Catalyst Testing in FCC Naphtha Hydrotreating

Key insights for smart selection

Cansu Mai | hte
Dan Miskin | Evonik

Who we are: hte in numbers

hte is the world leading solution provider for lab-scale R&D workflows

Clients from **38 countries** with **> 250 systems** delivered all over the world

Largest high throughput catalysis lab worldwide with **> 50 reactor units** and up to **1,000 reactors** running 24/7

> 350 employees with highly skilled scientists and engineers

Founded in 1999 in Heidelberg, Germany and **25 years of experience**

Financially sound & reliable ownership structure with BASF **since 2008**

Our approach

Downscaling commercial processes

Parallelization & automatization

Digitalization

High quality & commercially relevant data

Selected customer portfolio

Oil & Gas
bp, Chevron, ExxonMobil, IndianOil, JGC C&C, NESTE, PETROBRAS, REPSOL, saudi aramco, Shell, Sinopec, TotalEnergies

Refineries
bayernoil, CITGO, GC, idemitsu, MiRO, MOTIVA, MOLGROUP, NYNAS, OMV, Valero

Chemical
ARKEMA, EASTMAN, nic, sabic, SCA, SYNFUELS CHINA, VENATOR, YARA, BASF We create chemistry, Elevance Renewable Sciences, MITSUBISHI CHEMICAL, Sipchem, SOLVAY, TPC Group, VTT

Catalyst
ART Hydroprocessing, Axens, CLARIANT, CLG Chevron Lummus Global, EVONIK, Heraeus, Honeywell UOP, IFP Energies nouvelles, Ketjen, TOPSOE

Battery & Electrolysis
Chem4Batteries, Curtin University, JÜLICH Forschungszentrum, FUTURE BATTERY INDUSTRIES CRC, voltstorage, ZSW

hte technology for catalyst & process development

Technical Consulting

Catalyst Testing

Catalyst & Process Development

IDEATION	DISCOVERY	OPTIMIZATION	SCALE-UP

Workflow Analyses
Design and Feasibility Studies

High Throughput Reactor Systems

From 16-to 48-fold
Up to 10 ml
Powders / Shaped Materials

Active Material synthesis

Bench Scale Systems

From 4- to 16-fold
20 to 100 ml
Shaped Materials

From 4- to 8-fold
Up to 300 ml
Shaped Materials

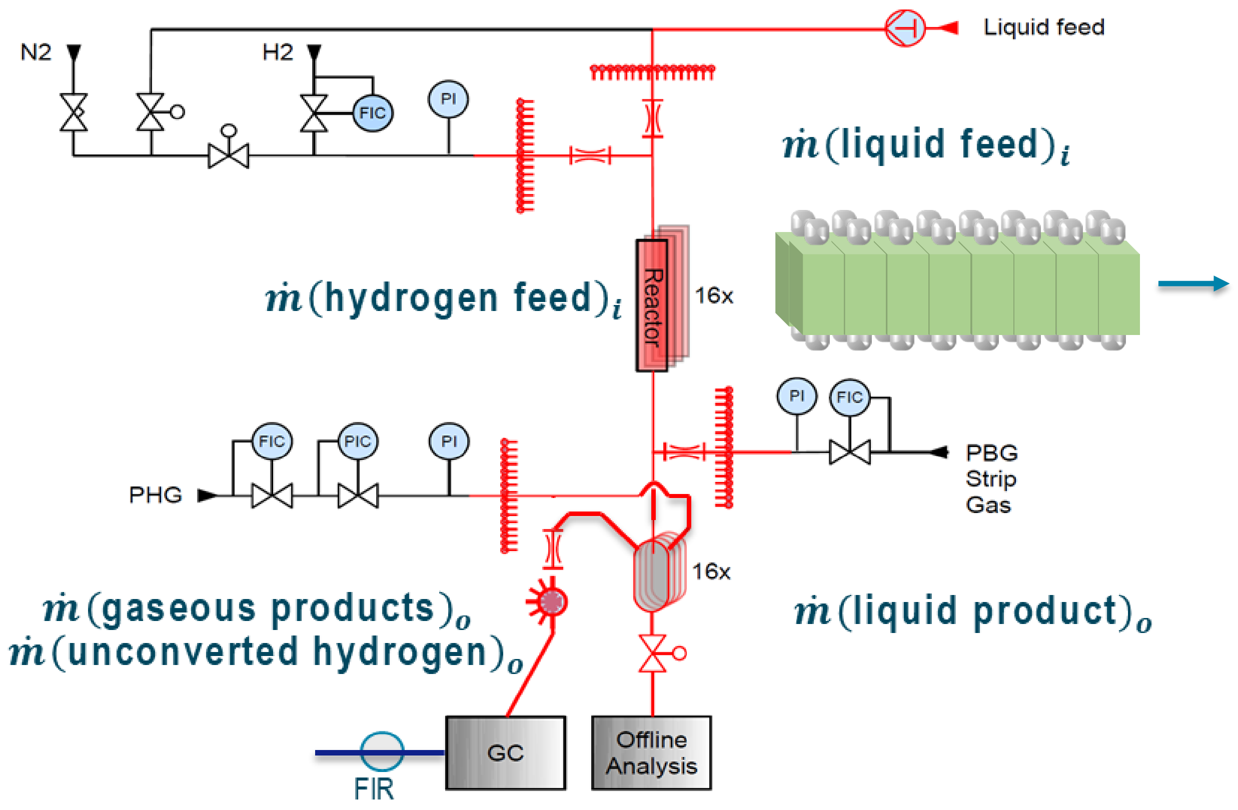
16/24-fold trickle bed reactor unit
Flexible tool for testing hydrocracking catalysts

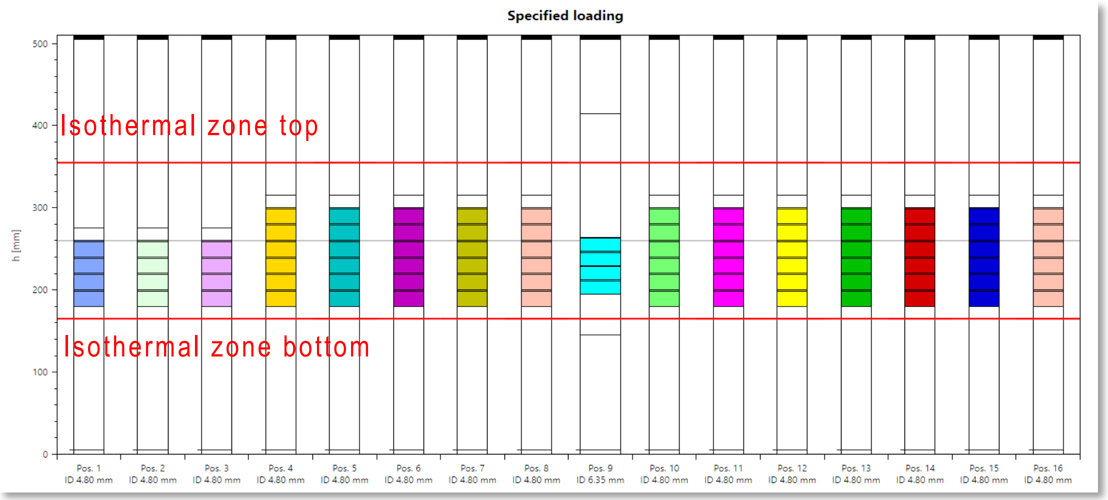
Parallelization	16 individual reactors or 8 x 2 reactors in series (= 8 x 3 reactors); interstage sampling and dosing
Temperature	• up to 450°C • 16 individual heating blocks
Pressure	15 to 260 bar
Catalyst volume	1-10 mL (Extrudates)
Feed requirements	~200 L/month operating 16 parallel trains
Product collection	~1 L of TLP for each reactor/week
Feeds	• H_2 feed gas, N_2 make-up gas • 1 or 2 liquid feeds • Diesel, VGO, resid, bio-based feed, etc.
Operation mode	Down or up flow, once-through, in series
Online analysis	Gas phase HC, H_2, H_2S, CO, CO_2
Offline analysis	SIMDIST, density, S, N...

