Shell Catalysts & Technologies

High-performance tail-gas treating

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Outline

WHY?

- The drivers for Shell developing SCOT technology and tail-gas treating catalysts
- Environmental Duty and Technology Advancements

HOW?

- Our approach to catalyst development projects, with a specific focus on tail-gas treating catalysts
- The processes, technology, analytics and equipment we use

WHAT?

- The catalyst products we have developed
- Key applications

934

- A new state-of-the-art SCOT tail-gas catalyst that sets superior performance standards in low-temperature operation
- Opportunities and the potential value to you

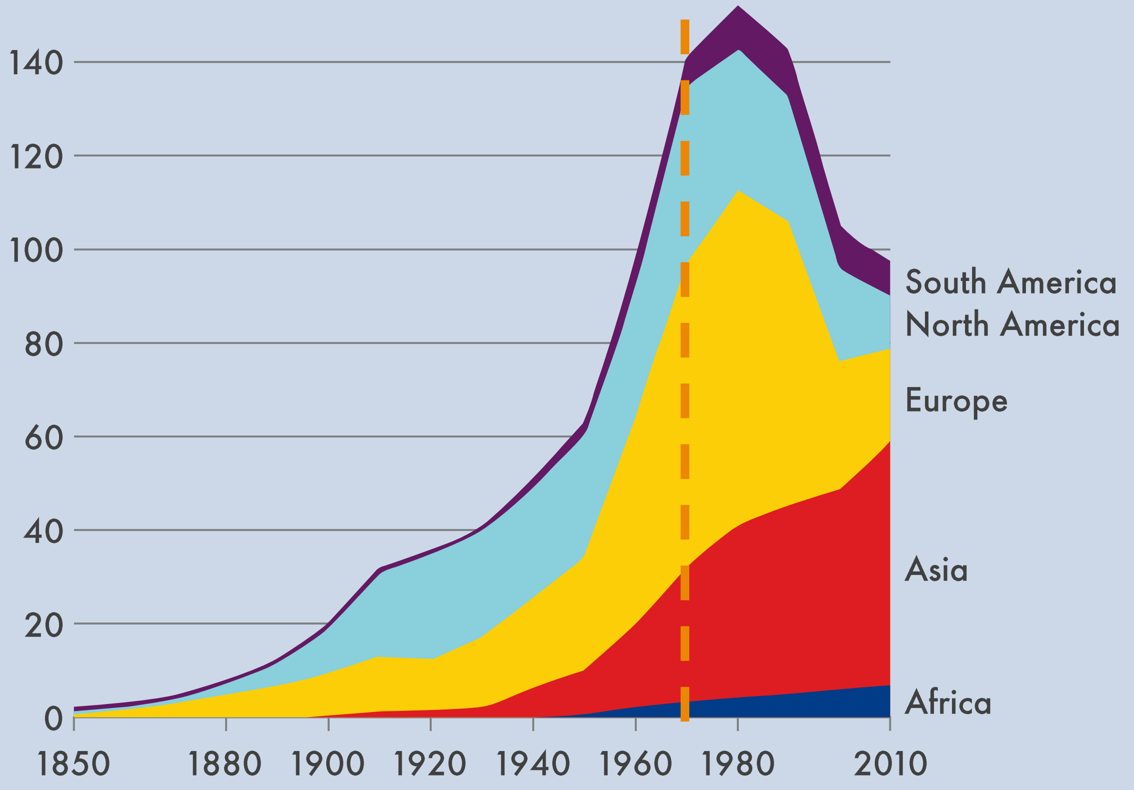
Shell Claus Offgas Treating (SCOT) process history

- Global initiatives in 1970s legislate reduction in sulphur emissions
- SCOT is the most widely applied TGU technology and catalyst
- 1970 – Shell awarded patent for using hydrotreating with amine for tail-gas treating
- 1972 – First application (Japan)
- 1975 – First US application (Norco)

50 years working on reducing SO_2

Global sulphur dioxide (SO_2) emissions by world region

Annual SO_2 emissions in million tonnes



Source: Clio Infra; Kilmont et al (2013)

Why SCOT

The industry standard
The most commercially proven tail-gas clean-up process when tail-gas recoveries in the 99.9% range are required

260+ units
worldwide

10ppmv H_2S specification in the SCOT vent gas can be achieved with Low-Sulphur SCOT

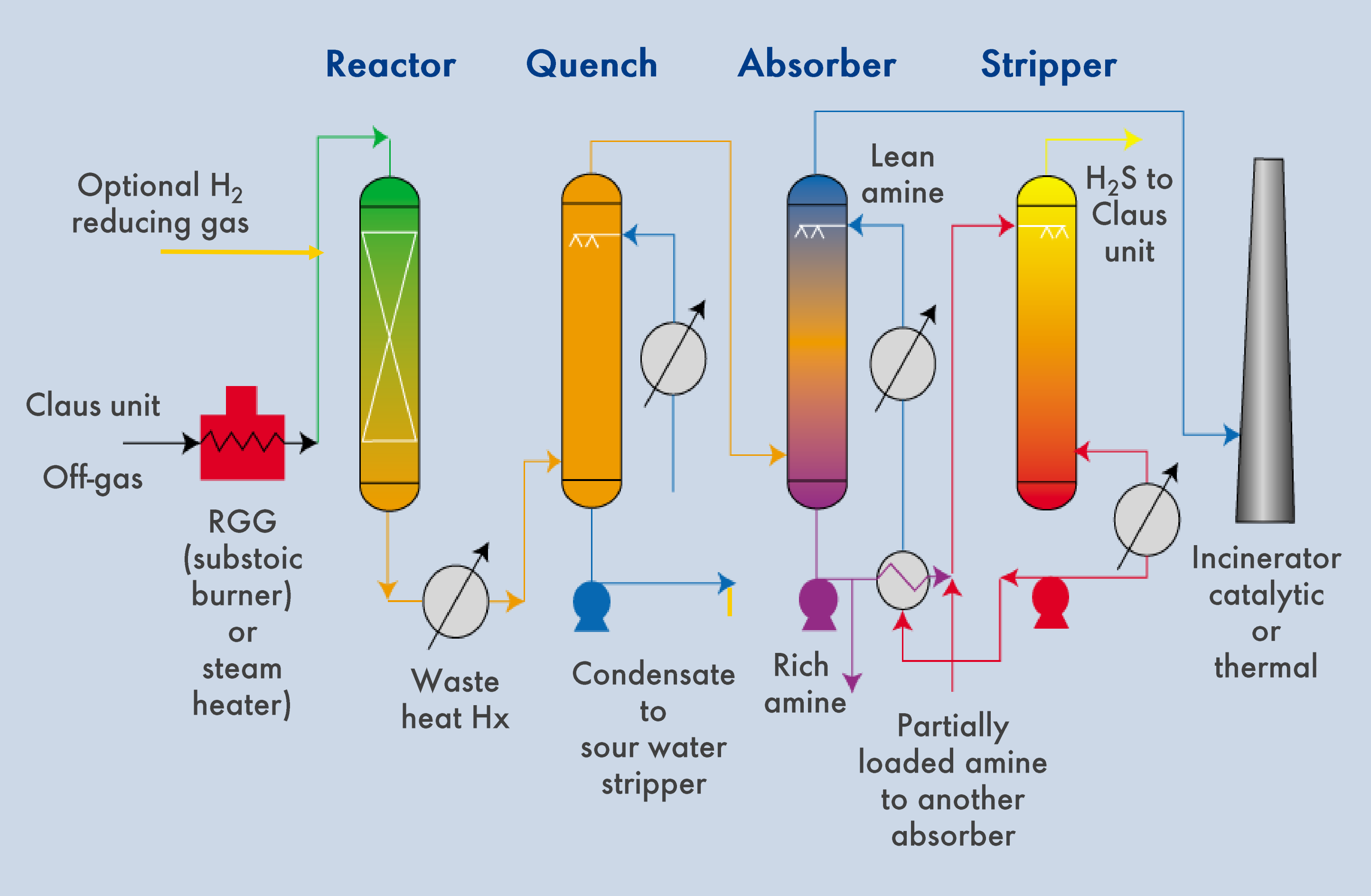
Application in **E&P** and **refining**

3 t/d to 4000 t/d
sulphur capacities of upstream Claus unit

Ultra-high sulphur recovery efficiency:
99.7+% (SCOT)
99.95% (SCOT ULTRA)

