Impact of Sulphur Exposure on °Catalytic Stripper Performance

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26th ETH Nanoparticles Conference

Zürich, 21.06.2023

Why Sulphur Exposure?

Sulphur is stored in the catalyst and

reduces the catalytically active surface

→ performance loss

Regeneration should be possible

How long does a °Catalytic **Stripper** work in sulphurous conditions?

When should it be serviced?

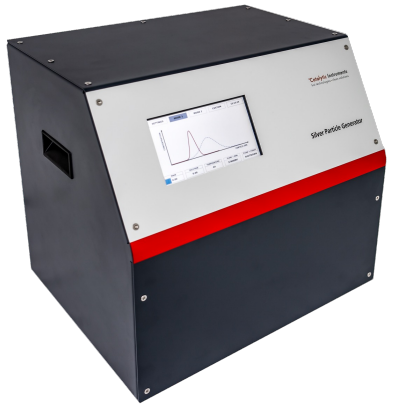
Test Methods

State of the art:

- °Catalytic **Stripper** is checked with **tetracontane** particles as defined by PMP
  - ✓ > 99.0% vaporisation of 30 nm tetracontane particles with an inlet concentration of ≥ 10,000 cm^{-3} ✓ (23 nm GTR)
  - ✓ > 99.9% vaporisation of tetracontane particles with a CMD > 50 nm and a mass above 1 mg/m^3 (10 nm / Brakes GTR)

- Aerosol measurement equipment[+] and know-how necessary to perform this check

[+]we use our SPG as Tetracontane Generator – at a touch of a button



Wanted:

- Quick,
  - easy and
    - reliable method

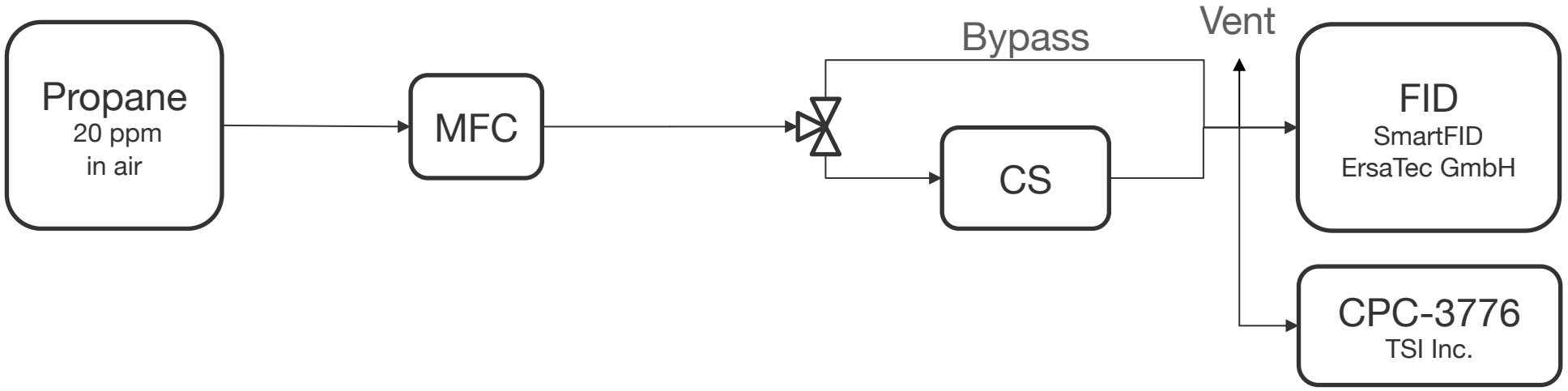
to check if °Catalytic **Stripper** is operational as designed and meets the above criteria

New Test Approach

Propane Oxidation Efficiency Measurement (**POEM**)

- Propane (C_3H_8)
  - Gaseous hydrocarbon
  - Low-cost
  - Easily available as calibration gas bottle
  - Bottle concentration is constant
  - Easy to detect with FID