Area of application	HDS, HDN, HDC, HDO, HDA, HDM, HydroIsom., Dewaxing, lubes, bio-feeds

Trickle bed test unit & reactor loading

General set-up



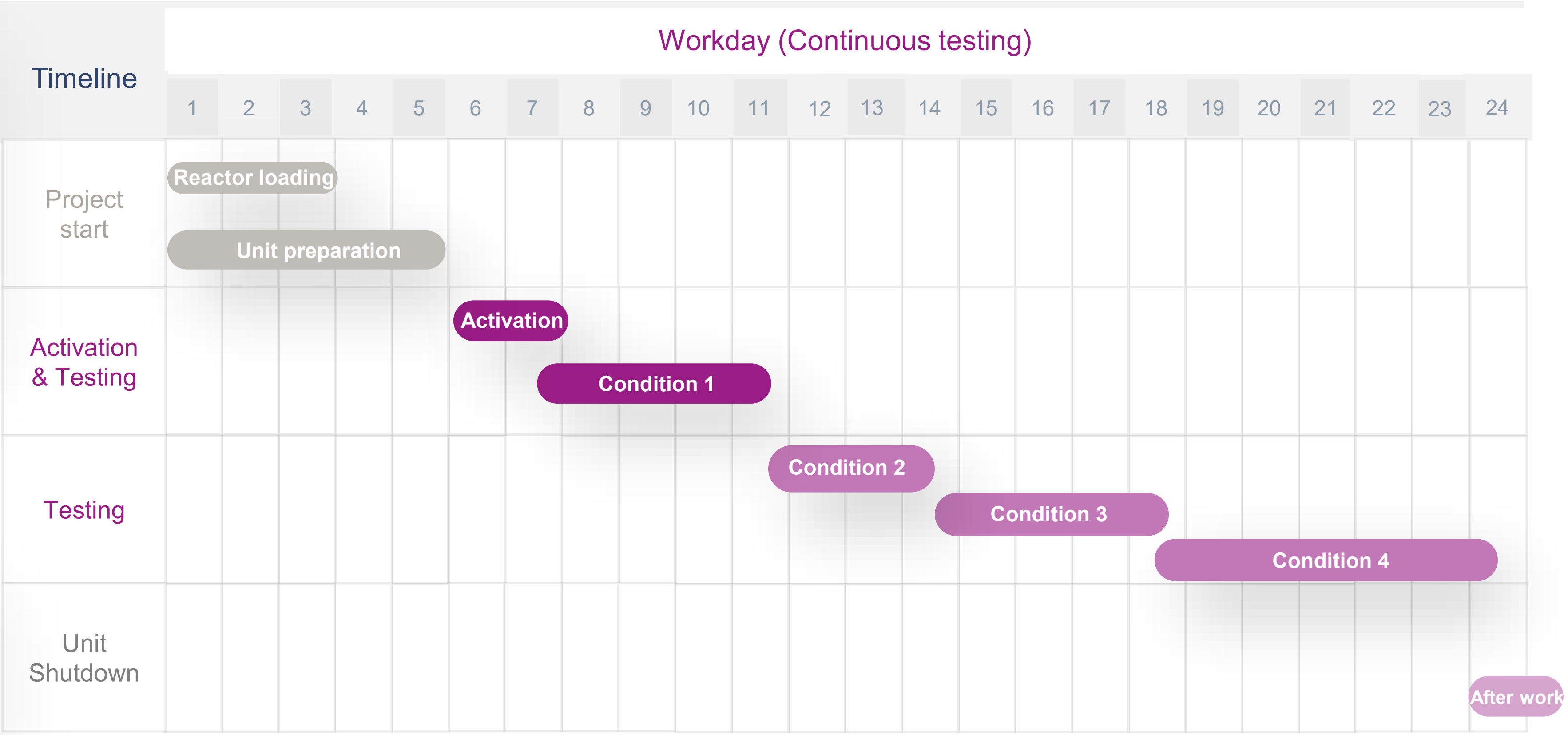


- **Catalyst extrudates of different sizes tested in**:
  - 15x 4.80mm and 1x 6.35mm trickle bed reactors
  - Individual capillary heating to adjust the pressure drop
- **12 Naphtha hydrotreating catalysts and 3 Selective hydrogenation catalysts** evaluated in parallel
  - Individual reactor heating system
  - Reactor temperature differences up to 150°C

Project timeline

- ○ ***6-8 weeks prior***
  - – Alignment on test protocol and reactor loading
  - – Catalyst and feed shipments

- ○ ***After stage***
  - – Final report issued
  - – Shipment of samples of interest



Case study - FCC naphtha hydrotreating
Balancing HDS activity with octane retention

➢ High HDS severity risks excessive hydrogenation, leading to octane loss and increased H_2 demand.

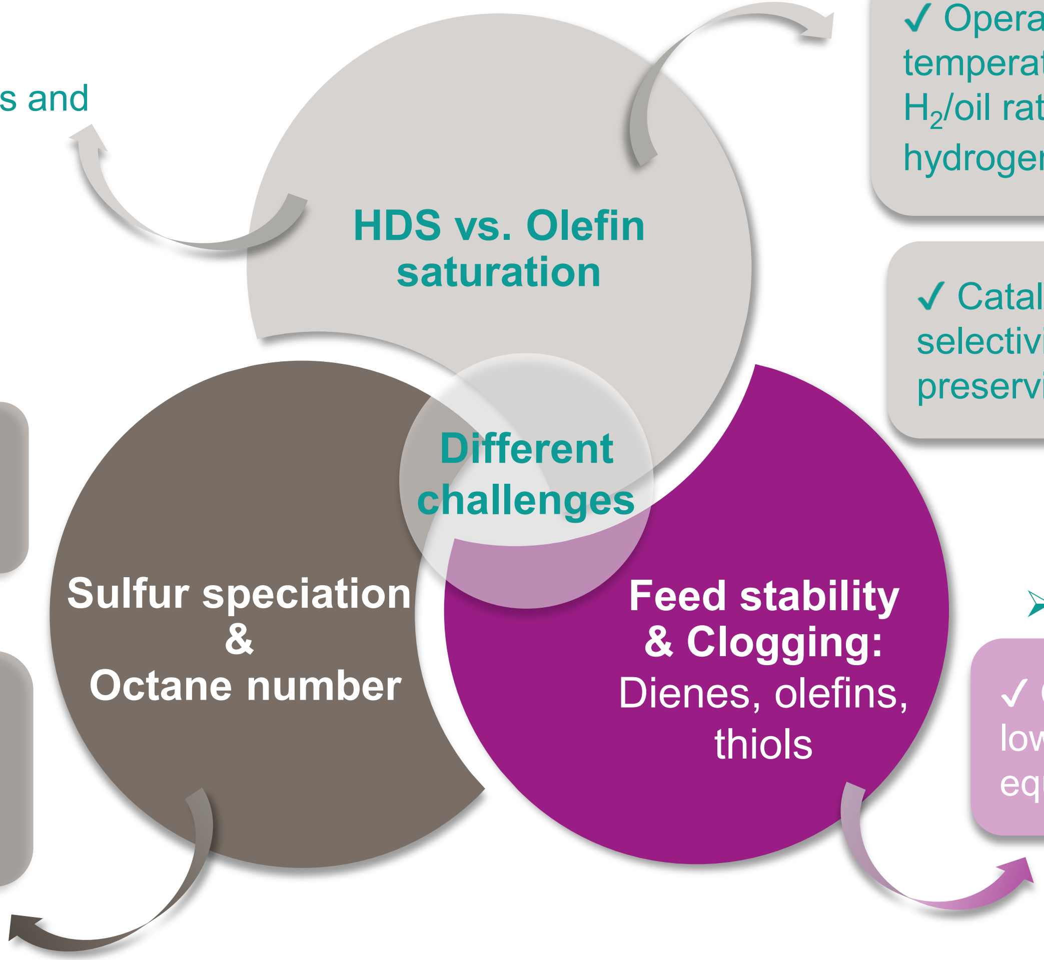
➢ Project specific advanced analytics

✓ Workflow for reactive sulfur species analysis: selective oxidation prep and SCD-based speciation

✓ Octane retention screening

Bromine number = *total unsaturation*

Maleic anhydride titration = selective reactivity of octane-contributing ***olefins*** and ***dienes***



✓ Operating conditions tuned to moderate temperatures (~140–310 °C) and optimized H_2/oil ratios (~320 Nm³/m³.h) to minimize hydrogen use.

