INNOVATIVE MANAGEMENT OF THE WASTEWATER PRODUCED IN THE H2S SCAVENGING OF NATURAL GAS

MARCO MASCHIETTI

Produced Water Club Meeting (Online)

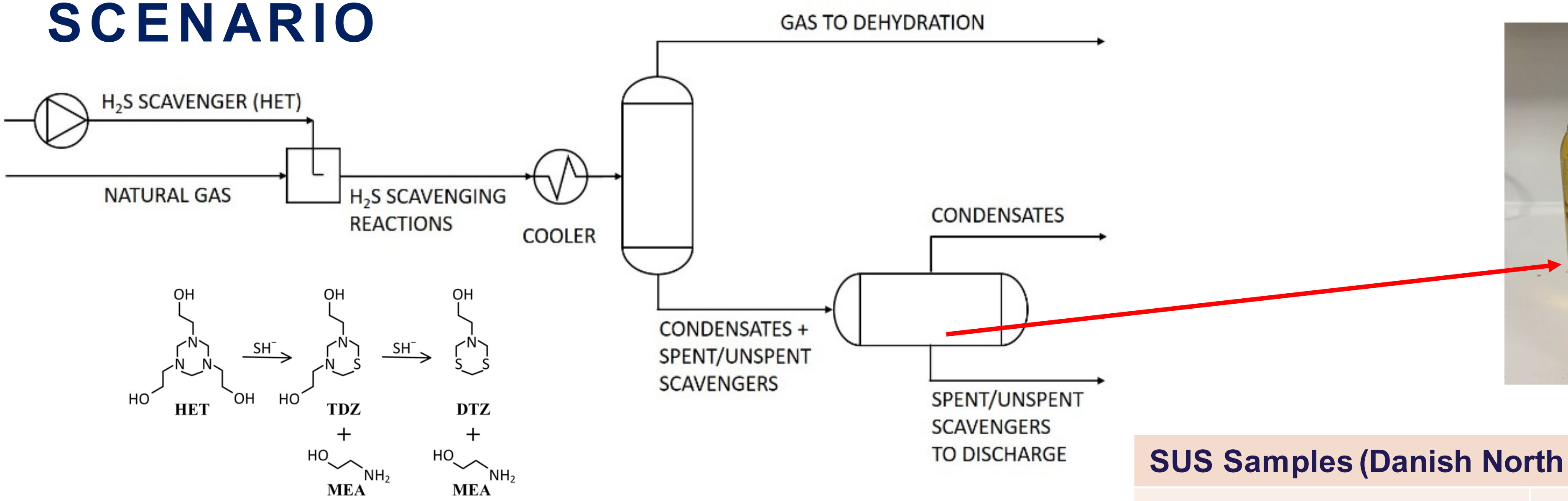
30 November 2023

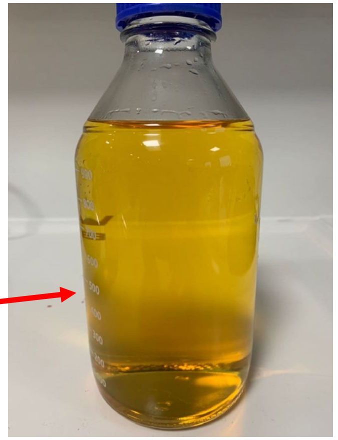
AALBORG UNIVERSITY

AGENDA

- Introduction to the ZeroH2S idea
- Membrane separation
- Hydrothermal oxidation
- New method for on-line analysis of spent/unspent H_2S scavengers

GAS-PHASE SCAVENGING OFFSHORE: CURRENT SCENARIO





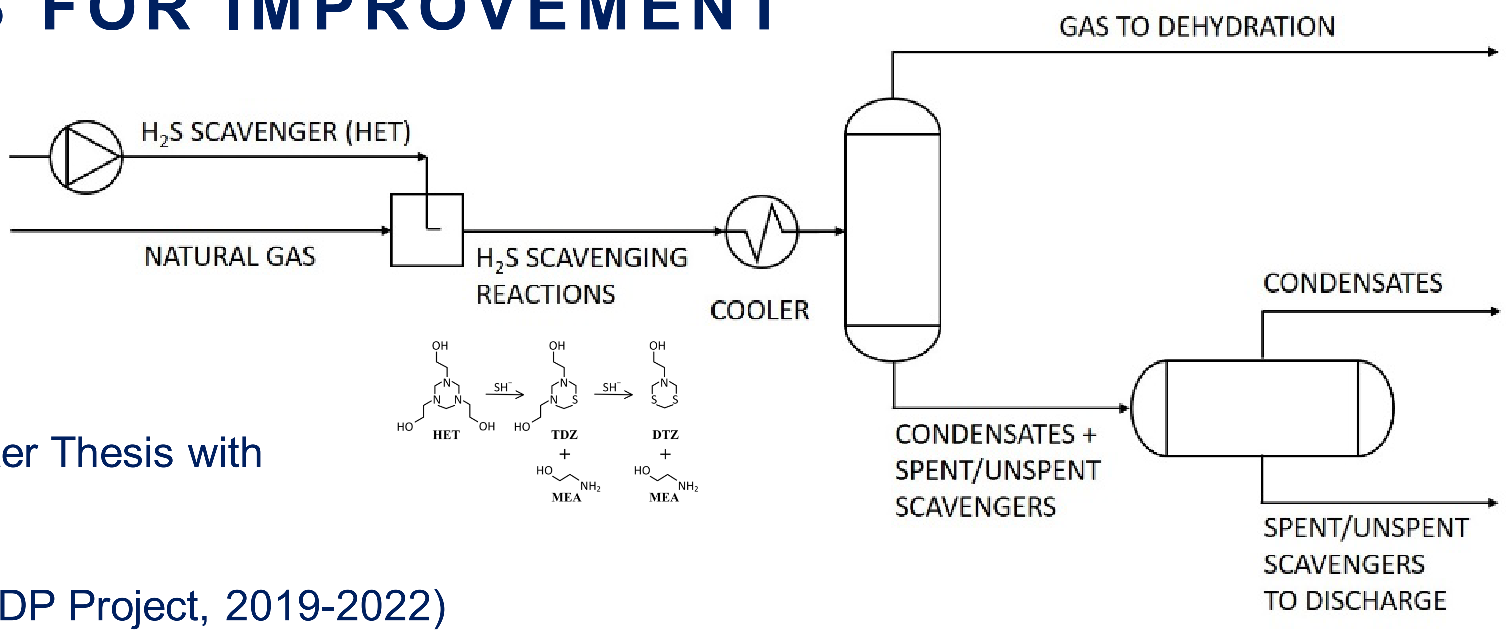
Opportunity for EIF reduction: Spent and Unspent H_2S scavengers (SUS) often discharged into the sea: small quantity (<0.1% of total water discharge) but high EIF (10-20% of total water discharge).

Opportunity for Cost Reduction: SUS contains large amounts of unreacted MEA-triazine. TDZ (present but difficult to quantitate) has also scavenging potential.