SCOT process: Sulphur species in Claus tail gas → H_2S → Claus

- High activity, low DP catalyst cobalt/molybdenum on alumina
- Reducing gas generator (RGG) burner for application w/o H_2
- Standalone amine system
- High reliability – 99%+ availability
- Turndown
- Configurations
  - Integrated/cascade
  - Low-Temperature SCOT
  - Low-Sulphur SCOT
  - SCOT ULTRA



SCOT process innovation
Continuing improvement across 50 years

Conventional
- RGG + Reactor + Quench + standalone amine
- Booster blower when required

Quench and amine
- Selectivity – CO_2 slip – DIPA, MDEA, Specialty solvent
- Pressure drop – trays to packing
- Booster blower deleted

Integrated and cascade options

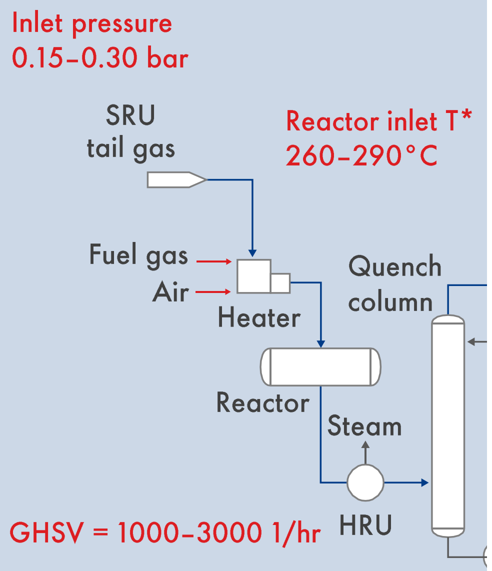
Low Sulphur performance
- Super stripper regeneration
- Acid aided regeneration
- Specialty sterically hindered solvent

Low temperature capability
- Reactor inlet as low as 200°C
- Higher activity catalyst
- Steam preheat and lower CAPEX
- OPEX reduction – energy

Design expertise and catalyst development combined with operational experience

Sulphur recovery system – Low-temperature tail-gas unit

Conventional configuration

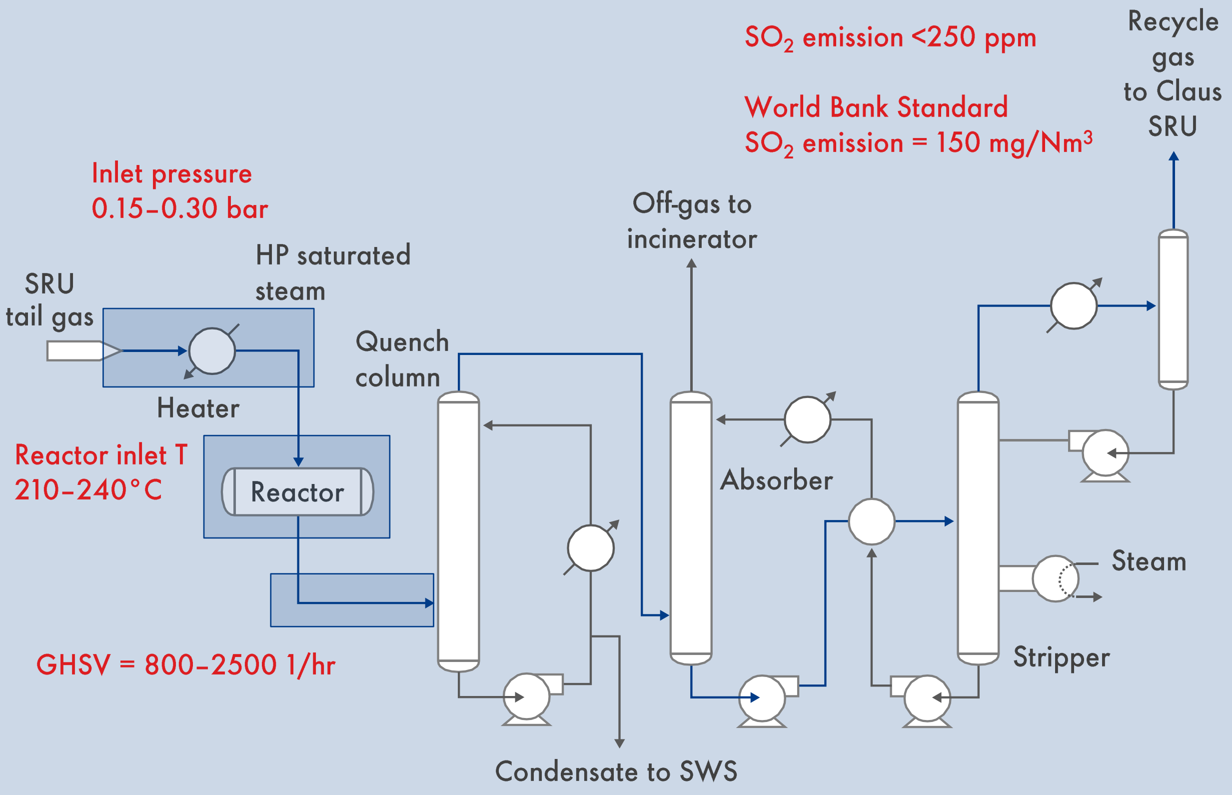


*In-line heater may operate either conventional or low-temperature mode

Benefits of low-temperature technology:

- Condensing steam preheat vs RGG burner
- HRU deleted
- Reduced CAPEX
- Lower temperature
  Reduced heat input
- Lower OPEX
- Improved operability
- Needed:
  Higher activity catalyst

Low-temperature trend in tail-gas technology



Higher activity catalyst is required

Low-temperature effects

Benefits

- Indirect preheat option (condensing steam)
- Burner and controls are eliminated – avoids major causes for catalyst damage
- 10–15% less CAPEX
- Lower fuel rate and less instrument and electrical maintenance means reduced OPEX
- Smaller carbon footprint

Challenges

- Diminished catalytic activity at low temperature; requires more catalyst or higher activity catalyst
- Impact of undesirable reactions,
  COS survival and mercaptan formation
  slip past the amine system and on to incinerator
- Requires a bit higher hydrogen concentration

SCOT catalyst development

Reactors utilise catalysts with cobalt and molybdenum sulfides on alumina support, active sites for hydrolysis, hydrogenation and water gas shift (WGS)

- First generation: Specifically developed from initial re-purposed hydrotreating catalysts
  - Second generation: developed high activity, high porosity, long life
    - Third generation: High activity contemporary low-temperature catalyst
  - 934 is newest, most active, more effective low-temperature activation

	RIT, °C	RIT, °F	WABT, °C	WABT, °F	aGHSV (1/hr)
First generation (534)	280	540	300–330	570–630	1000–2000
Second generation (234)	240	465	250–300	480–570	2000–2500
Third generation (LT-834)	220	430	230–250	445–480	1500–2000
Latest generation (LT-934)	200	392	210–230	410–445	1500 - 2000

Catalyst products (234 , 534, 834 or 934) arise from a continuing commitment by Shell for environmental improvement and a progression of development over 50 years for enhancing performance and activity