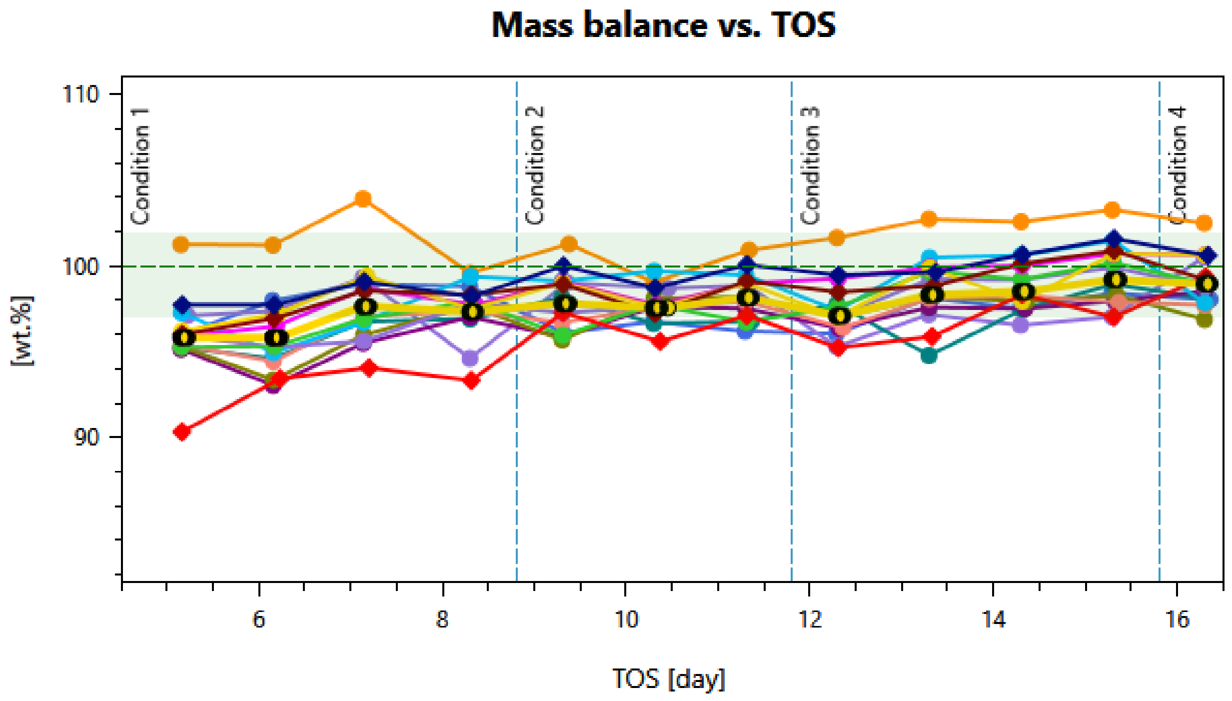
✓ Catalyst selection focused on high selectivity for thiophenic sulfur removal while preserving *olefins*.

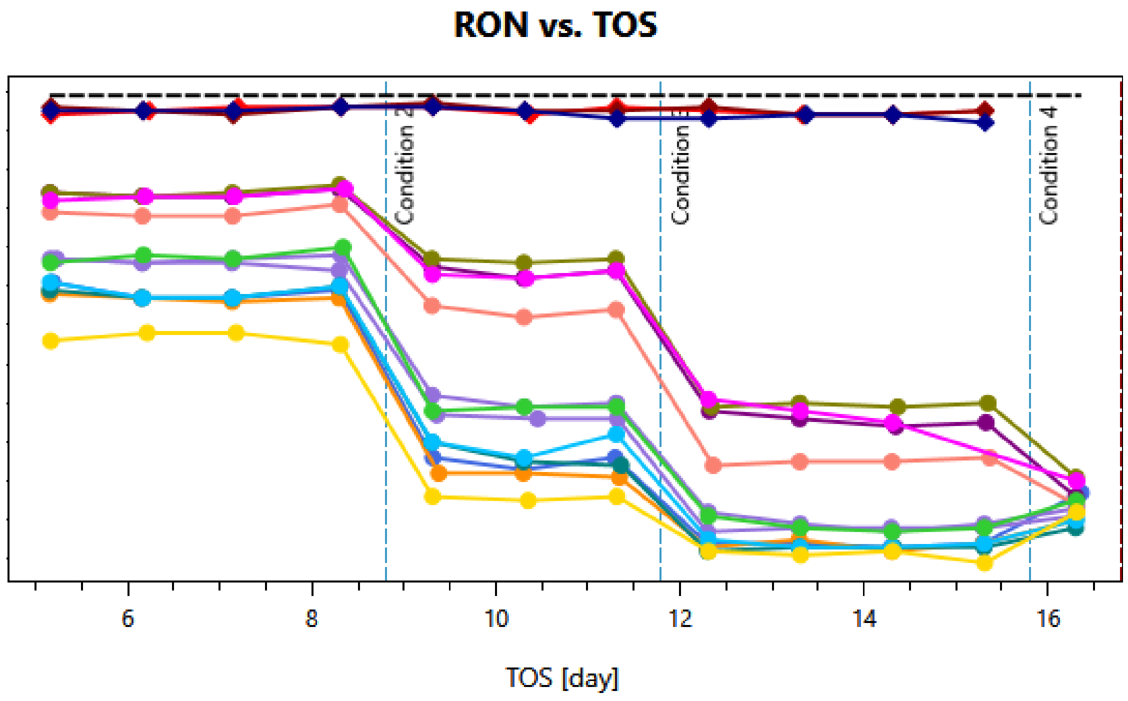
➢ Reactive feed handling

✓ Condenser temperatures were kept low (40–50 °C) to stabilize vapor–liquid equilibrium and minimize light-end losses