SUS Samples (Danish North Sea, 2014 to date)	
pH	8.9 – 9.6
COD	(120 – 320) g/L
Eco-toxicity	500 (marine bacteria) – 2000 (algae) times higher than Produced Water
TOC	(36 – 123) g/L
MEA-Triazine (HET)	(35 – 105) g/L
Monoethanolamine (MEA)	(8 – 19) g/L
MEA-Dithiazine (DTZ)	(7 – 25) g/L
MEA-Thiadiazine (TDZ)	substantial

POSSIBLE STRATEGIES FOR IMPROVEMENT

AAU COMMITMENT



- Optimizing the injection process

  (i) Sensors and Black Box approaches (2 Master Thesis with TotalEnergies, 1 completed, 1 on-going)

  (ii) Physicochemical modelling (SCAVOP – EUDP Project, 2019-2022)

- Green chemicals to substitute MEA-triazine (funded by DTU Offshore, on-going)

- Recover and recycle unspent MEA-triazine and on-site treatment of the residual wastewater before discharge (ZeroH2S projects, funded by DTU Offshore, on-going)

TotalEnergies

Crossbridge ENERGY FREDERICIA

RAMBØLL

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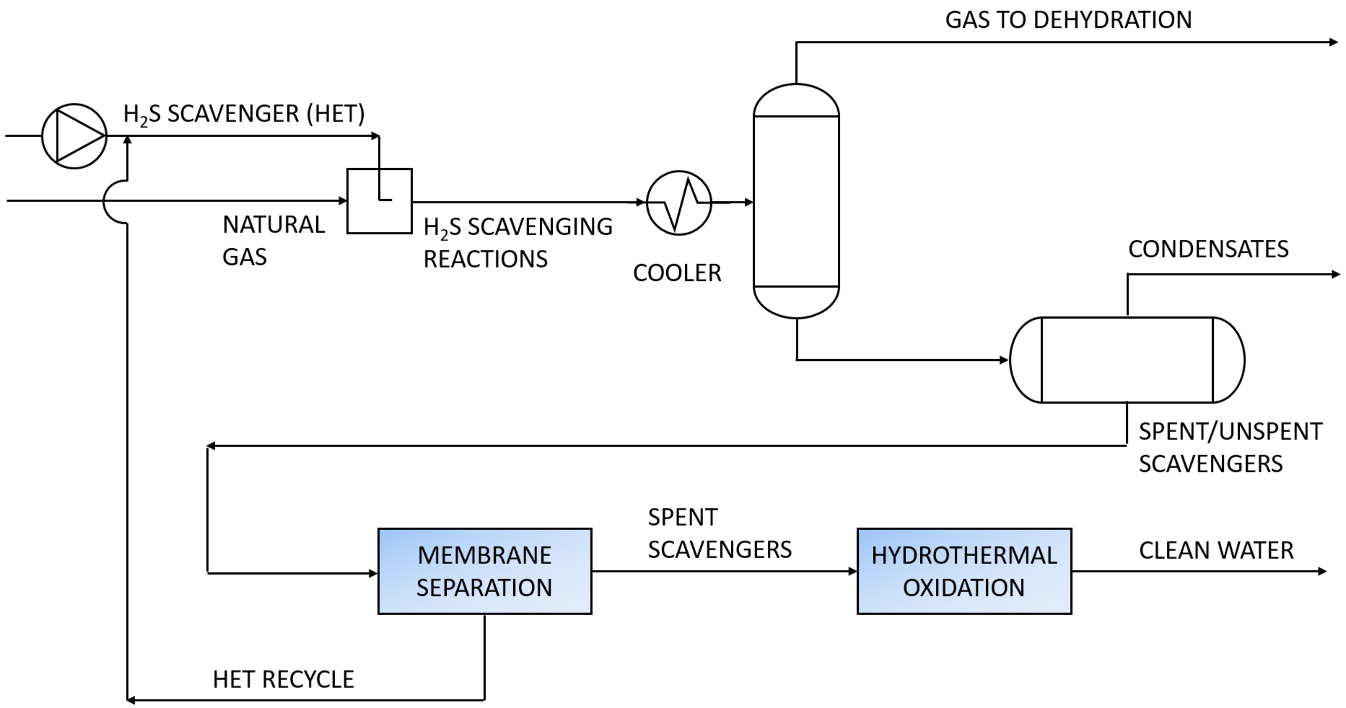
DTU Offshore
Danish Offshore Technology Centre

EUDP
The Energy Technology Development and Demonstration Programme

Aquarden TECHNOLOGIES

THE ZERO H2S IDEA

- Recovery of MEA-triazine (HET), and possibly other species with H_2S scavenging potential, by membrane nanofiltration and recycle
- Hydrothermal Oxidation (HTO) for removing toxicity of the water discharge



LAB-SCALE PROOF-OF-CONCEPT (2020-2022)

Experimental tests on commercial membranes for removal of SUS organics and separation of HET

Separation and Purification Technology 277 (2021) 119641

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

ELSEVIER

Performance evaluation of membrane filtration for treatment of H_2S scavenging wastewater from offshore oil and gas production

Mahdi Nikbakht Fini, Nikolaos Montesantos, Marco Maschietti, Jens Muff [*]

Journal of Environmental Chemical Engineering 10 (2022) 108735

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

ELSEVIER

Facile fabrication of high performance nanofiltration membranes for recovery of triazine-based chemicals used for H_2S scavenging

Alaa Khalil [a,b,*], Nikolaos Montesantos [a], Marco Maschietti [a], Jens Muff [a,b]

Experimental tests on hydrothermal oxidation of SUS

Chemical Engineering Journal 427 (2022) 131020

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

ELSEVIER

Proof of concept of hydrothermal oxidation for treatment of triazine-based spent and unspent H_2S scavengers from offshore oil and gas production

Nikolaos Montesantos, Mahdi Nikbakht Fini, Jens Muff, Marco Maschietti [*]

Water Research 230 (2023) 119507

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

ELSEVIER

Reducing the environmental impact of offshore H_2S scavenging wastewater via hydrothermal oxidation

Nikolaos Montesantos [a], Lars M. Skjolding [b,*], Anders Baun [b], Jens Muff [a], Marco Maschietti [a,*]

ADVANCEMENT IN THE KNOWLEDGE OF THE H2S SCAVENGING REACTION

I&EC research
Industrial & Engineering Chemistry Research
pubs.acs.org/IECR
Article

Experimental Study of the Aqueous Phase Reaction of Hydrogen Sulfide with MEA-Triazine Using In Situ Raman Spectroscopy

Iveth Romero, Sergey Kucheryavskiy, and Marco Maschietti*

Cite This: *Ind. Eng. Chem. Res.* 2021, 60, 15549−15557 Read Online

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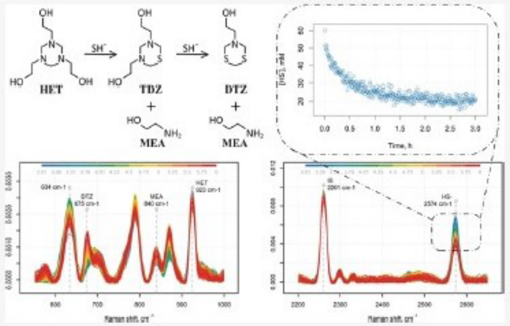
ABSTRACT: A method for quantitation of bisulfide in the aqueous phase reactions of H_2S scavenging with MEA-triazine is proposed. The method is based on time-resolved in situ Raman spectroscopy, thus allowing in situ monitoring of the reactions. The method is applied to obtain the kinetic data of the reactions in batch configuration at room temperature for initial pH values of 9, 10, and 11 and MEA-triazine/bisulfide initial concentration ratios in the range of 0.5−10. The pH increases remarkably during the reactions, causing a substantial decrease in the rate of disappearance of bisulfide. If the system is reacidified, complete depletion of bisulfide can be achieved, evidencing the irreversibility of the scavenging reactions. The results are also supported by a qualitative analysis of the trends of the characteristic Raman peaks of MEA-triazine, dithiazine, and monoethanolamine. These trends are in line with the currently accepted reaction scheme, consisting of two scavenging reactions in series.