Key technology differentiators

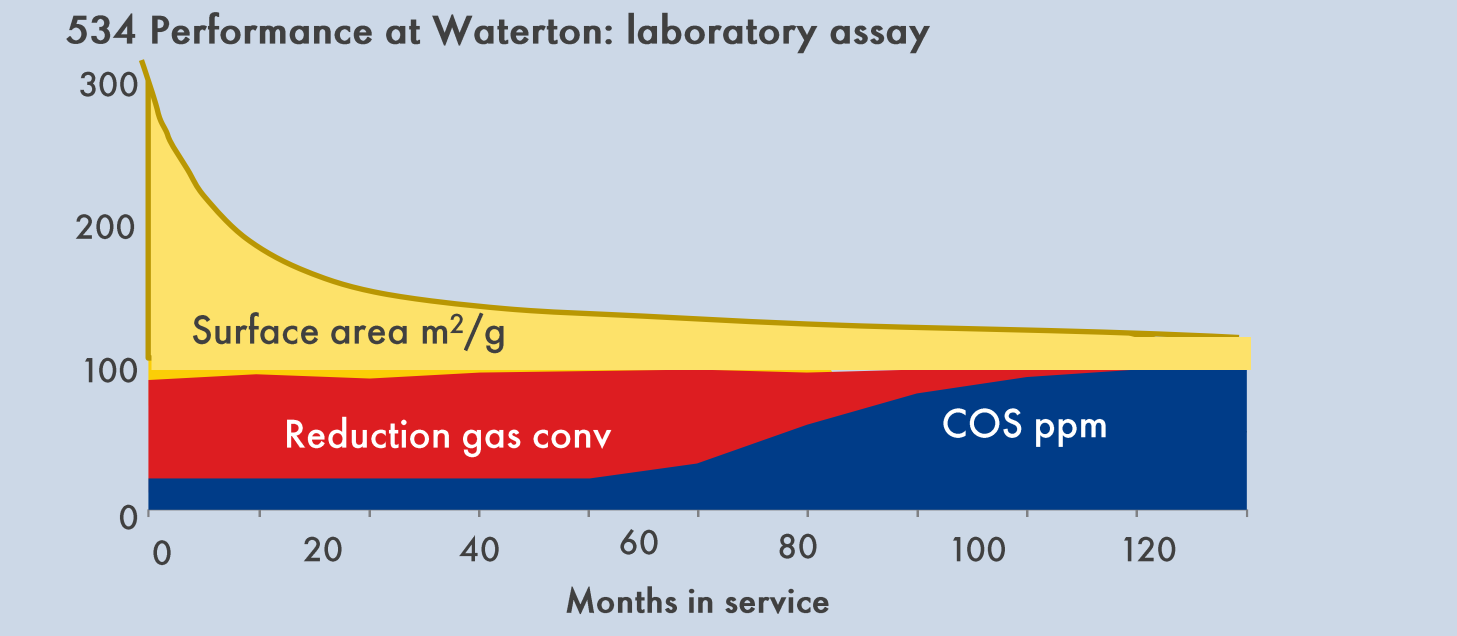
- Advanced low temperature SCOT catalyst means reactor inlet can be as low as 200°C
- Cascaded SCOT unit offering reduces the overall solvent requirement
- SCOT process demonstrates robust operability
  - good overall sulphur recovery even during substantial upsets in the Claus
  - downtime experience is ~0.5% for SCOT units
- SRU can operate on a continuous basis at 10–100% of design capacity
- SCOT can start up with less than 10% of design feed

Catalyst innovations and process technology advancements have enhanced operability and provided significant savings in CAPEX and OPEX

SCOT process and operational support

SCOT catalyst life

- Aging factors include hydrothermal, carbon, sulfation, whacking
- Activity follows surface area, declining to 50% from SOR to EOR
- 4–6 years is typical service life
- 12+ years has been achieved
- Catalyst activity is stronger at higher temperature
- 934 is a more active catalyst, performing at lower temperature, with operating allowance to raise temperature and extend run



What we provide

- **SCOT catalyst**: Selection assistance for best practice in catalyst life
- **Assessment**: Evaluate catalyst activity from plant performance data, Project remaining catalyst life
- **SCOT process**: Providing operations guidelines, training and advice

Drivers for tail-gas catalyst improvement

Shell responding to demand for higher activity catalyst

Industry focus on further reducing OPEX (fuel) and enhancing operability

World Bank standards tighter emission requirements

Requirement to operate at lower temperatures

Our new catalyst should offer lower energy consumption, full activation at low temperature, higher activity at low temperature, increased catalyst lifecycle and improved conversion and lower emission of SO_2, CO and CO_2

The catalyst is the key

Low-temperature operation is only possible with high-activity catalysts

Traditional catalysts simply don't perform reactions fast enough to be operated at low temperature

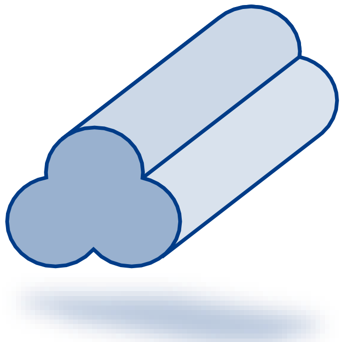
$SO_2 + 3H_2$	→	$H_2S + 2H_2O$	→	SO_2 hydrogenation
$SO_2 + 2H_2$	→	$S + 2H_2O$	→	SO_2 hydrogenation
$S + H_2$	→	H_2S	→	S hydrogenation
$COS + H_2O$	→	$CO_2 + H_2S$	→	COS hydrolysis
$CS_2 + 3\ H_2$	→	$CH_3SH + H_2S$	→	CS_2 hydrogenation
$CS_2 + H_2O$	→	$COS + H_2S$	→	CS_2 hydrolysis
$CH_3SH + H_2$	→	$CH_4 + H_2S$	→	Mercaptan hydrogenation
$CO + H_2O$	→	$CO_2 + H_2$	→	CO WGS

Composition of commercial tail-gas treating catalysts

Bifunctional tail-gas catalyst

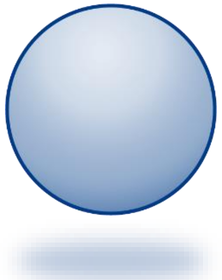
Oxidic support (Hydrolysis)
- Al_2O_3
- TiO_2