Results

Mass balance & RON

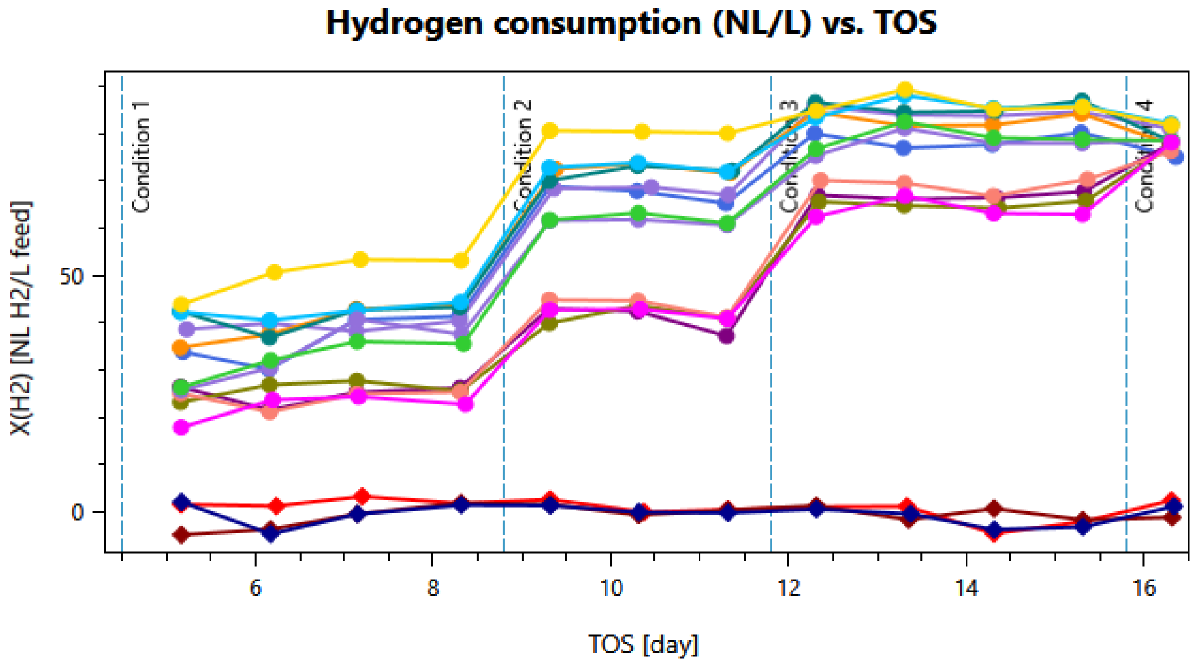


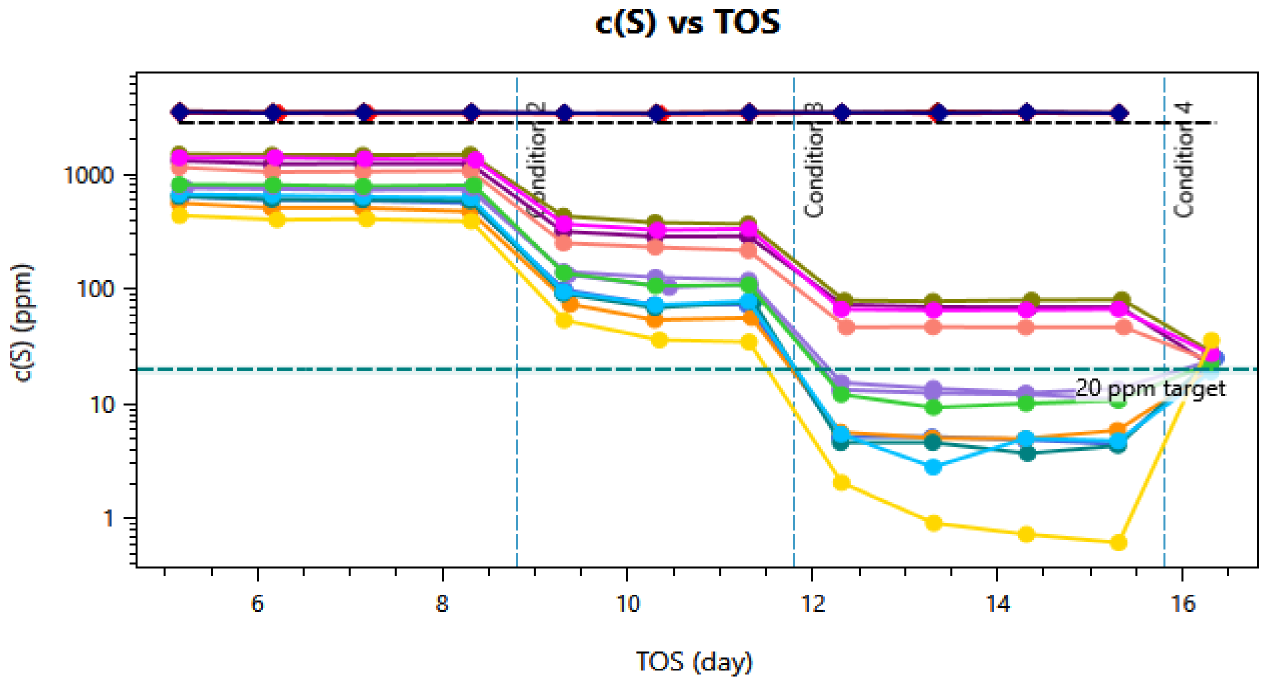


- Carbon mass balance accounted across gas and liquid phases, resulting in 100% (±3%) for most datapoints collected

- RON calculated from GC composition analysis
- Bromine number and maleic anhydride titration also performed throughout experiment conditions

Results
Hydrogen consumption & HDS

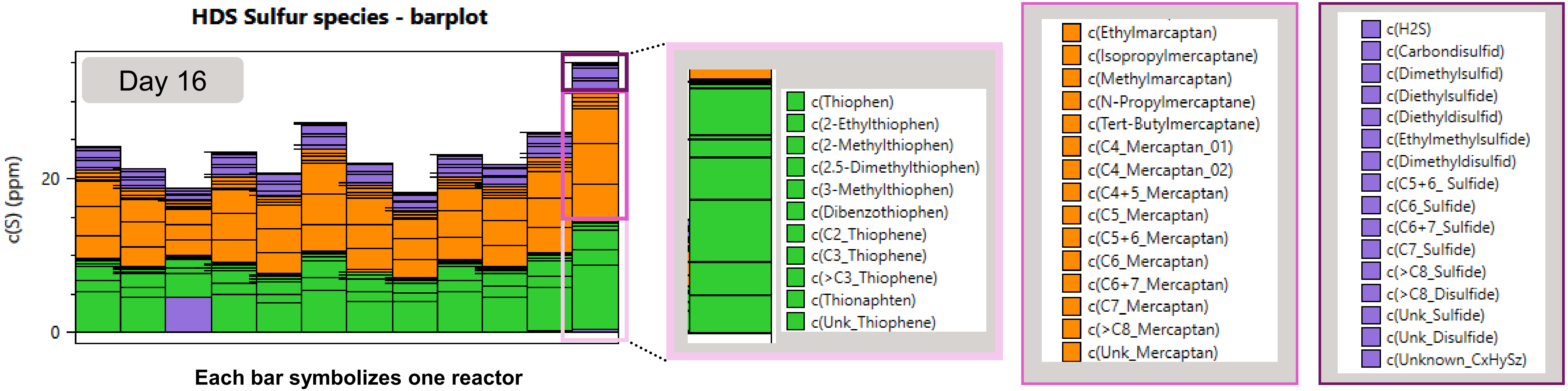




- Hydrogen consumption for SHU catalysts close to experimental error.
- HDS catalysts could be clearly differentiated in terms of H_2 consumption which correlated with catalyst activity

- Top performing catalysts reduced total sulfur below 20 ppm at the highest temperature of the screening program
- For the final test all catalysts were brought close to 20 ppm total sulfur concentration via individual reactor temperature control
- SHU reactors with slightly higher S in product concentration due to evaporation of light ends (quantified via GC)

Results
Sulfur speciation



- Sulfur speciation achieved GC-SCD analysis and sample derivatization to remove Mercaptanes and Sulfides;
  - The derivatization process involves a two-step selective oxidation, followed by sample work-up for analysis.
- Bottom purple block for H_2S still dissolved in sample