I&EC research
Industrial & Engineering Chemistry Research
pubs.acs.org/IECR
Article

Temperature- and pH-Dependent Kinetics of the Aqueous Phase Hydrogen Sulfide Scavenging Reactions with MEA-Triazine

Iveth Romero, Fernando Montero, Sergey Kucheryavskiy, Reinhard Wimmer, Anders Andreasen, and Marco Maschietti*

Cite This: *Ind. Eng. Chem. Res.* 2023, 62, 8269−8280 Read Online

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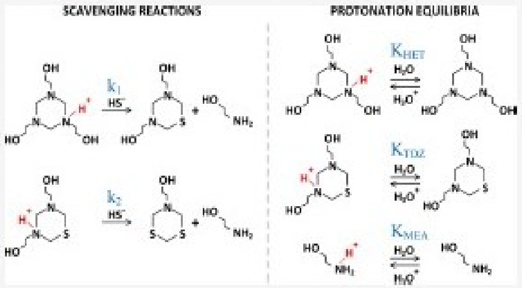
ABSTRACT: A novel kinetic model for the aqueous phase hydrogen sulfide scavenging reactions using MEA-triazine (HET) is proposed. The assumptions of the model are based on experimental observations obtained by NMR spectroscopy, supporting the existence of 3,5-bis(2-hydroxyethyl)hexahydro-1,3,5-thiadiazine (TDZ) as a quantitative reaction intermediate and showing the protonation behavior of HET and the lack of protonation of 5-(2-hydroxyethyl)hexahydro-1,3,5-dithiazine (DTZ). Experimental kinetic data were obtained with a new in situ Raman spectroscopy setup, which enabled monitoring the time-variation of bisulfide concentrations in a batch stirred reacting system at temperatures of up to 75 °C for HET/HS^- initial concentration ratios from 0.5 to 5. The optimal model parameters were regressed from the experimental data using a brute force optimization method. The rate constants of the first and second scavenging reactions were estimated to be 0.435 and 0.004 L mol^{-1} s^{-1} at 25 °C, and the activation energies were 68 and 57 kJ mol^{-1}, respectively.



EUDP
The Energy Technology Development and Demonstration Programme

RAMBOLL

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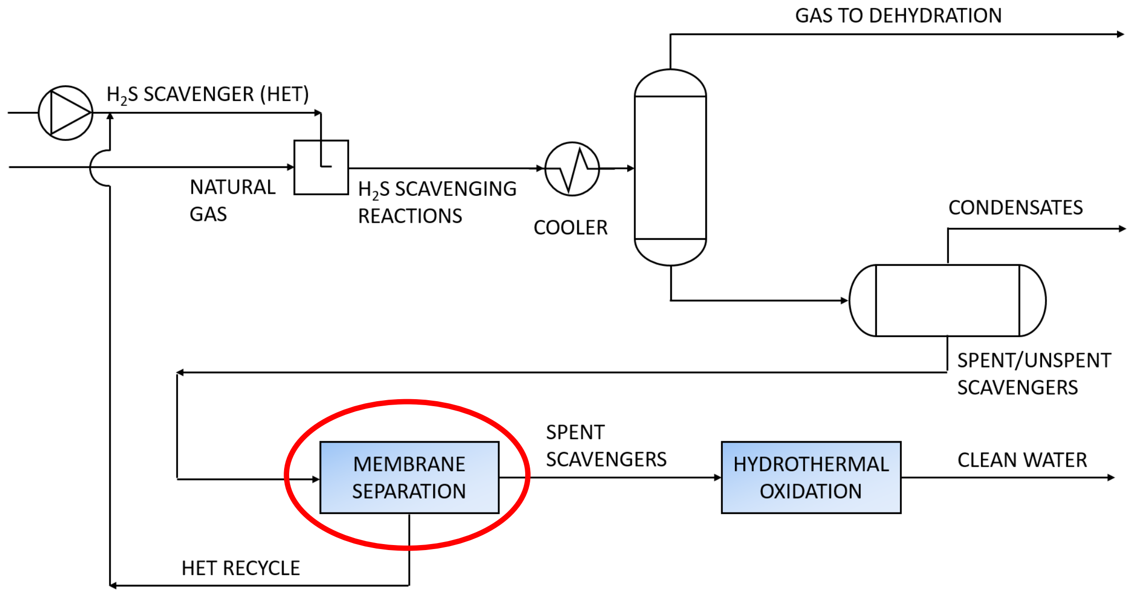
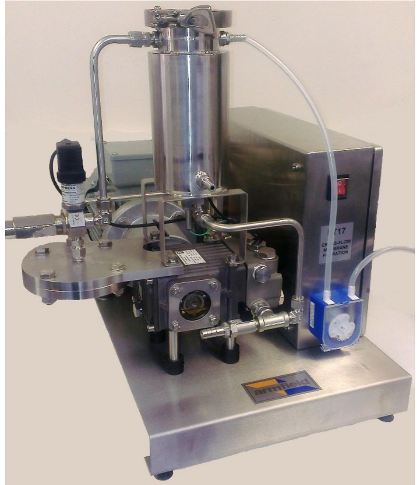
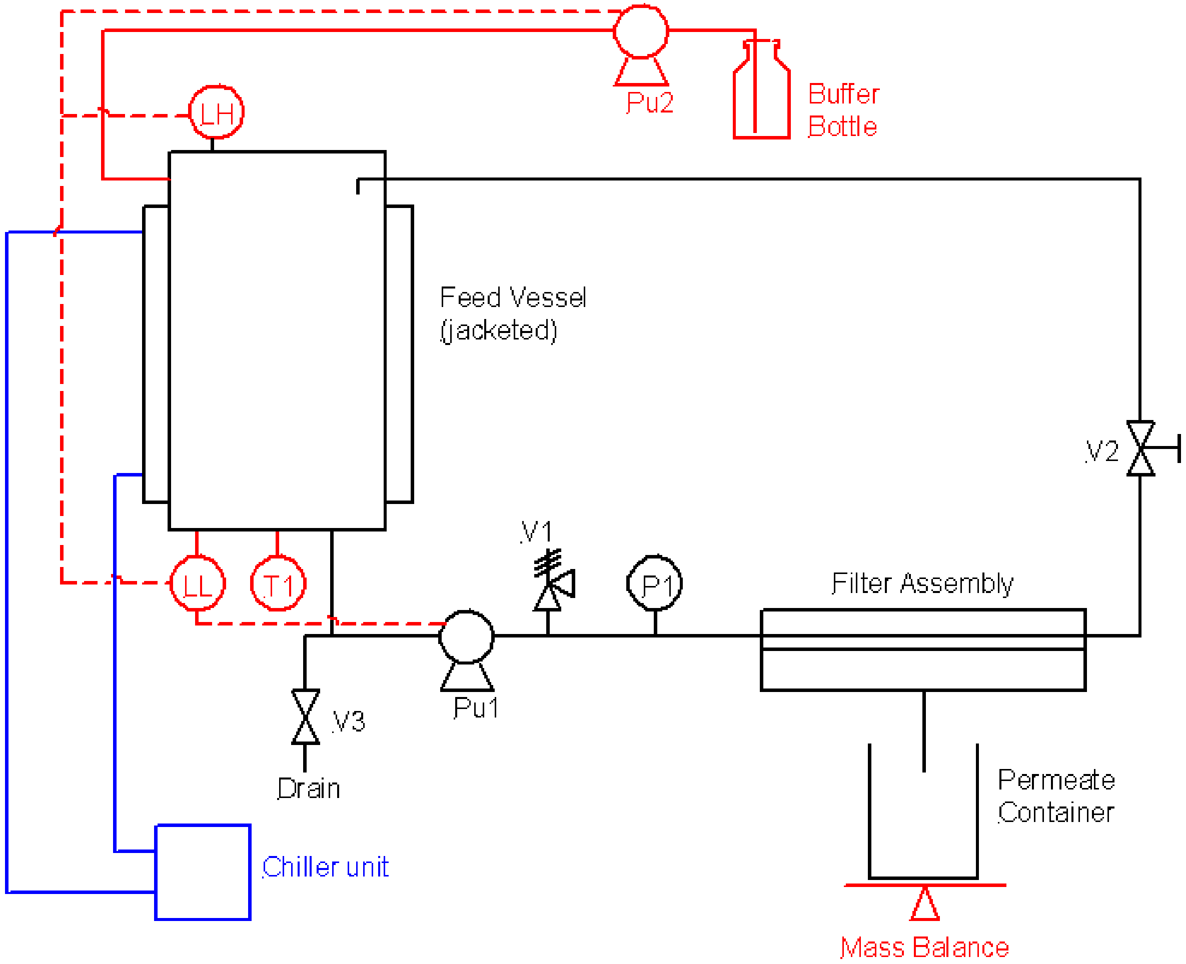