Metal sulfides (Hydrogenation and WGS)
- Mo, Co



Shapes: Trilobes extrudates

Sizes: 3.2 mm

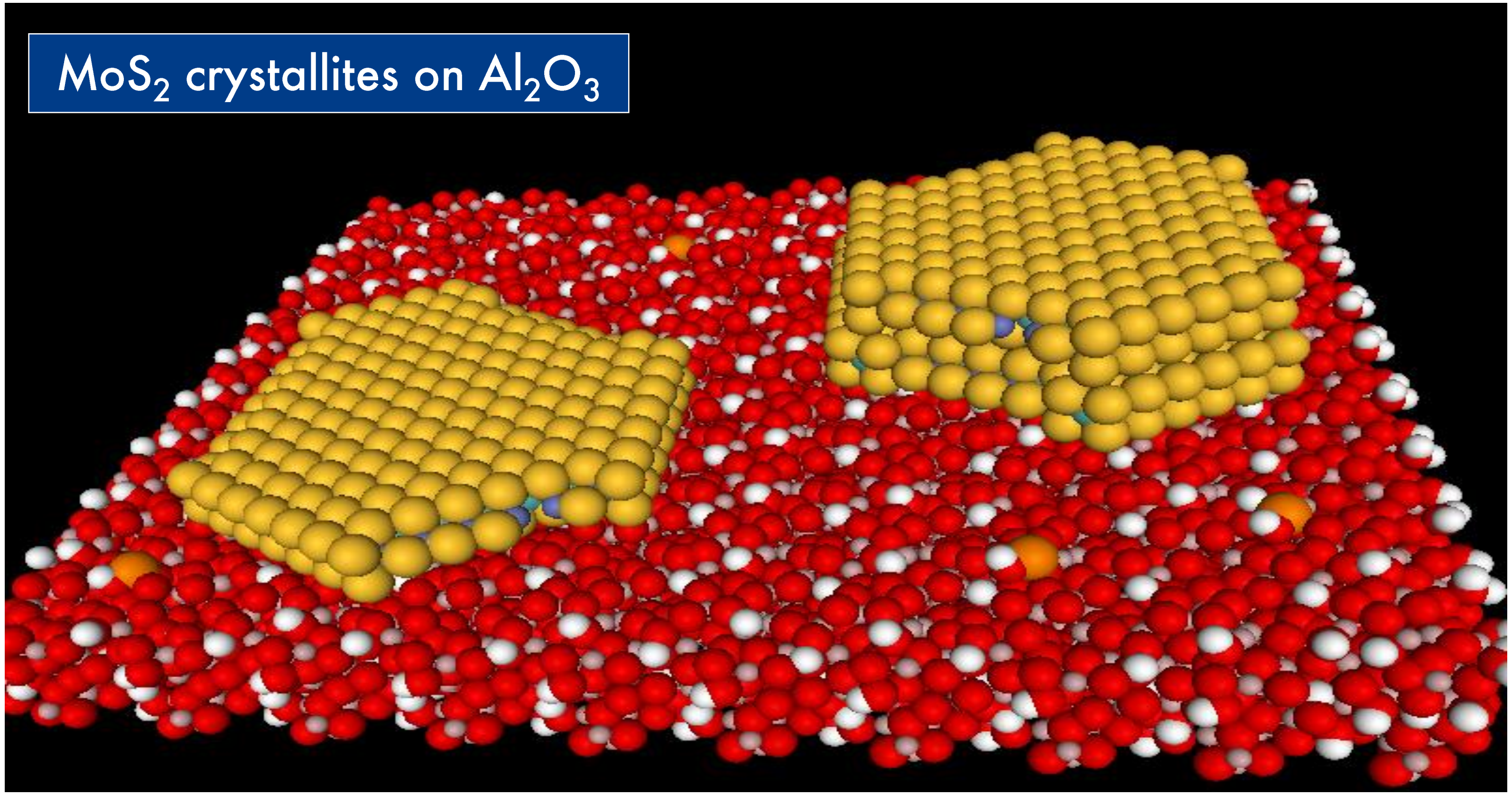


- Spheres
- 4 and 8 mm

Tail-gas catalyst active sites

Co-Mo-S phase: Hydrogenation and WGS occur on these slab structures

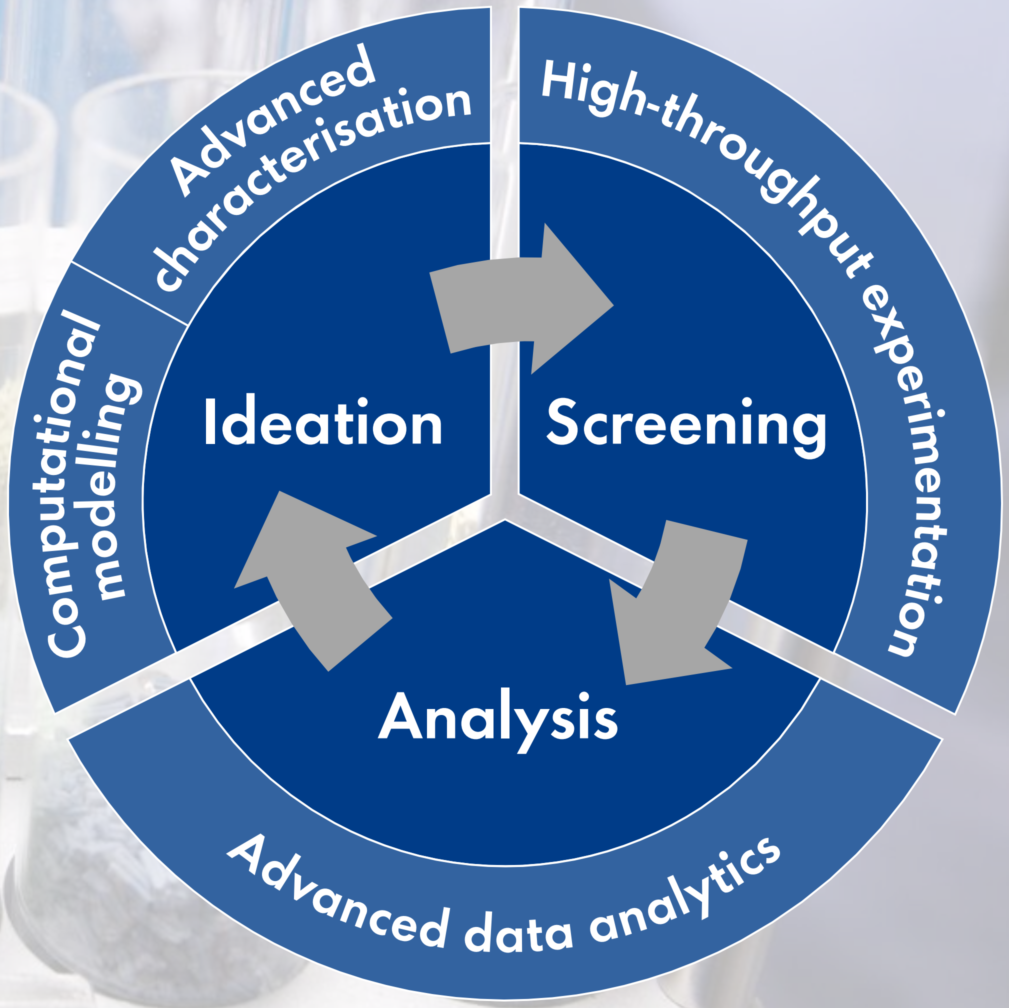
Alumina: Hydrolysis occurs on the highly porous support (alumina phases affect activity)



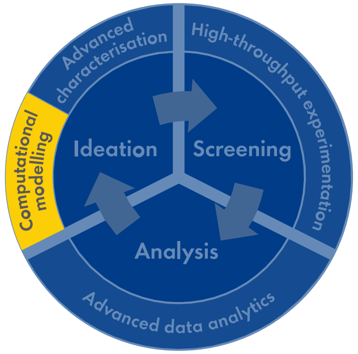
	S
	Co
	O
	O
	Al
	Dopants

Shell Catalysts & Technologies' catalyst development process

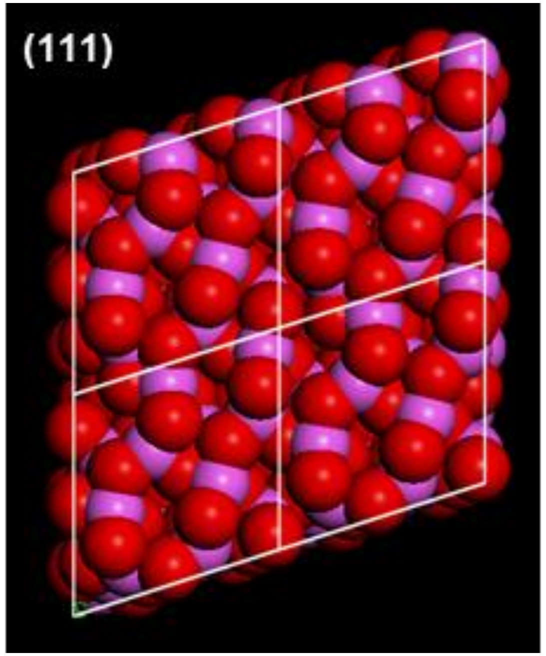
- Parallel workflow: Ideation, screening and analysis occur simultaneously
- Eliminates barriers to invention
- Enabled by major investments in:
  - Computational modelling
  - Advanced characterisation
  - High-throughput experimentation
  - Advanced data analytics
- Recognises the importance of each part of the process

