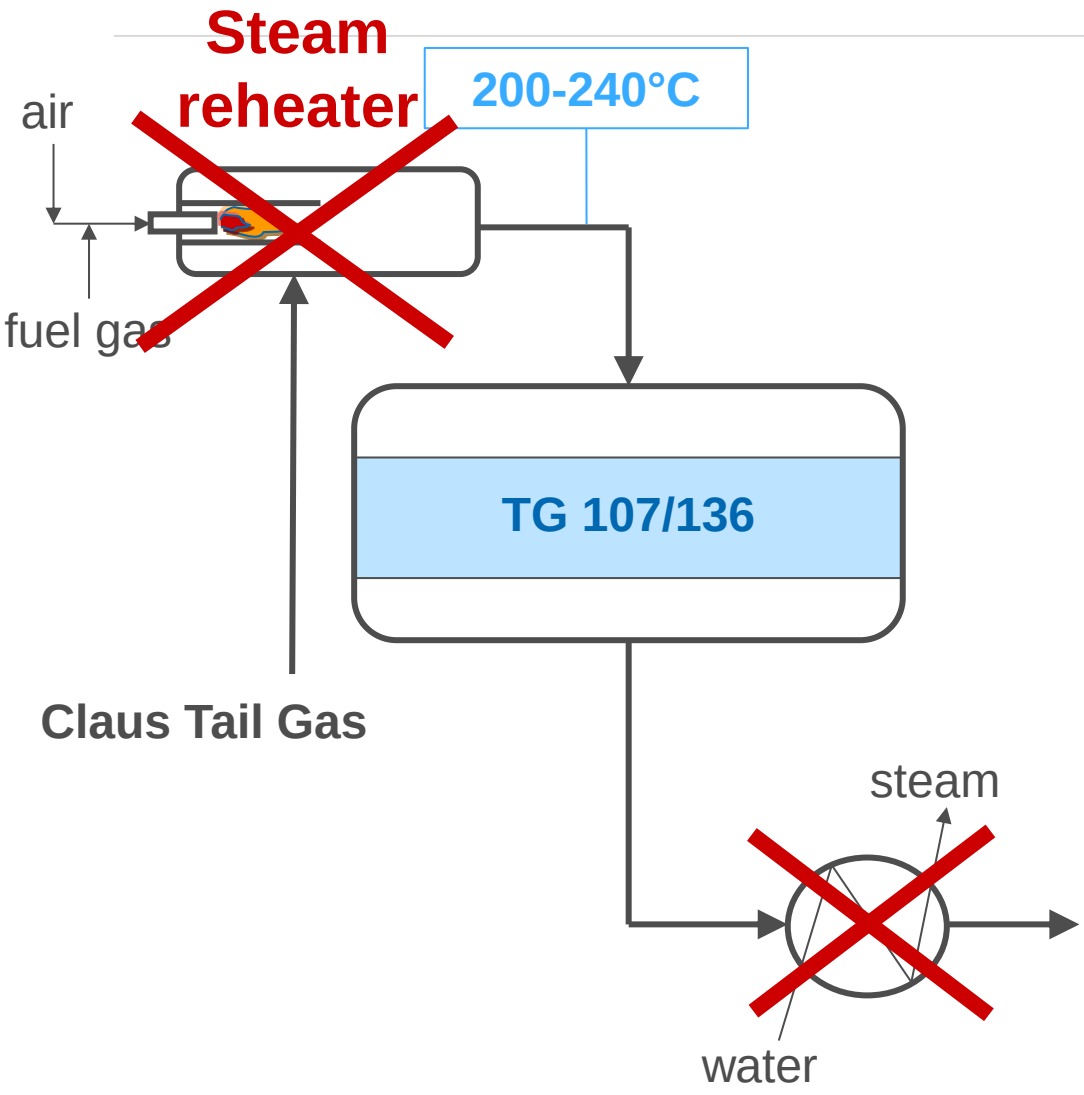
Conventional Temperature Catalysts



Low Temperature Catalysts



A Revolution for Existing / New Units



Operation at low temperature

- **40 % savings on energy**
  Catalyst payback < 1 year
- **Lower CO_2 emissions**
- **Tripled temp. safety margin**

From direct to indirect reheater

- **Less risk of misoperations (soot or excess air)**
- **Longer catalyst lifetime**
- **Equipment downsized 10%**
- **Capex reduction 10-15%**
- **OpEx reduction 20%**

Ref.: Marco van Son, Sept. 15th 2005 Brimstone, Vail (CO)

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Driving Sulfur Recovery Towards Excellence

Axens pioneered every evolution in sulfur recovery catalysis over the past 50 years:

- **Al_2O_3/TiO_2 hybrid : CRS 21 (1972)**
- **Fe Oxygen scavenger: AM (1976) & AMS**
- **Pure TiO_2: CRS 31 (1984)**
- **Optimized Alumina: CR-3S (1994)**
- **LT hydrogenation: TG 107 (2004) & TG 136**
- **BTX management: CSM 31 (2007)**
- **Low turndown catalyst: CR-3S LG (2014)**
- **HT hydrogenation catalyst: TG 203 (2015)**

Focusing on the benefits of our customers made us Sulfur recovery catalyst World leader

Axens Complete Portfolio for SRU

Claus Catalysts



- CR: Claus alumina
- CR-3S: Improved Claus alumina
- DR Series: Active bed supports
- CRS 31: Titanium dioxide catalyst
- AM & AMS: Oxygen scavengers
- CSM 31: BTX management

Tail Gas Treatment Catalysts


- TG 103: TG hydrogenation catalyst, spherical
- TG 203: TG hydrogenation catalyst, spherical
- TG 107: Low temperature TG hydrogenation catalyst, spherical
- TG 136: Low temperature TG hydrogenation catalyst, extrudate

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