CROSS-FLOW FILTRATION (LAB SCALE)

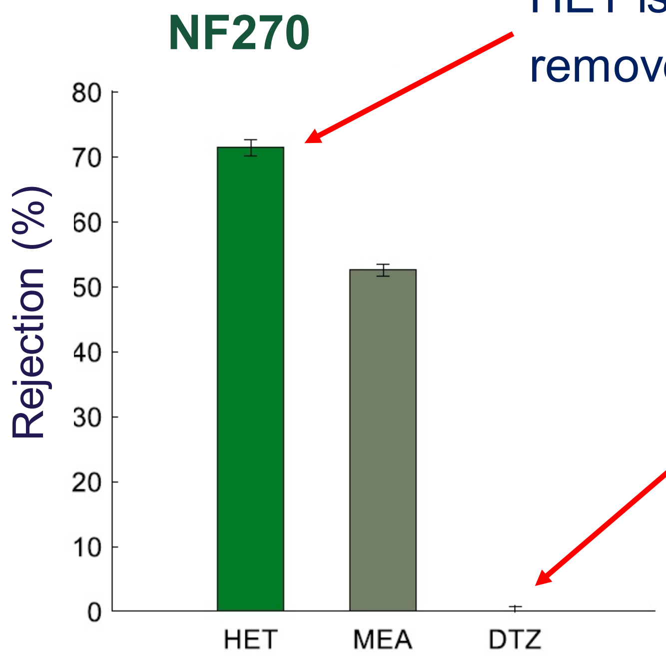
- 30 bar and 40°C
- Flow rate: 100 L/h
- Flat sheet membrane
- Recovery of 250 mL of permeate out of 500 mL of feed (P/F = 0.5) or recycle of permeate for 24 h fouling tests
- Duration: (2 – 10) hours





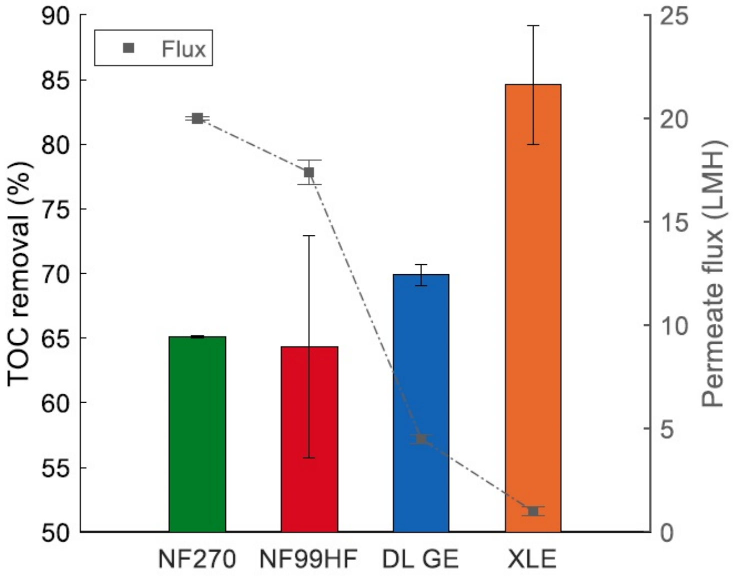
MEMBRANE RECOVERY OF MEA-TRIAZINE – KEY RESULTS

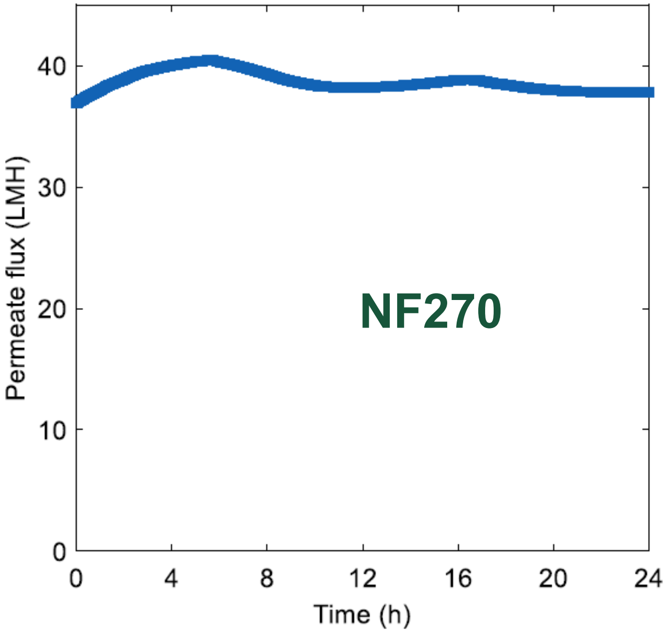
The separation HET/DTZ is possible!