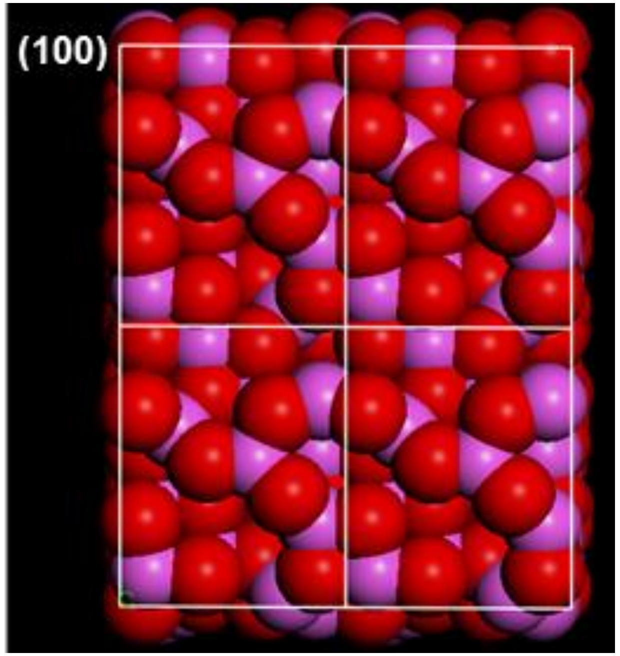


Computational modelling



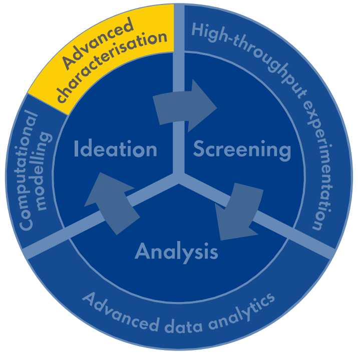
- Elucidates key descriptors of catalyst activity
- Allows the optimisation of these descriptors as well
- Synthetic strategies are guided by these learnings
- Fewer physical experiments needed to obtain higher activity



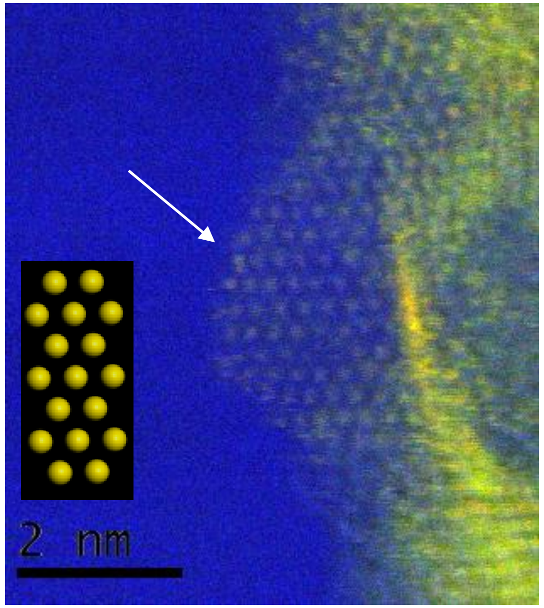


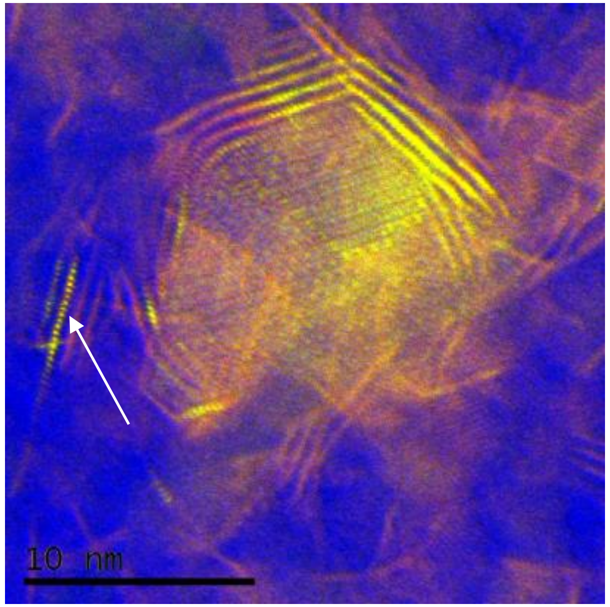
Density function theory calculation to determine optimal aluminum and oxygen placement in the catalyst support

Advanced characterisation

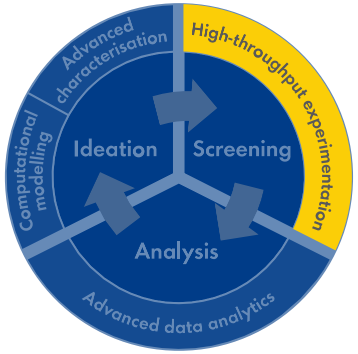


- Provides a fundamental understanding of the structure/function relationship
- These learnings allow the custom tailoring of catalysts for high performance
  - E.g. Incorporating direct and indirect desulphurisation active sites into individual MoS_2 slabs





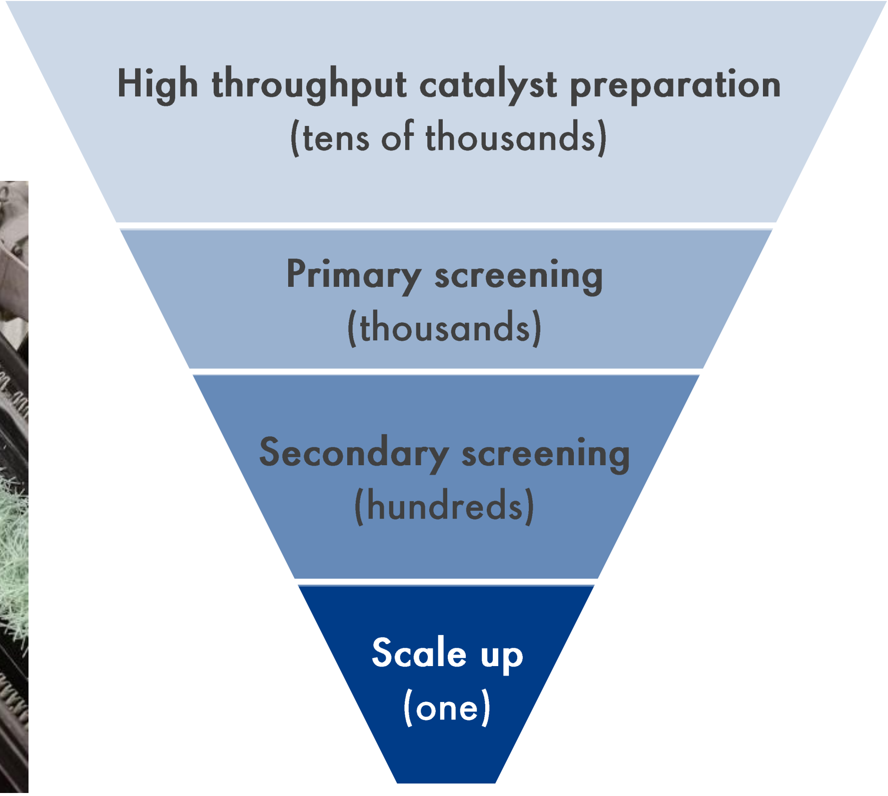
Aberration-corrected transmission electron microscopy allows us to see the active sites of real catalysts operating on customer feedstocks



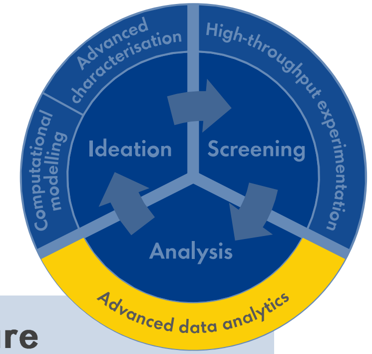
High-throughput experimentation

- Screen ideas as quickly and accurately as possible
- Funnel systematically sieves through formulations
  - High-throughput catalyst preparation
  - Fit-for-purpose catalyst testing
- Allows ideas to be screened that would normally have been ignored