Experimental Setup - POEM

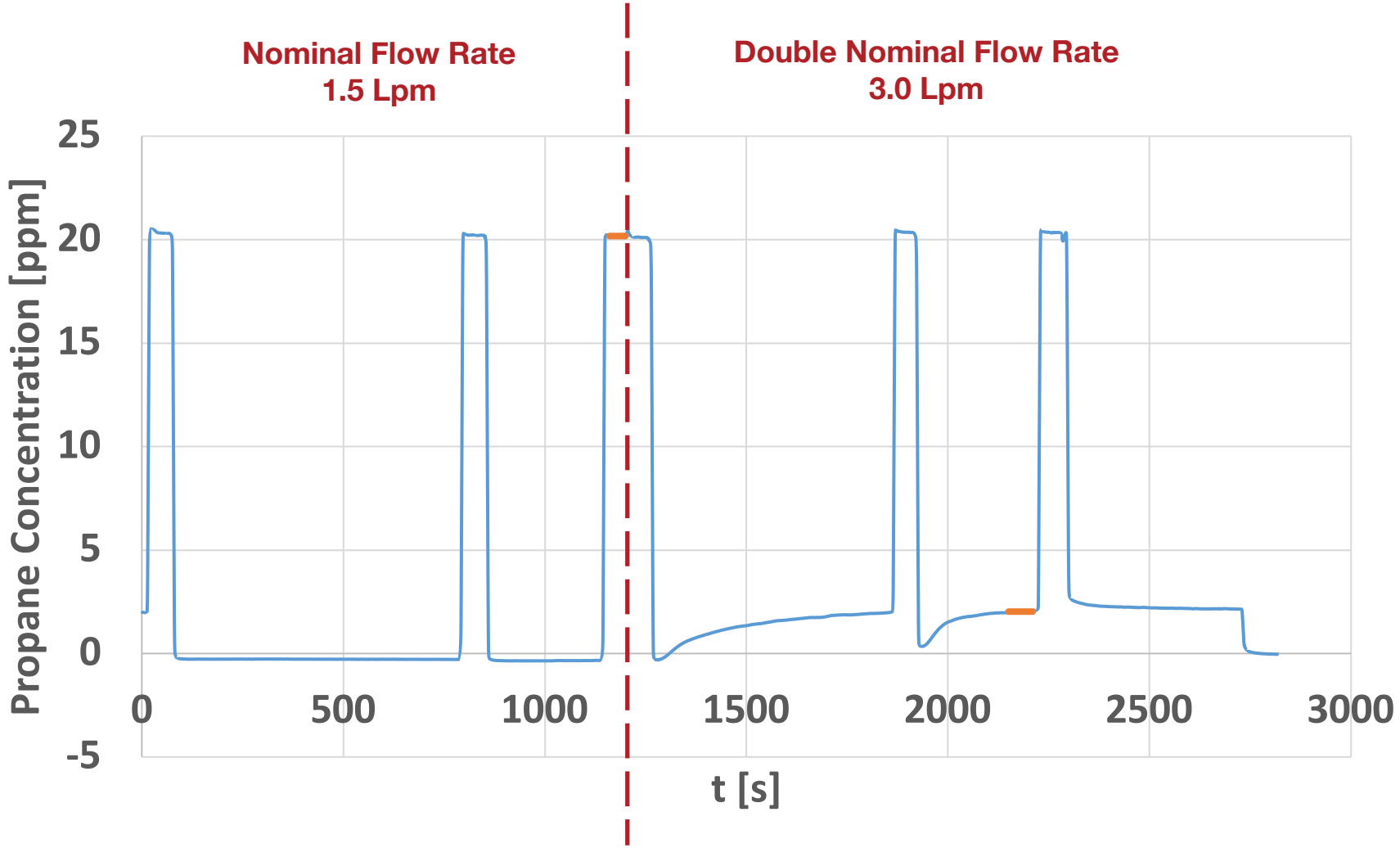


Tasks:

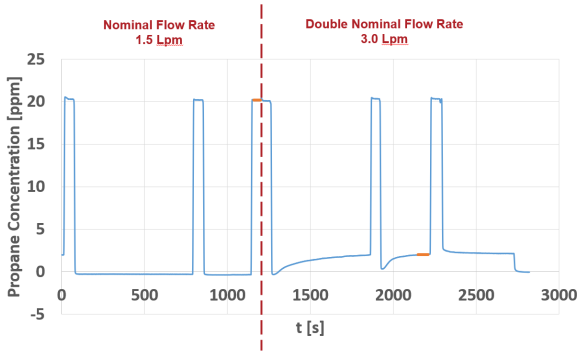
- Find suitable propane concentration
- Characterise new °Catalytic Stripper
- Expose °Catalytic Stripper to sulphur
- Evaluate sulphur-exposed °Catalytic Stripper

Comparison of 3 New CS015

CS015
1.5 Lpm



Comparison of 3 New CS015

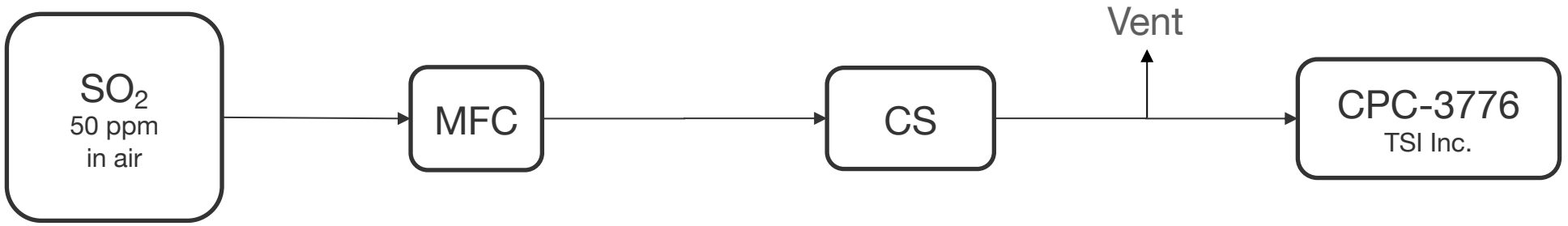


Device	Eta_nominal [%]	Eta_Double [%]
CS015 #1	100	90
CS015 #2	100	94
CS015 #3	100	93

→ **Performance of three similar CS015 at double nominal flow is similar**

- No particle emission observed

Experimental Setup – Sulphur Exposure



Tasks:

- Expose the °Catalytic **Stripper** to sulphur from SO_2 gas (50 ppm SO_2 in air)
  - 3 x 1h SO_2 exposure, POEM and tetracontane testing in between
- Calculate exposed sulphur mass with known concentration and flow rate of SO_2
- Calculate emulated operating time with assumptions regarding fuel, engine operating point, dilution

Performance after Sulphur Exposure

[%]	After **1x 1h of SO2**, i. e. 1.24 g/L		After **2x 1h of SO2**, i. e. 2.48 g/L		After **3x 1h of SO2**, i. e. 3.72 g/L	
Device	Eta_POEM	Eta_Tetracontane	Eta_POEM	Eta_Tetracontane	Eta_POEM	Eta_Tetracontane
CS015 #1	100	99.999	100	99.998	100	99.965
CS015 #3	100	99.999	100	99.990	100	99.566

PMP Limit: 99.9%

Particle emission observations:

- CS015 #1:
  - No PN emission during SO_2 exposure and POEM, minor tetracontane PN
- CS015 #3:
  - Increasing PN emission (1E3/cm³) during last minutes of 3rd SO_2 exposure
  - Large PN emission (2E4/cm³) during 3rd POEM for CS015 #3
  - Very large PN emission (5E5/cc) after tetracontane test, sampling ambient air

Conclusions:

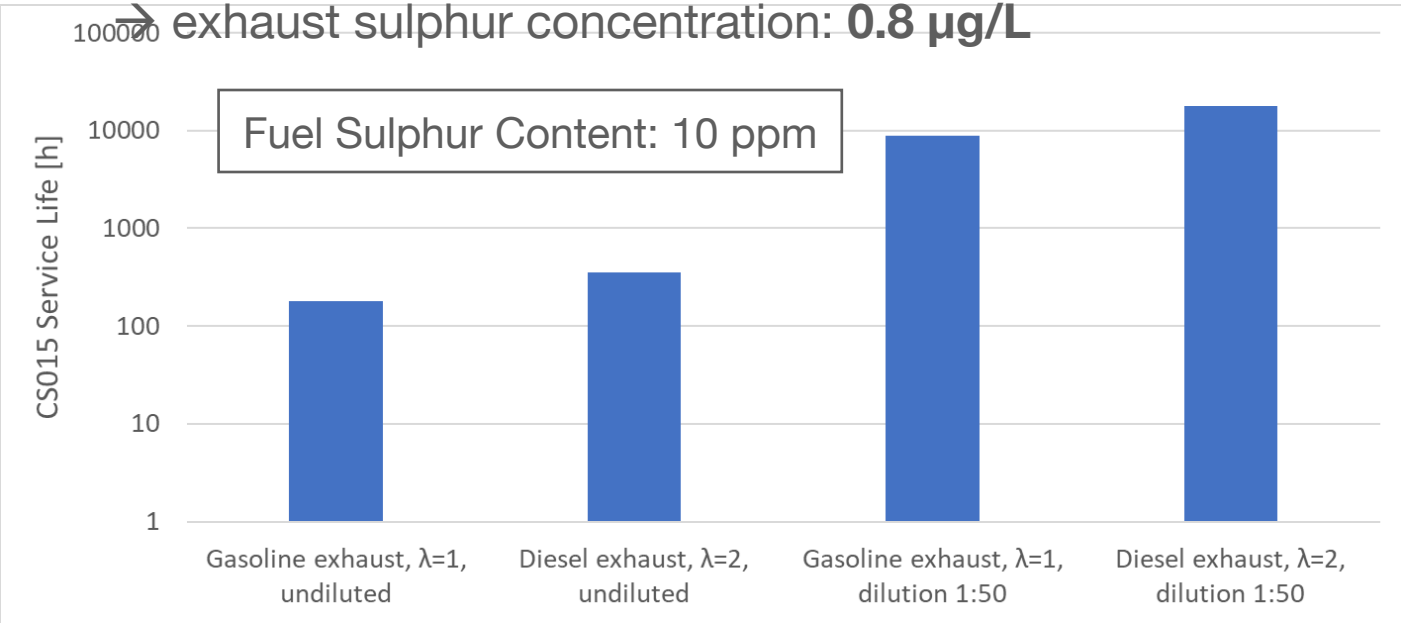
- POEM in this configuration not sensitive enough
- **Both CS015 can be safely used up to 2.5 g/L sulphur loading** (gram sulphur per liter catalyst)

Estimating CS015 Service Life

Assumptions for calculating exhaust sulphur content:

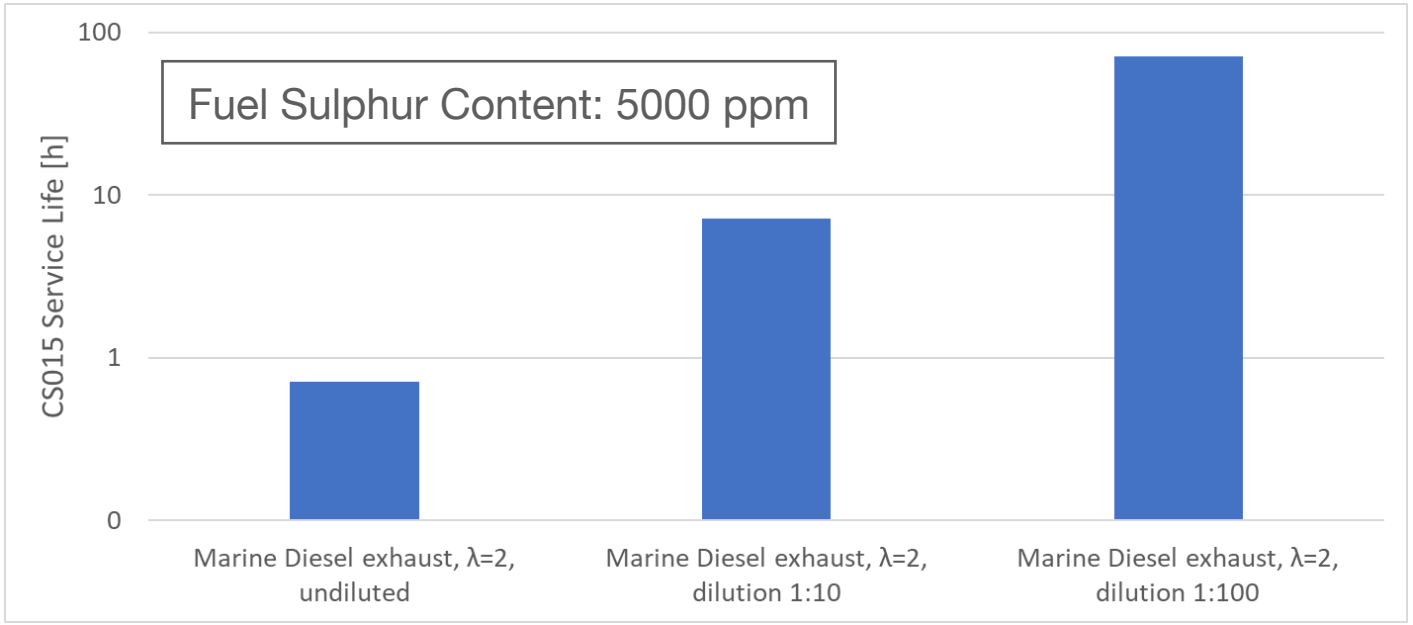
- Complete, stoichiometric (λ = 1) combustion of octane
- No sulphur contribution from engine oil
- 10 ppm fuel sulphur content