HET is removed

DTZ permeates through the membrane



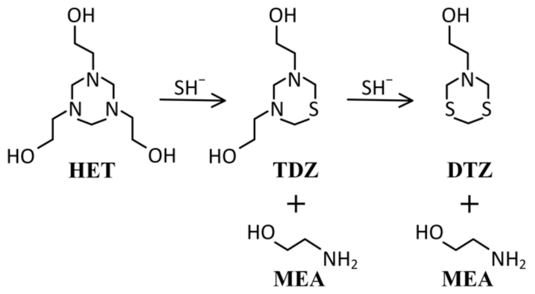


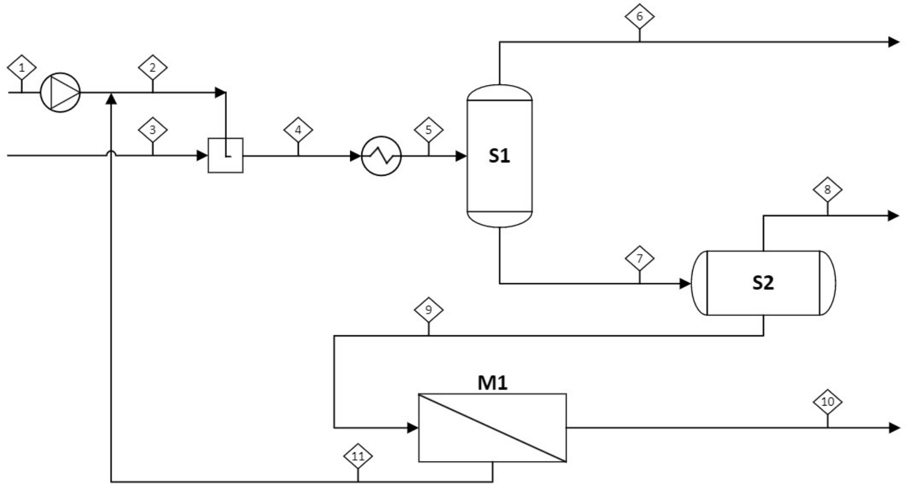
- NF270: best compromise between recovery, selectivity and permeability
- No evidence of fouling up to 24 hours of operation

MEMBRANE FILTRATION – BASIC DESIGN: ASSUMPTIONS

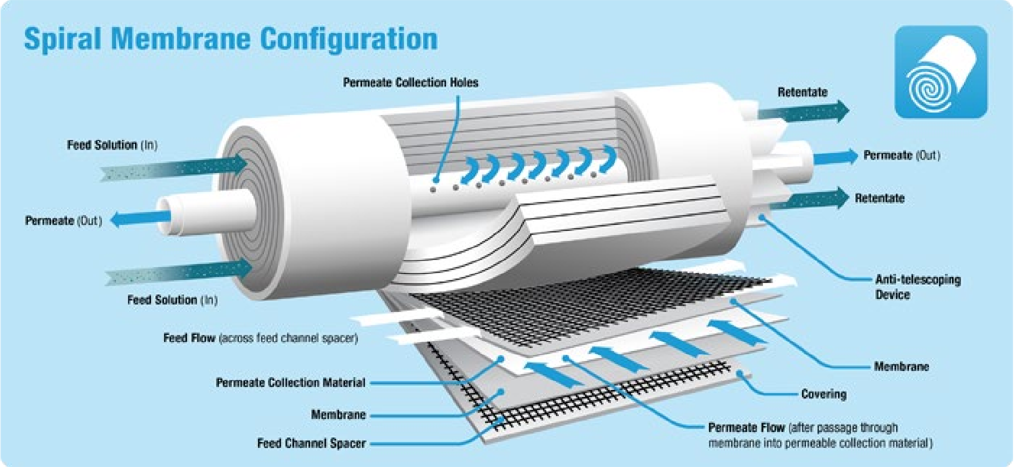
Addition of an NF unit – Design Assumptions

- It is assumed that all the excess MEA-triazine is available for potential recovery.



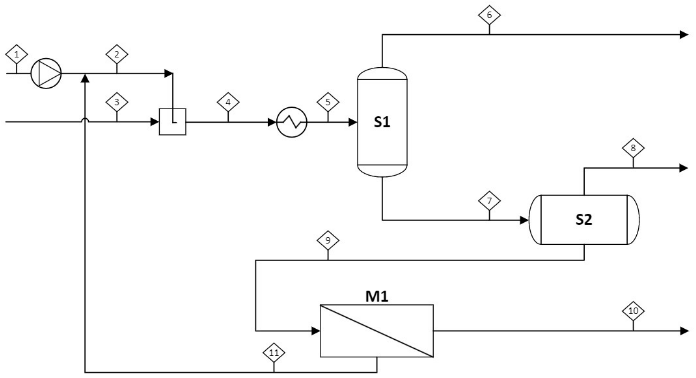


- One membrane module (spiral wound) for permeate-to-feed ratio 0.5
- TMP 30 bar
- Rejection of MEA-triazine: 70%



MEMBRANE FILTRATION – BASIC DESIGN RESULTS

Resource recovery and reduction of discharge:



Current dosage (kg_{scav}/kg_{H2S})	Reduction of HET consumption	Reduction of discharge of organics
12	40%	34%
20	58%	53%
40	72%	68%

Size and cost:

- To get an idea: the photo shows a 24 m^3/day NF unit (2 modules)
- Cost of the membrane unit in the photo (incl. pump, gauges, membranes, and controls, 2-6 bar, no ATEX, VAT excl.): 24 000 EUR (Silhorko)
- Pump energy requirement (if needed): in the order of 1 kW