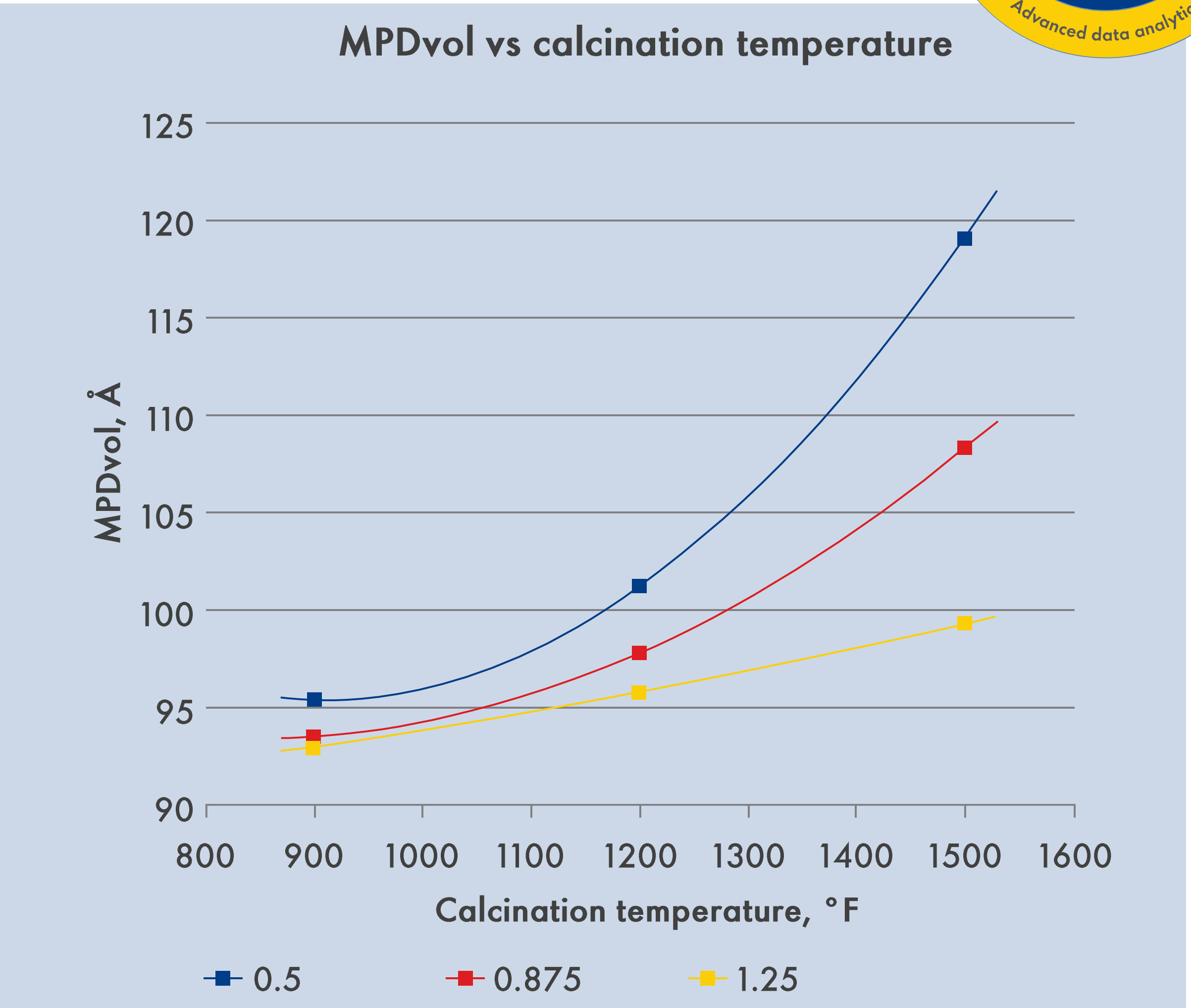
High throughput funnel



Advanced data analytics



- A natural and essential partner to high-throughput experimentation
- A custom designed software suite encompasses the entire workflow from experimental design to data processing
- Allows the vast data gathered from high-throughput experimentation to be managed and processed
- Statistical models are developed using the entire database rather than incomplete subsets



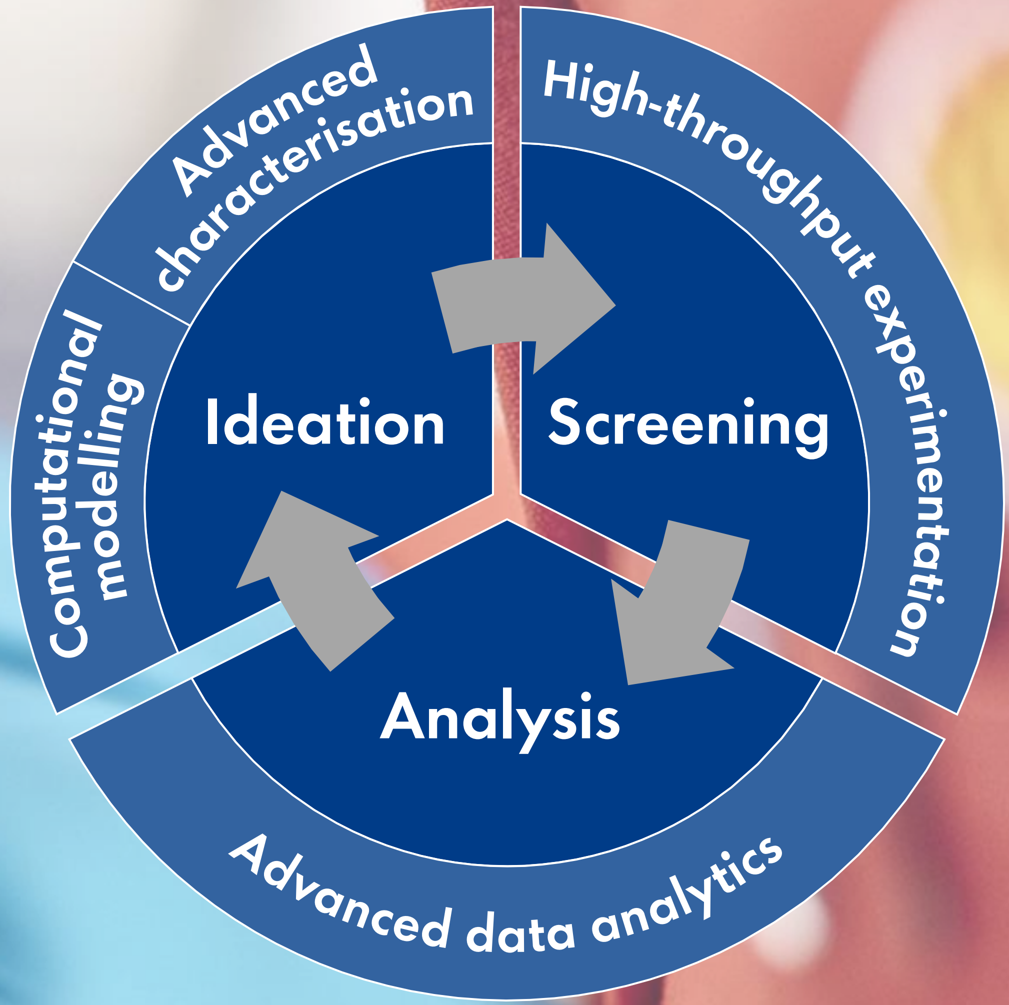
Statistical analysis finds correlations between variables

Our catalyst development process helps us to...