Summary

- **HDS activity & Octane retention**
  - Benchmarking OctaMax for HDS activity and octane retention
  - Deep HDS with minimal olefin saturation
- **Operational efficiency**
  - Dedicated pilot plant testing under realistic conditions
- **Sulfur speciation performed in liquid products**
  - Product Distribution: PIONA analysis of both vapor and liquid products
- **Advanced analytics:**
  - Validation of S conversion, yield, mass balance and octane retention

hte

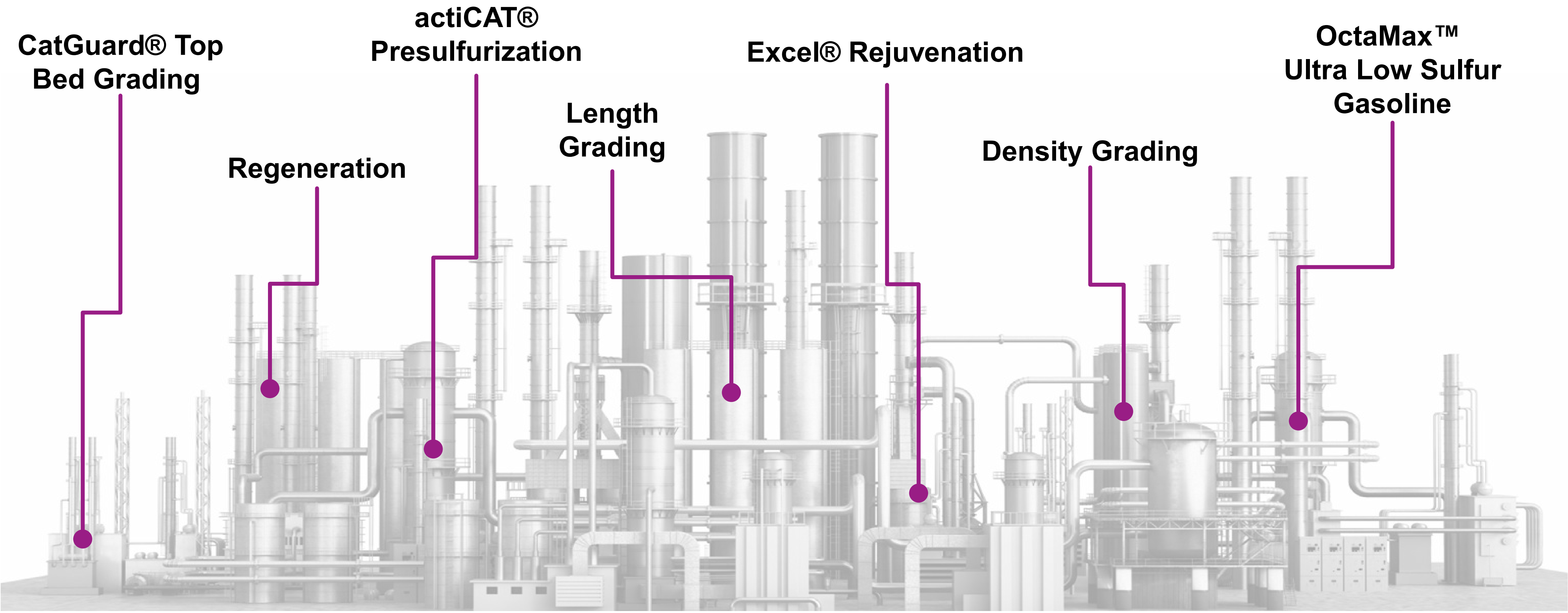
hte

EVONIK
Leading Beyond Chemistry

Evonik in figures

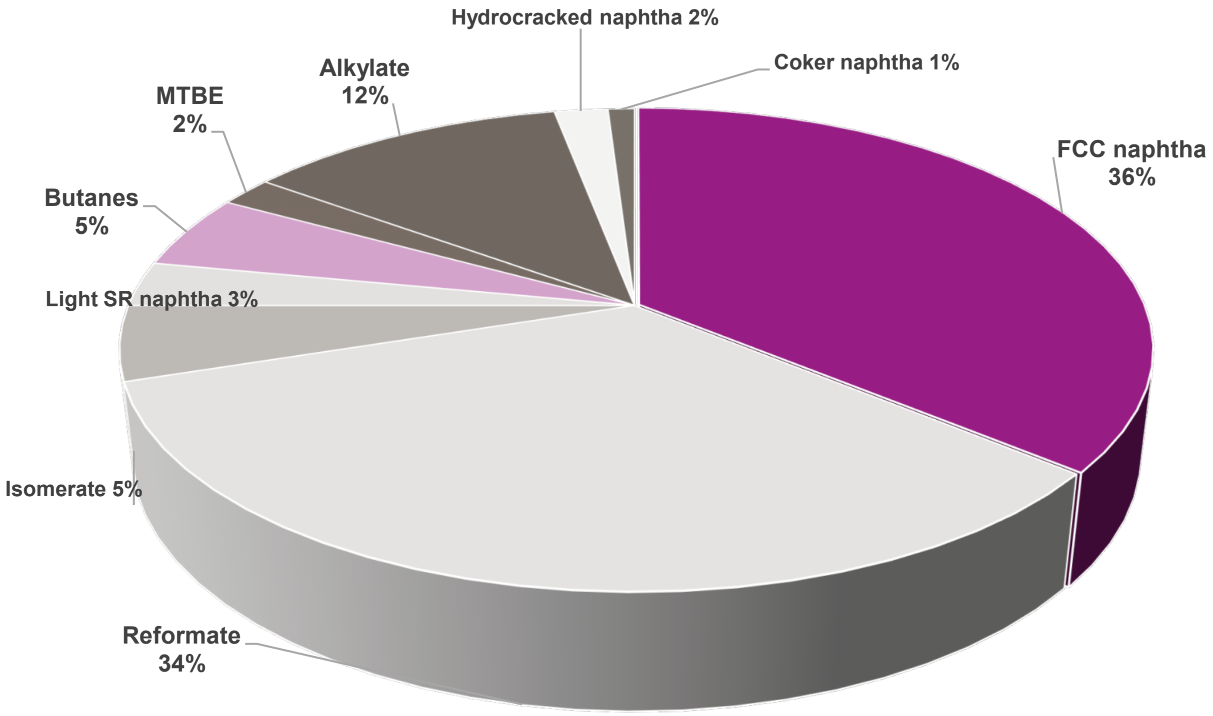
FINANCES	BUSINESS	INNOVATION	PEOPLE
€15.2 **billion** in sales generated by our company in the 2024 fiscal year.	**9,200** **products** in our portfolio – from ABIL® to NANOPOX® and ZETASPERSE®. **104** **production locations** ensure close proximity to customers and markets, whether in North America, South America, Europe or Asia.	**21,400** **patents** stand for Evonik's innovative spirit. Our first patent dates back to 1882/83. **€459** **million** invested in our company's research and development activities in 2024.	**32,000** **employees** represent 110 nations. Plenty of potential to develop tailor-made solutions for every market in the world.