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TotalEnergies

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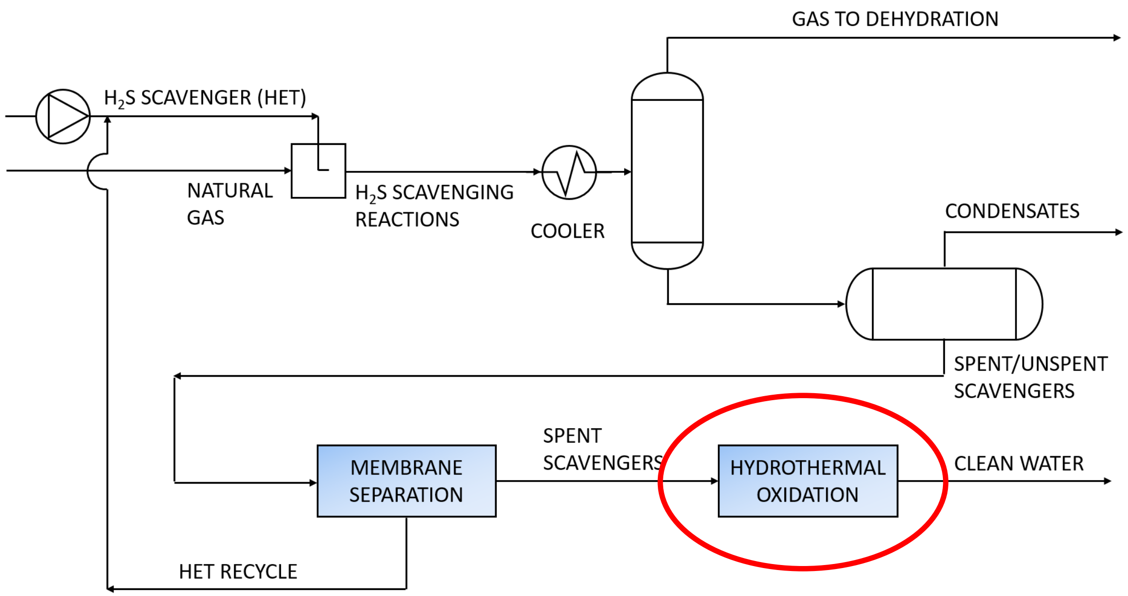
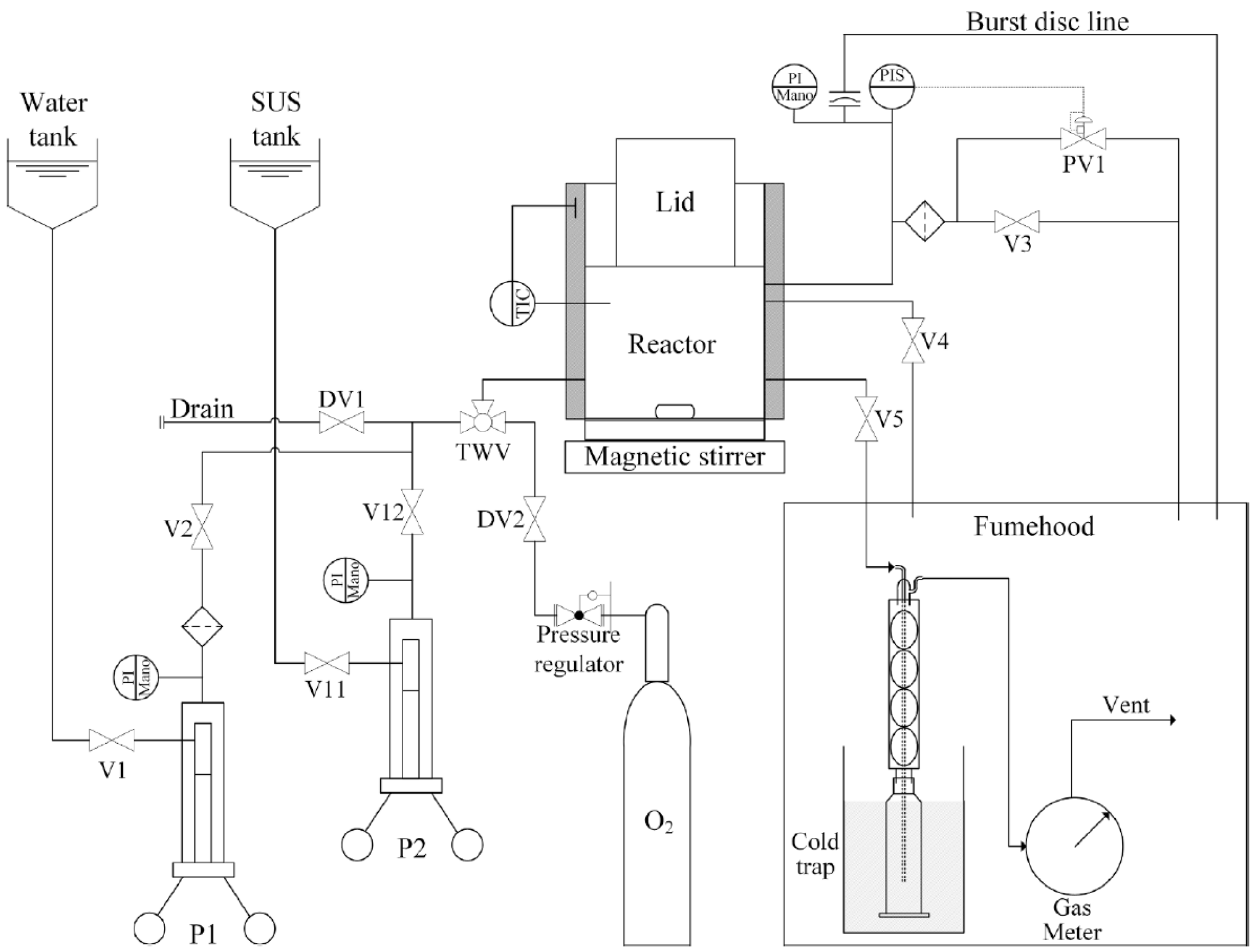
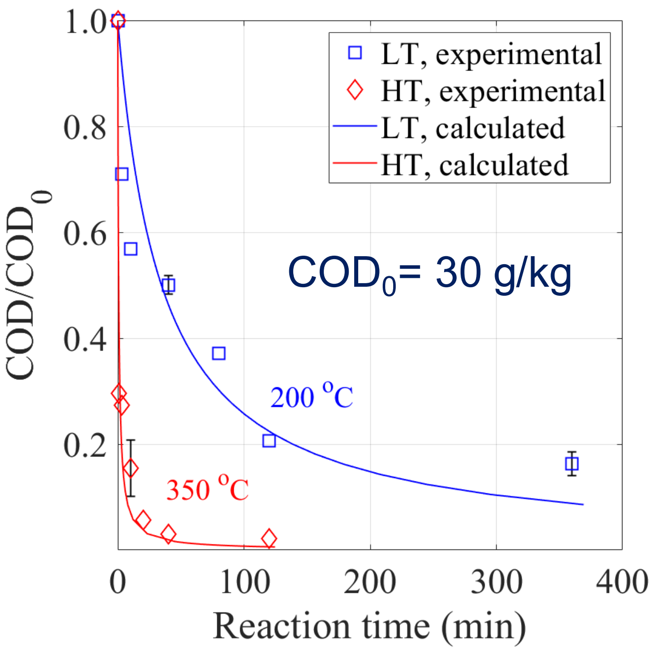