...generate ideas with a high probability of success

...screen those ideas as quickly as possible

...extract as many learnings as possible from that data



Our tail-gas treating catalyst portfolio

- Operating temperature: as low as 220°C – 428°F
- High activity
- Excellent pressure drop performance

- Typical operating temperature: 240°C – 465°F
- Balances fill cost and activity
- Excellent pressure drop performance

- Typical operating temperature: 280°C – 540°F
- Suitable for in-line burner configurations
- Industry-leading pressure drop performance

Our tail-gas treating catalyst portfolio just got better

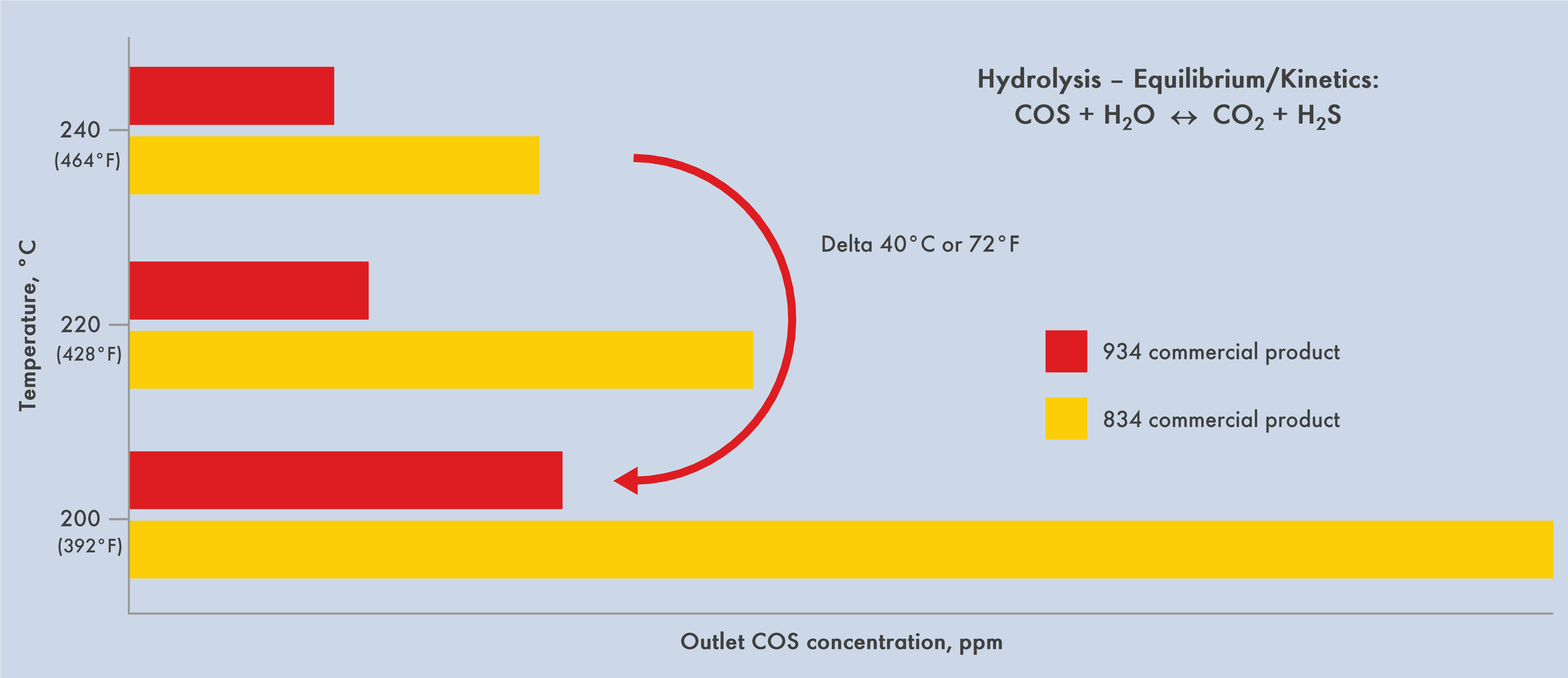
- Operating temperature: As low as 200°C – 392°F
- Highest activity, hydrogenation and hydrolysis performance
- Excellent pressure drop performance

- Operating temperature: as low as 220°C – 428°F
- High activity
- Excellent pressure drop performance

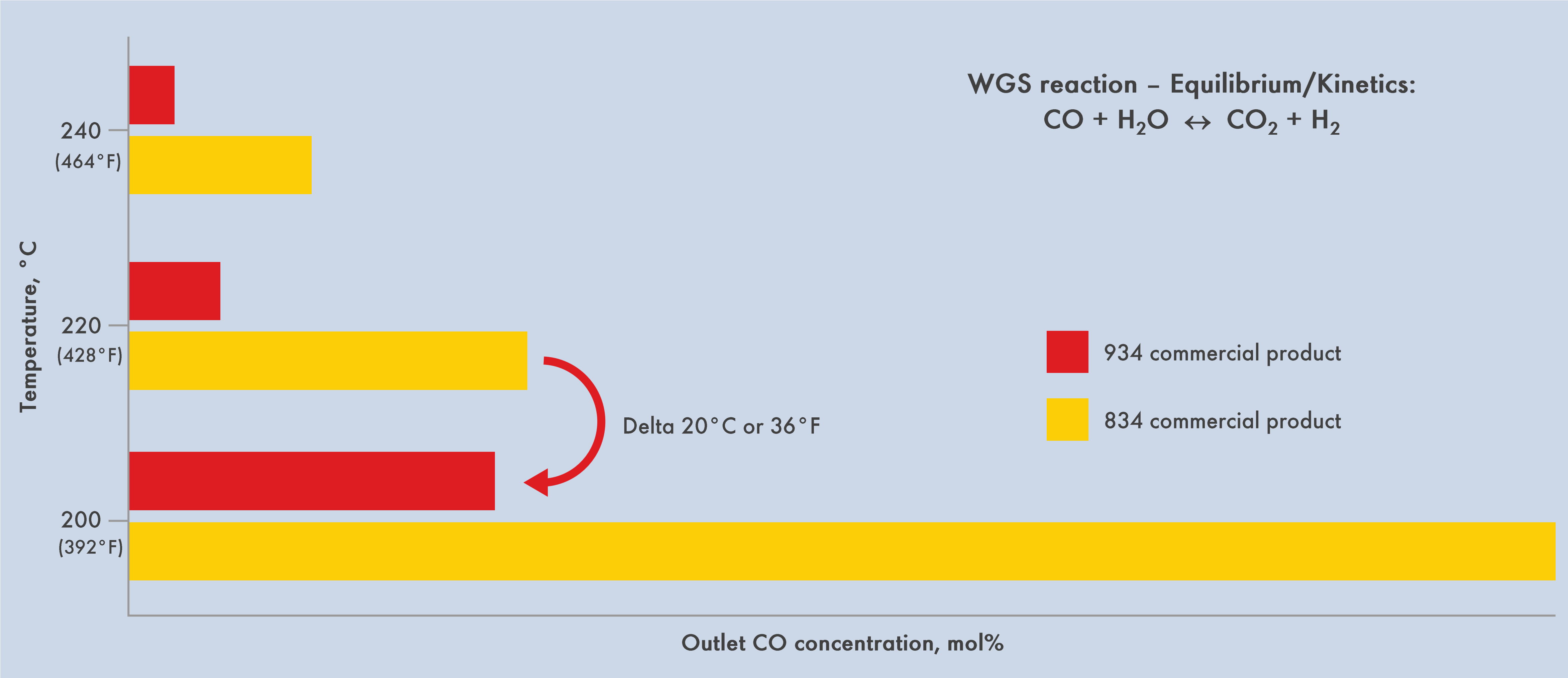
- Typical operating temperature: 240°C – 465°F
- Balances fill cost and activity
- Excellent pressure drop performance