→ exhaust sulphur concentration: **0.8 µg/L**



- Decent service life even without dilution
- Typical PMP-compliant systems use 1:50 to 1:100 dilution before CS, extending service life to years

Estimating CS015 Service Life

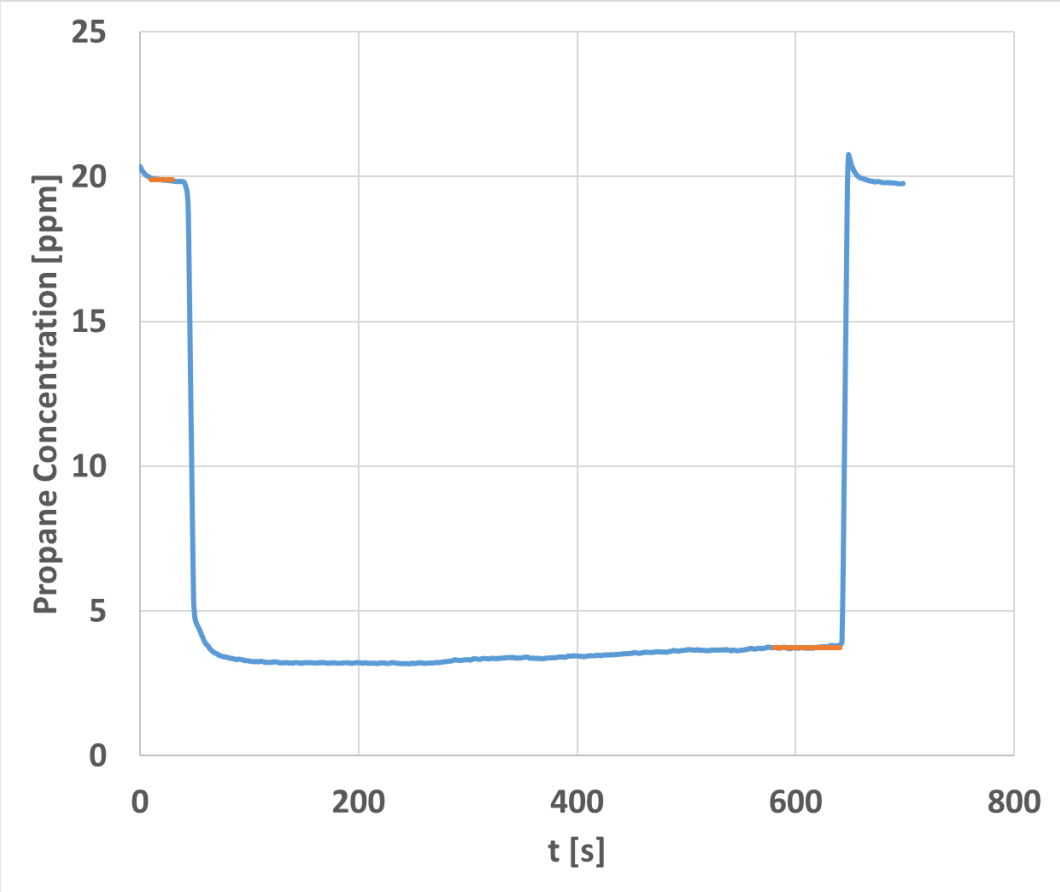


Marine fuel sulphur content 5000 ppm:

- Raw exhaust is very challenging
- High dilution factors are recommended
- Sulphur exposure should be roughly estimated and monitored
- PN emission should be checked from time to time

Successful Regeneration

CS015 #2 was SO_2-exposed for
1x 5h / 6.2 g/L = sulphur poisoned!



eta_POEM = **81%**

eta_Tetracontane = **0%**

PN emission of **3E7/cm³**

90 min of
0.3 Lpm Camping Gas
+
1.2 Lpm N2

@ 600 °C

Tetracontane test = 100 %,
zero particles measured

(POEM not performed)

Summary

Propane oxidation efficiency measurement is a quick and easy approach

- Sensitivity needs to be increased
- PN should be measured in parallel

SO_2-exposure enables service life estimation:

- A °Catalytic **Stripper** CS015 has a service life of several thousand hours in typical automotive applications
- High sulphur applications should roughly estimate sulphur exposure and use high dilutions

Confirmation that sulphur-impaired °Catalytic **Stripper** can be regenerated

Outlook

Increase POEM sensitivity

Test more °Catalytic **Strippers** for statistically robust results

More detailed investigation of how to best regenerate a °Catalytic **Stripper**

Investigate phenomenon “self-regeneration”

Investigate whether regeneration fully removes sulphur, or residual sulphur impairs CS performance in a way that replacement is necessary at some point

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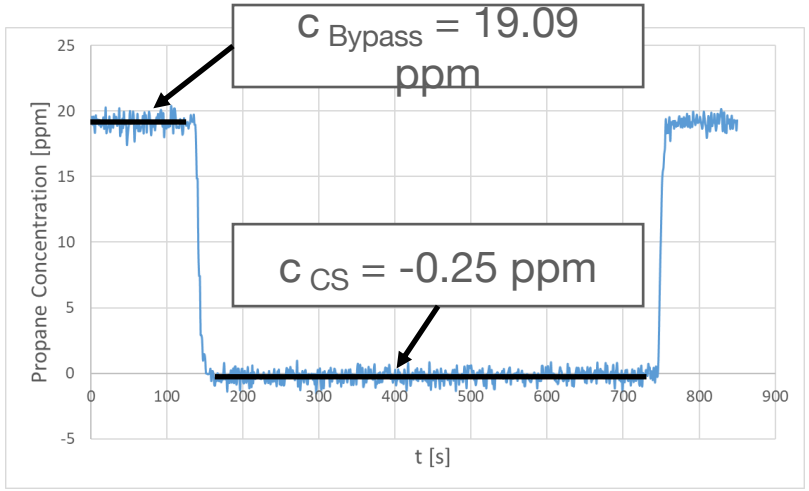
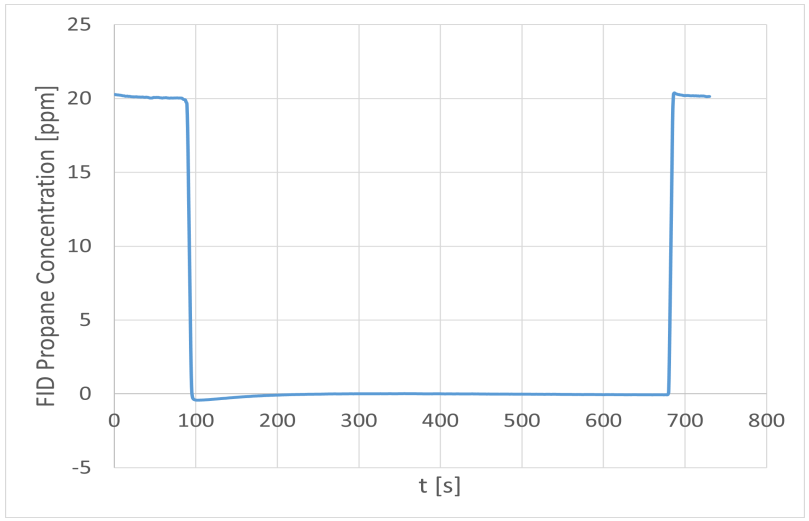
Appendix