Hydroprocessing Catalyst: Products & Services

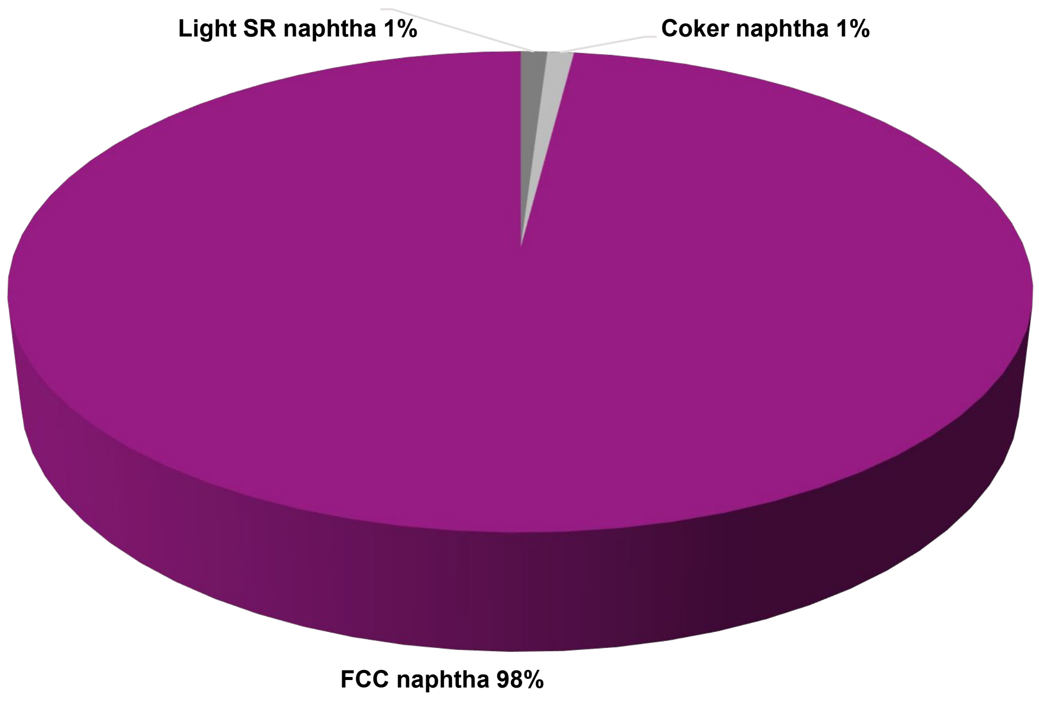


OctaMax: Typical Gasoline Pool Composition

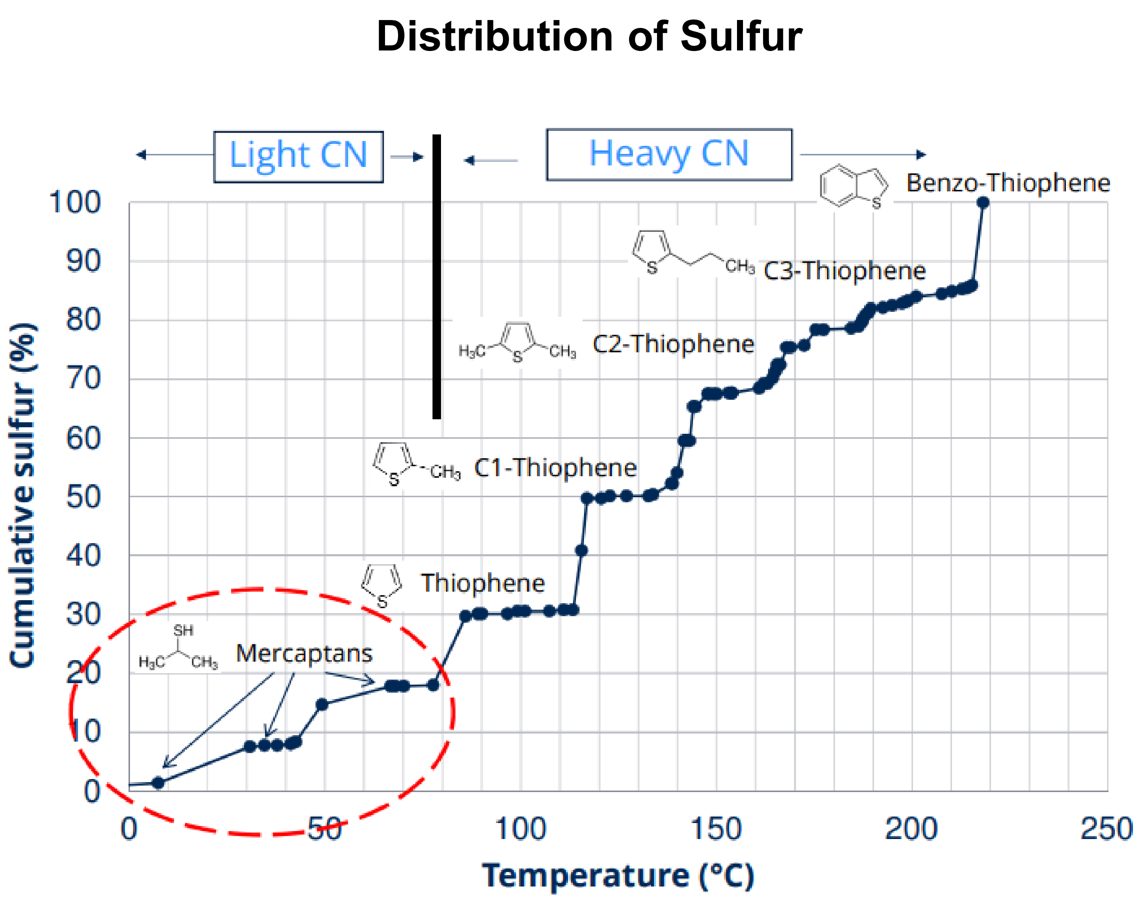
% Blend Stocks of Gasoline Pool

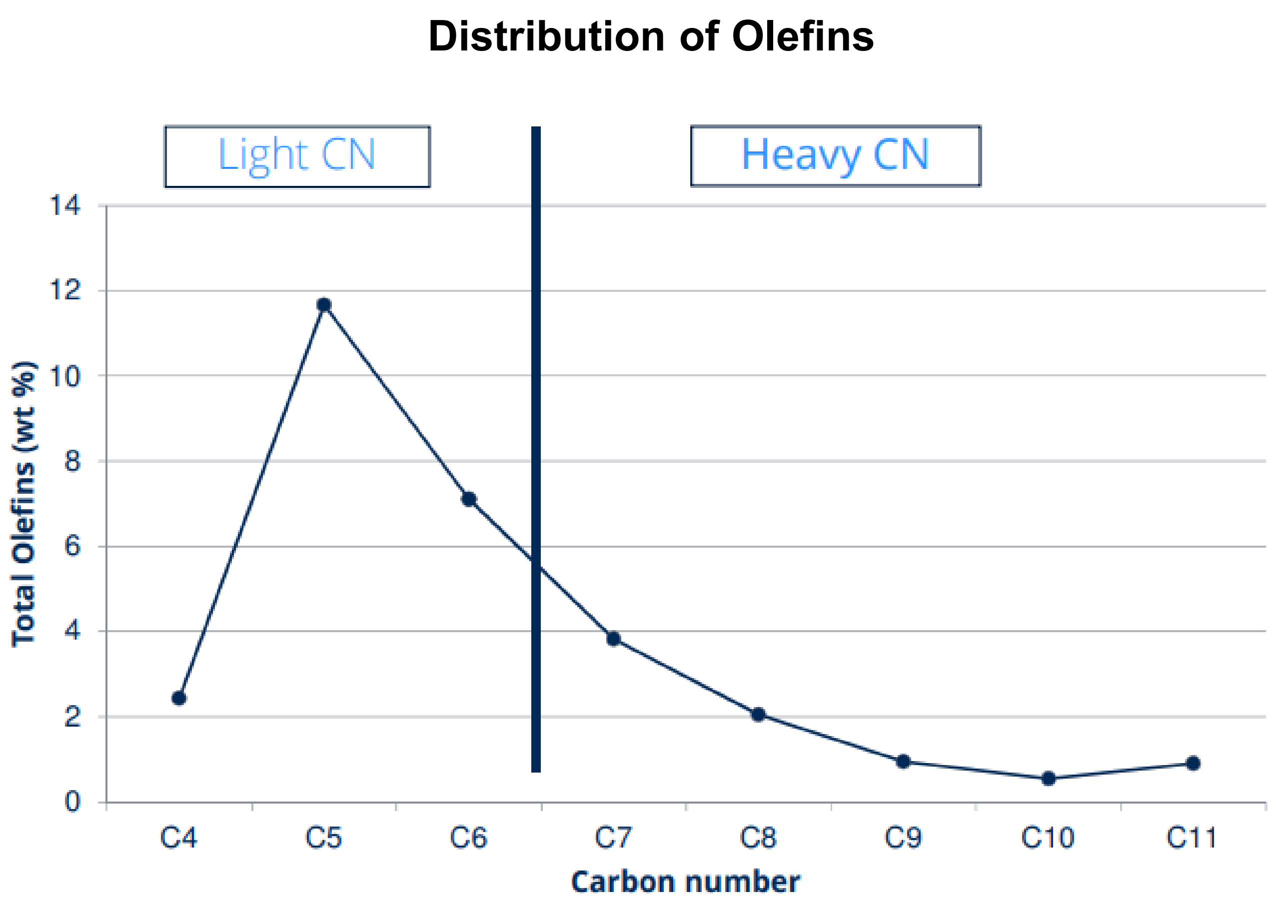


Distribution of Sulfur in Blend Stocks



OctaMax: Sulfur and Olefin Distribution in FCC-Naphtha



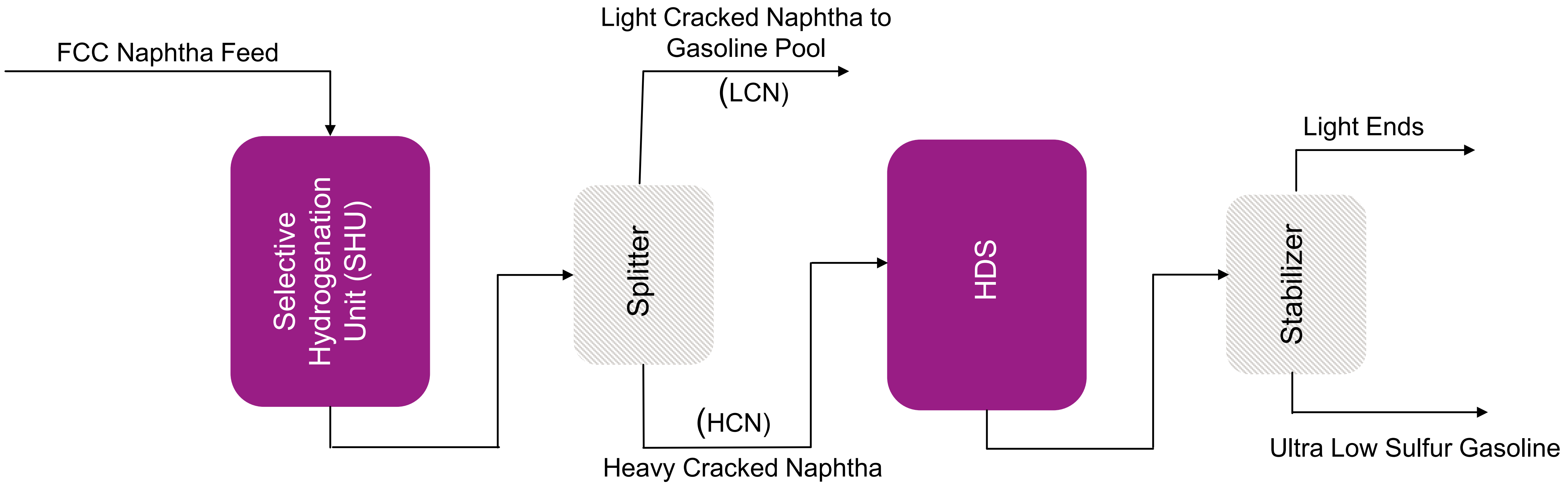


The goal is to minimize olefins saturation while deeply desulfurizing

hte