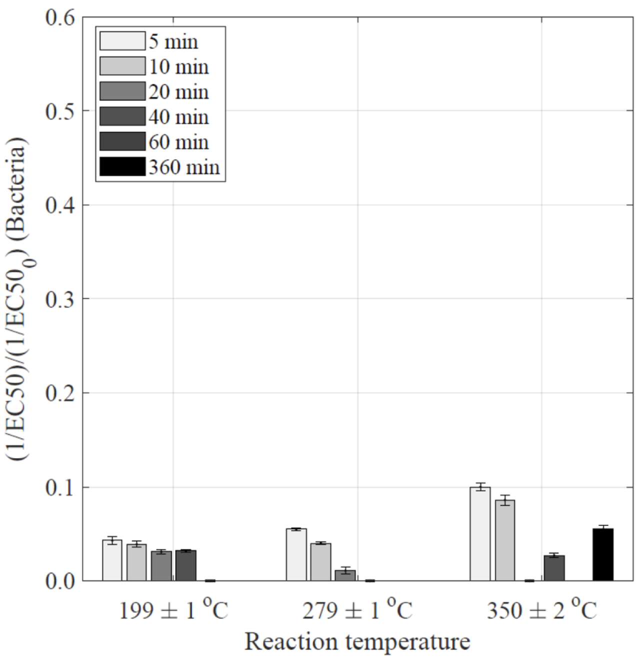
HYDROTHERMAL OXIDATION (LAB SCALE - BATCH)

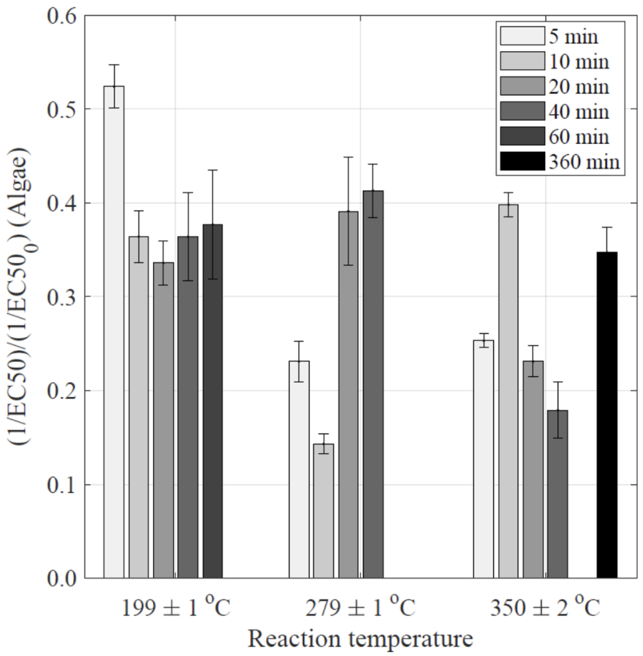


- ➢ Low temperature experiments: 200°C and 70-90 bar
- ➢ High temperature experiments: 350°C and 210-250 bar
- ➢ Excess of oxygen
- ➢ Reaction time: from 1 to 360 min

REMOVAL OF TOXICITY VIA HYDROTHERMAL OXIDATION

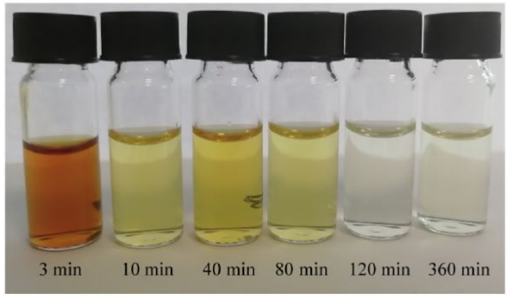




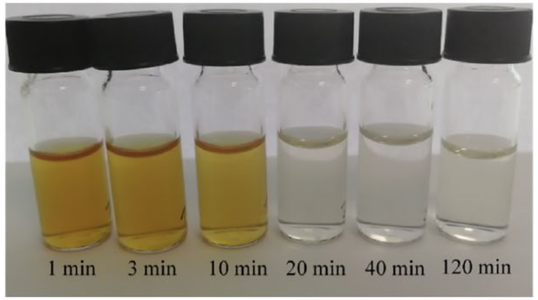


- HET, MEA, and DTZ rapidly decompose
- COD reduction ca. 70 times faster at 350°C
- C, N, S converted into CO_2, ammonium, nitrate, and sulfate
- Sunstantial eco-toxicity reduction: >90% towards marine bacteria, 48% to 86% towards algae

Feed



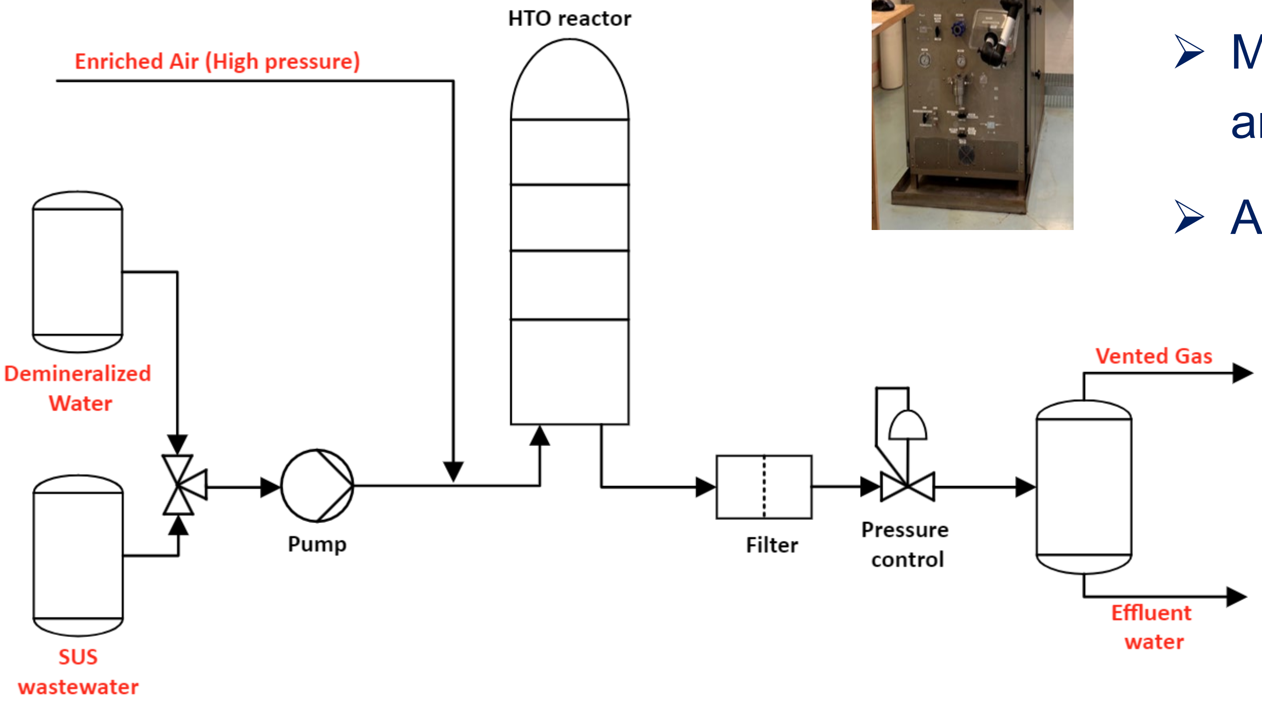
200°C



350°C

HYDROTHERMAL OXIDATION (CONTINUOUS FLOW)

Experimental campaign on-going in Aquarden Technologies.