- Typical operating temperature: 280°C – 540°F
- Suitable for in-line burner configurations
- Industry-leading pressure drop performance

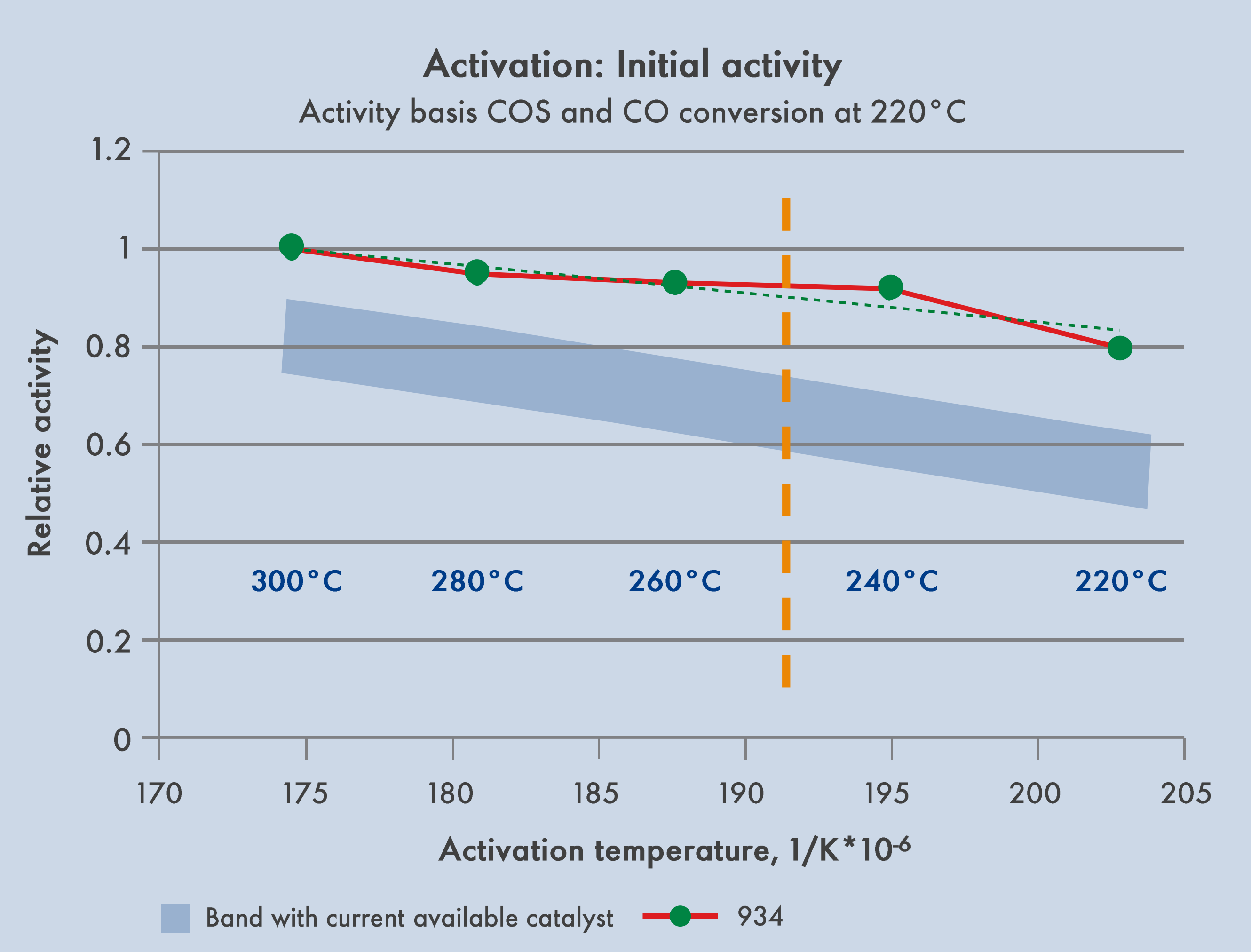
934 higher activity and higher selectivity for COS conversion

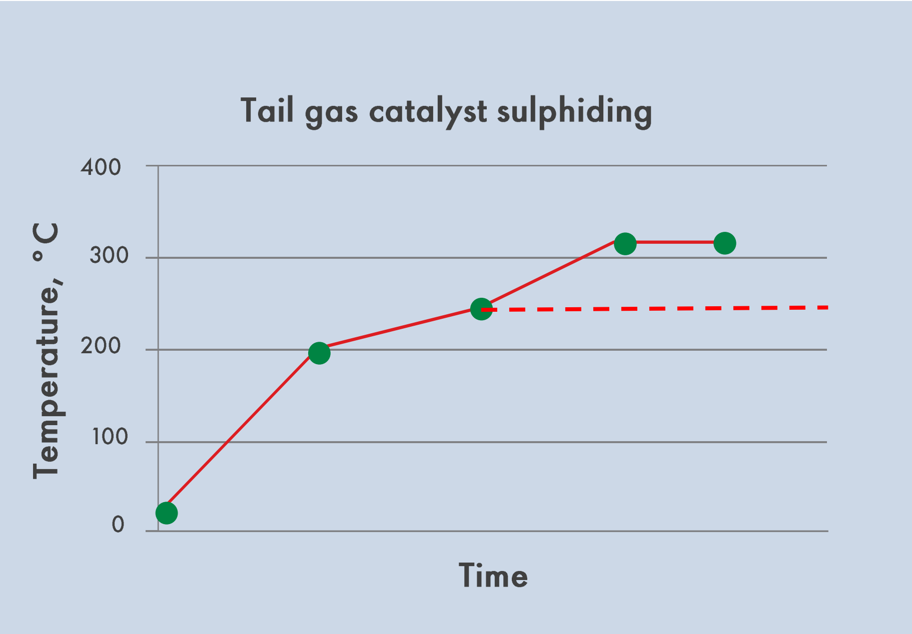


934 higher activity and higher selectivity for CO conversion



934 benefits from improved catalyst activation





- **Catalyst Sulfiding**
  - CoO + H_2S → CoS + H_2O
  - MoO_3 + $2H_2S$ + H_2 → MoS_2 + $3H_2O$

934 is likely to be a strong candidate for your unit if you...

...are able to operate at lower temperatures (Energy reduction)

...experience SO_2 emission issues from COS or CS_2 (Emission constraints)

...have tight limits on CO emissions (Emission constraints)

...are designing a new unit that operates at low temperature using steam or electrical heating (Greenfield)

...have an older type unit and the current burner can undergo a basic upgrade for operation at low temperature (Brownfield)

934 case study

Customer drivers

- Energy reduction target: >10% and reduce CO_2
- OPEX cost reduction target: 15%
- COS level EOR max 25 ppm
- Catalyst life cycle of 4 years

Results

- System can handle a 210°C RIT using 934
- Even at lower temperature the expected COS value at EOR will be met
- Lowering temperature from 240°C to 210°C reduces Energy consumption

Impact

- $221k/y fuel gas savings
- Reduced SOx emissions by lowering COS
- Reduced CO_2 emissions
- Reducing energy use

$

- Energy savings for four units $884k/y
- Energy and OPEX saving of 20.5%
- COS at EOR will be lower that 15 ppm

$

The takeaways

WHY?	To help refiners respond to ever-tighter emissions mandates, and other business drivers, we have been developing innovative tail-gas treating catalysts and processes for over 50 years because the environment matters
HOW?	Our catalyst development process is key: It helps us to generate ideas with a high probability of success, screen those ideas as quickly as possible, and extract as many learnings as possible from that data
WHAT?	Our portfolio of 234, 534 and 834 is designed to help meet a wide range of refiners' performance objectives, and we just launched 934, which offers a step change in activity
934	■ Operating temperatures as low as 200°C are possible; can help extend cycle life ■ Potential energy reductions of 20% (case specific) ■ higher hydrolysis performance, higher WGS, low pressure drop