EVONIK Leading Beyond Chemistry

OctaMax: Typical Process Configuration of FCC Naphtha -HDS Units



SHU

- Always a NiMo catalyst
- Also known as Di-Olefin Reactor

HDS

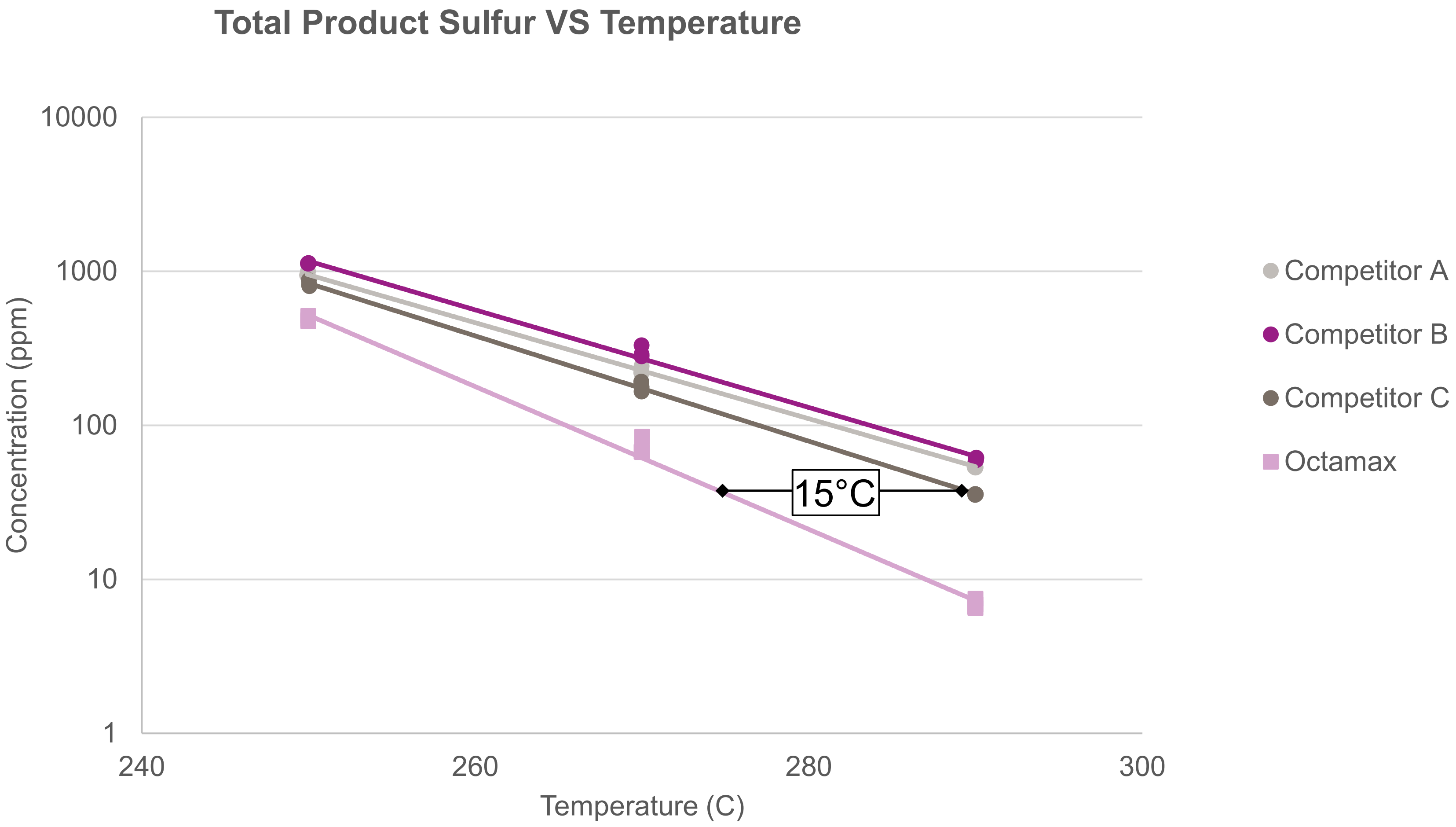
- Always a CoMo catalyst for HDS (and Ni catalyst for mercaptan recombination)
- Hydrodesulfurization. Reduce sulfur levels to allow gasoline pool blend to be <10wppm

Uniquely selected catalyst regenerated at optimal conditions for FCC naphtha HDS units