Results: FTIR vs. FID



FTIR



FID

FID has much better Signal-to-Noise ratio

= it is better suited for the task of measuring a single chemical component

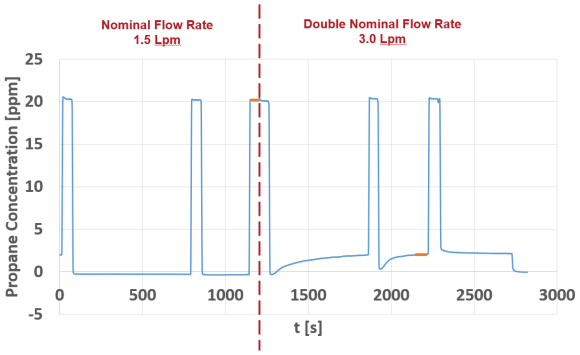
Oxidation Efficiency Calculation:

$$\eta = 1 - \frac{c_{CS}}{c_{Bypass}}$$

Error calculation:

Mean + SD → Error Propagation
→ ± σ

Comparison of 3 Similar CS015



Device	Eta_nominal [%]	Eta_Double [%]
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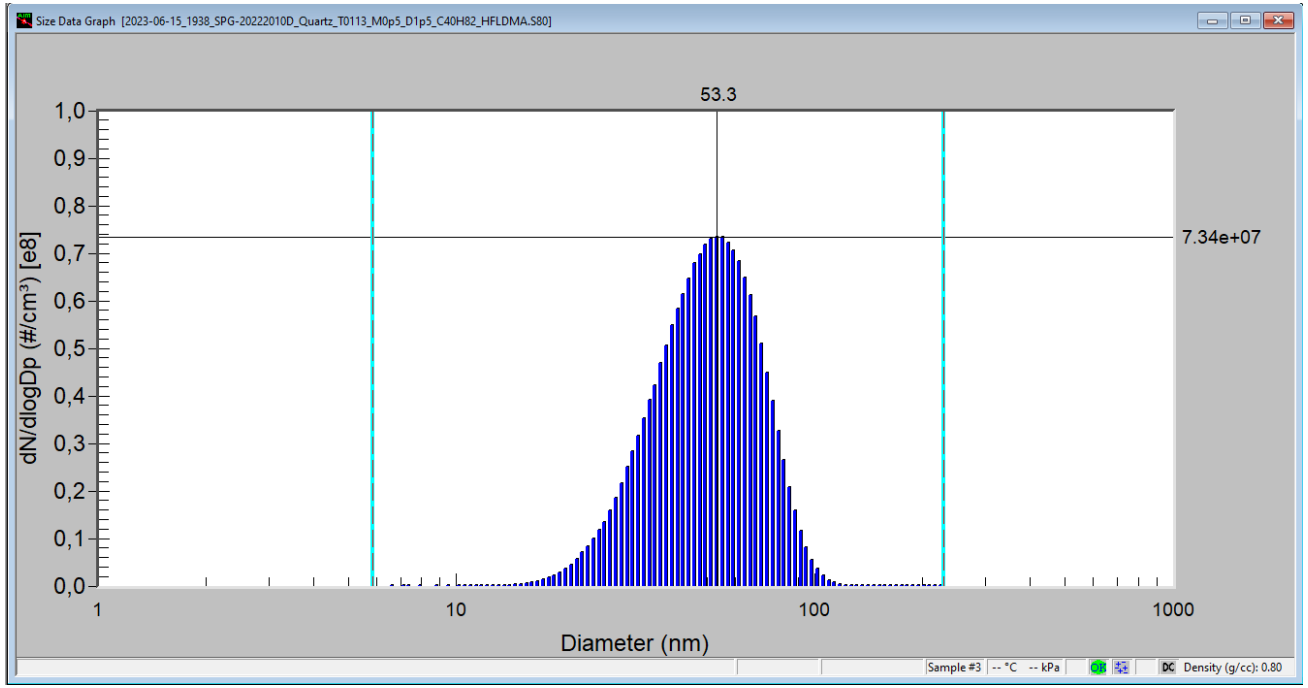
- Why all 100%?
  - FID zero calibration is done with thermodenuder = removes less HC than CS = CS below zero level
  - 20 ppm propane not challenging enough?