Very good news so far:

- Operability proved so far up to feed COD 200 g/L
- COD reductions in the range 93-98%
- Main products: sulfate, ammonium (and nitrate), and CO2
- Autothermal process and excess heat generated

Possible problems with the vent gas:

- H_2S (10^2 ppm) detected in the vent gas, but only at low temperature (280°C)
- CO (10^3 ppm) in the vent gas, at all temperatures.

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Aquarden TECHNOLOGIES

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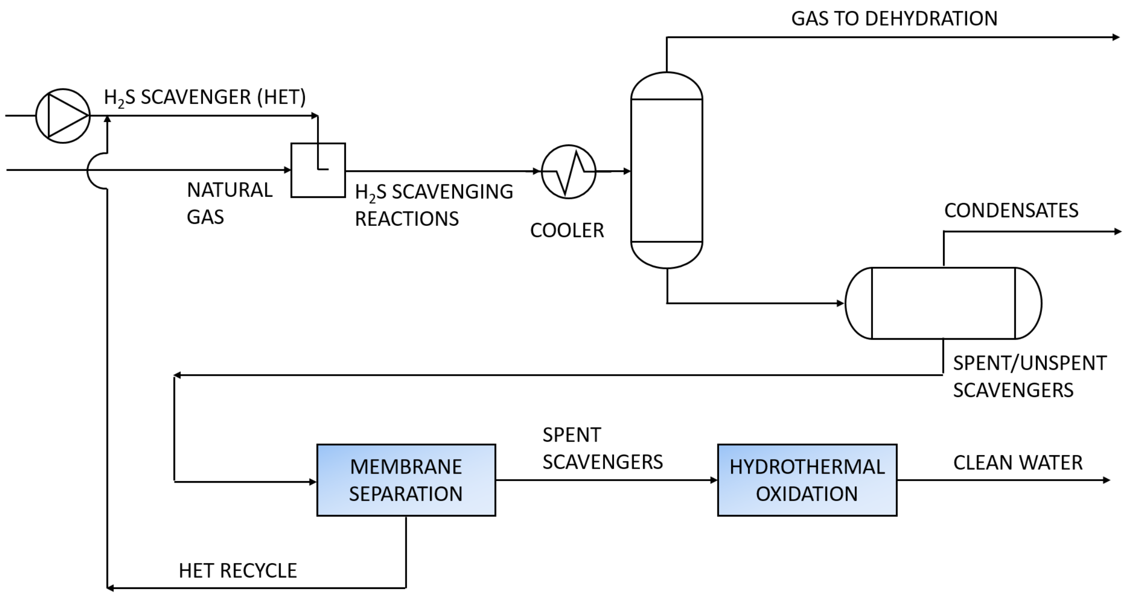
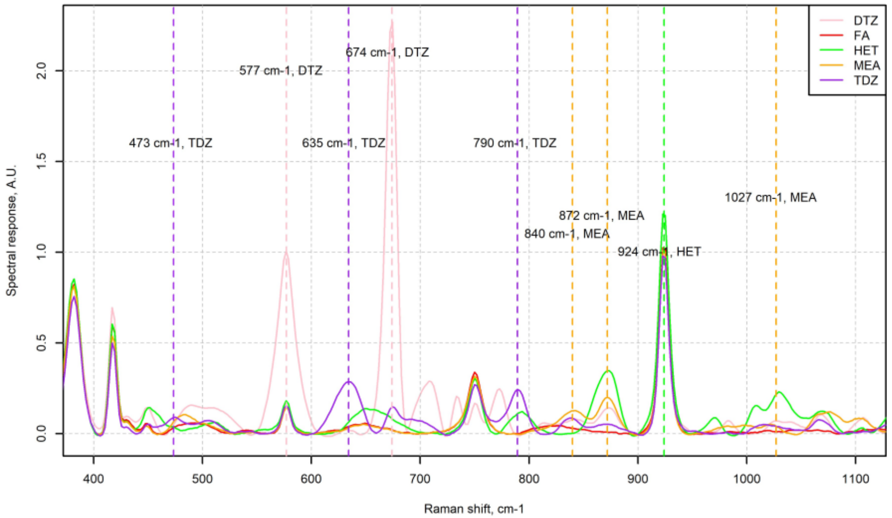
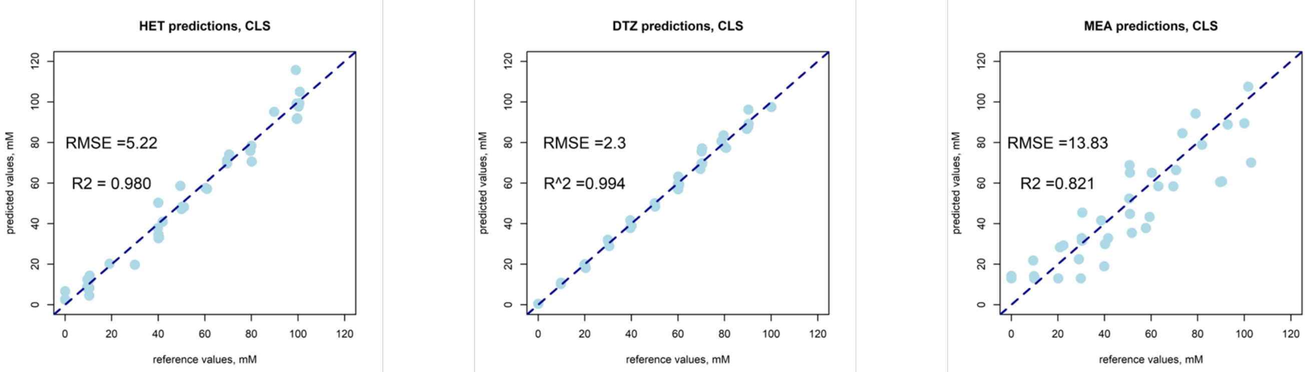
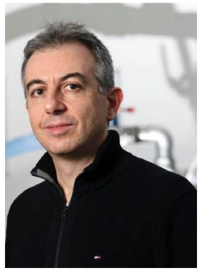


ANALYSIS OF SPENT/UNSPENT SCAVENGERS BY MEANS OF RAMAN SPECTROSCOPY





THE ZEROH2S TEAM



Marco Maschietti
Associate Professor,
HPHT processes, topside offshore oil and gas

Jens Muff
Associate Professor
Advanced oxidation and membrane processes

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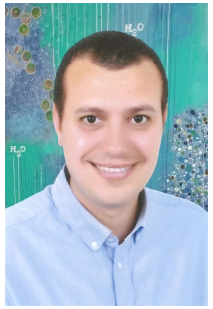
Sergey Kucheryavskiy
Associate Professor
Spectroscopy and chemometrics



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Karolina Agata Szlek
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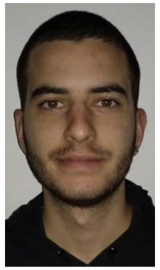
Spectroscopy and chemometrics



Alessandro Perrucci
PhD student
Hydrothermal oxidation

Collaborations: Aquarden TECHNOLOGIES, DTU

DTU Offshore
Danish Offshore Technology Centre