OctaMax™

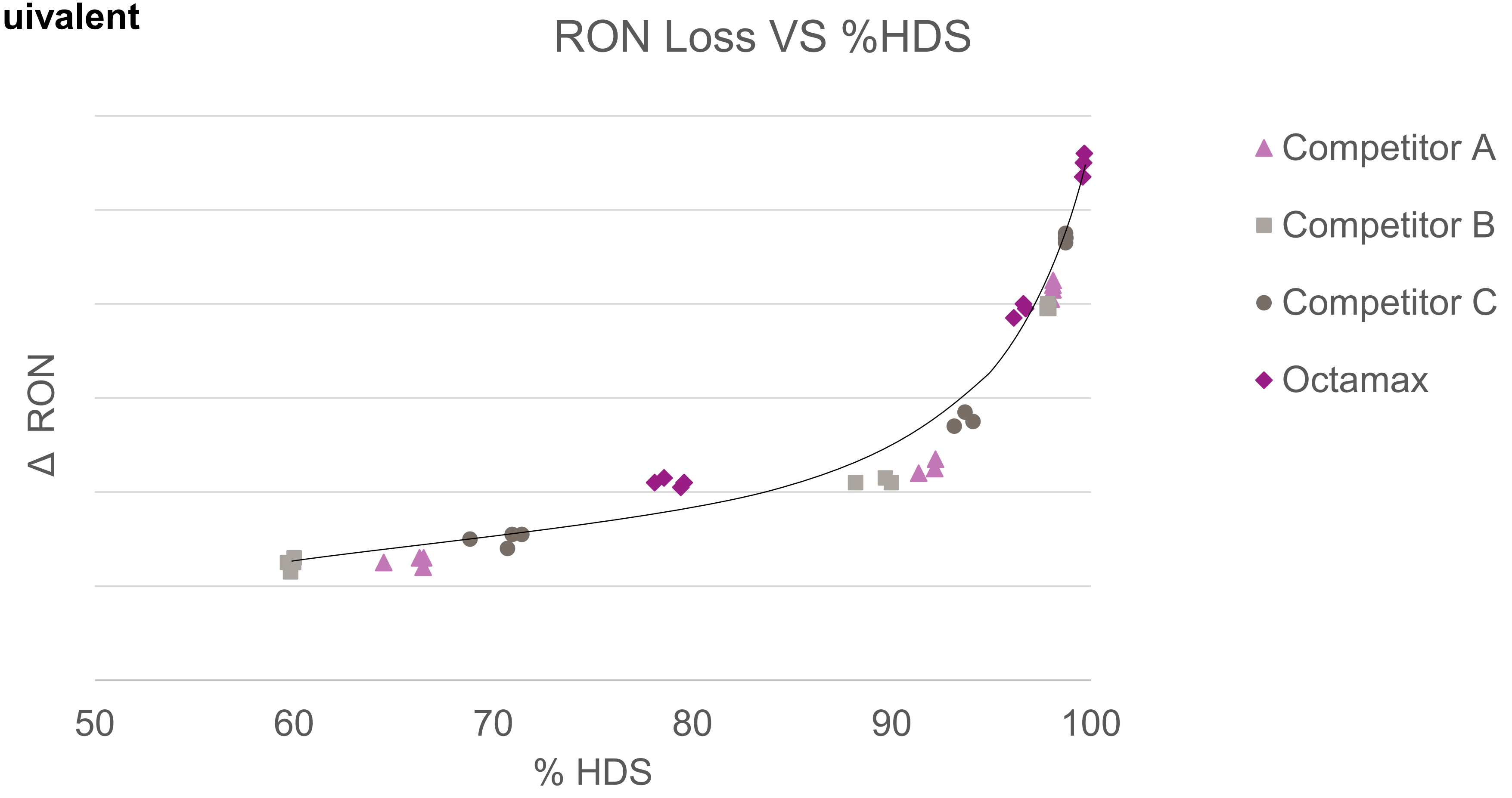
HDS vs. Temperature

- Competitor A, B, and C catalysts are the most commonly utilized FCC naphtha catalysts from three different manufacturers
- **OctaMax catalyst demonstrates significantly increased desulfurization activity**

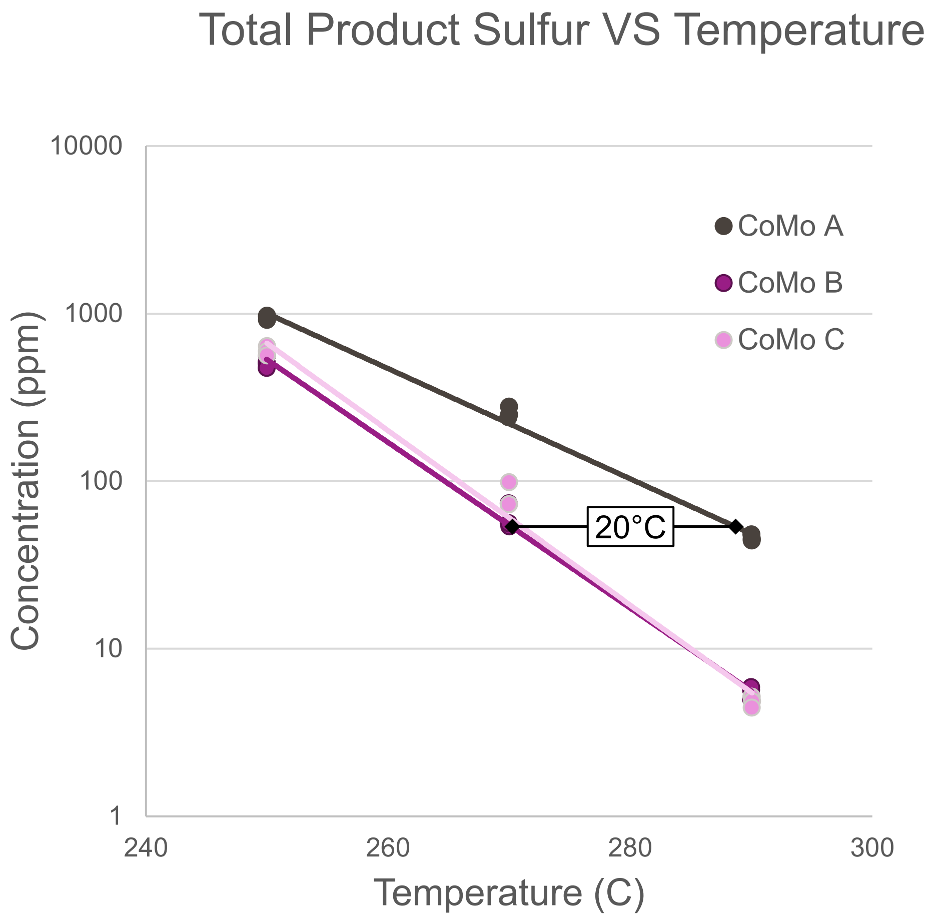


Selectivity

- **OctaMax demonstrates equivalent octane selectivity to fresh competitive catalysts.**



OctaMax Candidates



- Not all regenerated CoMo catalysts are equivalent for FCC naphtha desulfurization
- All CoMo catalysts in the graph met Evonik's standard internal specifications for regeneration for reuse
- CoMo A does not meet OctaMax specifications as it has significantly reduced desulfurization activity

Testing confirmed performance projections in our Technical Model

Able to Predict Typical Parameters
Able to predict typical parameters such as WABT requirements, hydrogen consumption, cycle length projections, and generate loading diagrams

Typical Parameters

Predict RON

Ability to Predict RON
Uniquely for this application, we also have the ability to predict RON loss

- Can model FCC naphtha post-treaters with or without an interstage splitter

Comparing Feed Slate Cases
With this information we can help our customers optimize run strategies by comparing different feed slate cases

Compare

Guarantee

Guarantee
All modeling is backed by a performance guarantees consistent with industry peers

Why this matters
OctaMax

Enhanced HDS activity

Advantages:

- Can treat more difficult feedstocks
- Increase feed rates
- Increase catalyst cycle lengths

Equivalent selectivity toward octane retention

Advantages:

- Flexibility to overtreat when economics are favorable

Lower fill cost

Advantages:

- Compared to fresh, OctaMax is a more cost effective catalyst

Sustainability benefits

Advantages:

- Reduced CO_{2e} compared to manufacturing fresh catalyst

Why Testing with hte is valuable

1

Reliable, independent testing institution

2

Ability to test a large number of catalyst systems simultaneously

3

Experience and assets to accurately test many different applications

4

Willingness to customize test set-up and analytical methods to precisely fit customers needs

5

Flexibility to alter plans mid-test to best capture the intended data

EVONIK
Leading Beyond Chemistry

&

hte