    → FID with catalyst for zero gas is ordered

→ **Performance of three similar CS015 at double nominal flow is similar**

- No particle emission observed

Example Tetracontane PSD



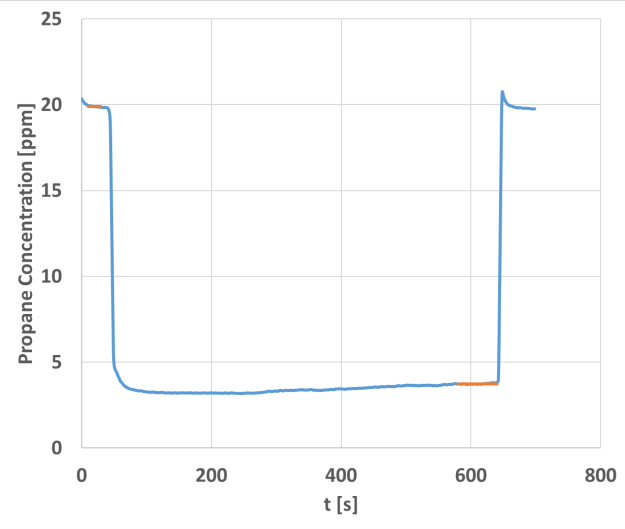
Statistics Table [2023-06-15_1938_SPG-20222010D_Quartz_T0113_M0p5_D1p5_C40H82_HFLDMA.S80]

	Number Particle Size	Diameter Particle Size	Surface Particle Size	Volume Particle Size	Mass Particle Size
Median (nm)	50.5	56.3	61.7	66.5	66.5
Mean (nm)	51.9	57.2	62.3	67.0	67.0
Geo. Mean (nm)	49.2	54.6	59.8	64.7	64.7
Mode (nm)	53.3	61.5	66.1	71.0	71.0
Geo. St. Dev.	1.40	1.37	1.34	1.31	1.31
Total Conc.	2.74e+07(#/cm³)	1.42e+03(mm/cm³)	2.56e+11(nm²/cm³)	2.65e+12(nm³/cm³)	2.12e+03(µg/m³)

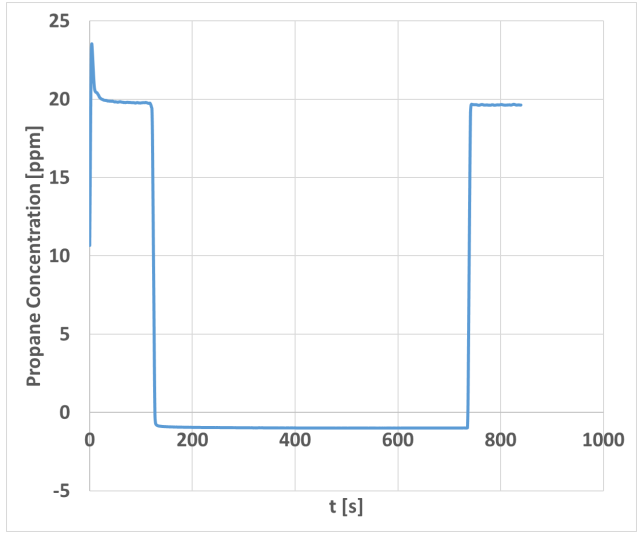
Sample #3 -- °C -- kPa DC Density (g/cc): 0.80

Self-Regeneration?

CS015 #2 was SO_2-exposed for 1x 5h



Same measurement one week later



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PN emission of 3E7/cm³

eta_POEM = 100 %

Tetracontane test not performed

PN emission during POEM 5E4/cm³