Membrane-based Recovery of MEA-triazine and Hydrothermal Oxidation of Spent Scavengers: A Proof of Concept

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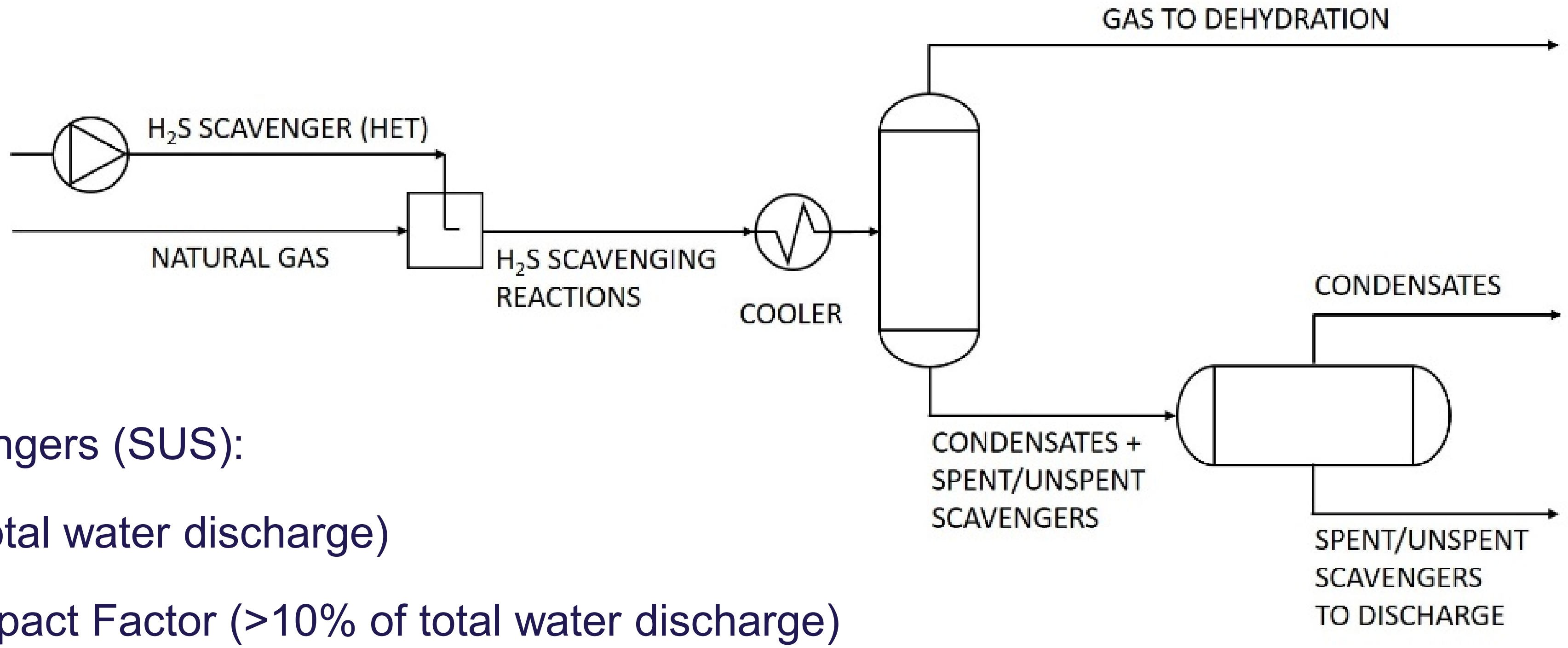
PRODUCED WATER CLUB MEETING
Online Meeting, 23 February 2022

AALBORG UNIVERSITY

H_2S SCAVENGING OF NATURAL GAS: NECESSARY BUT EXPENSIVE AND PROBLEMATIC FOR THE ENVIRONMENT



THE PROBLEM

- Spent and Unspent Scavengers (SUS):

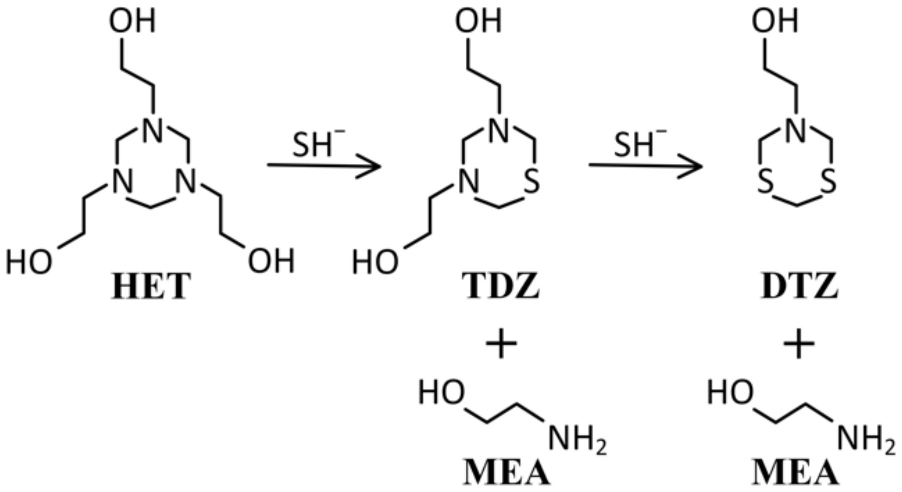
  small quantity (<0.1% of total water discharge)

  but high Environmental Impact Factor (>10% of total water discharge)

- HET: >50% of total expenditure of production chemicals

CHARACTERISTICS OF THE SUS

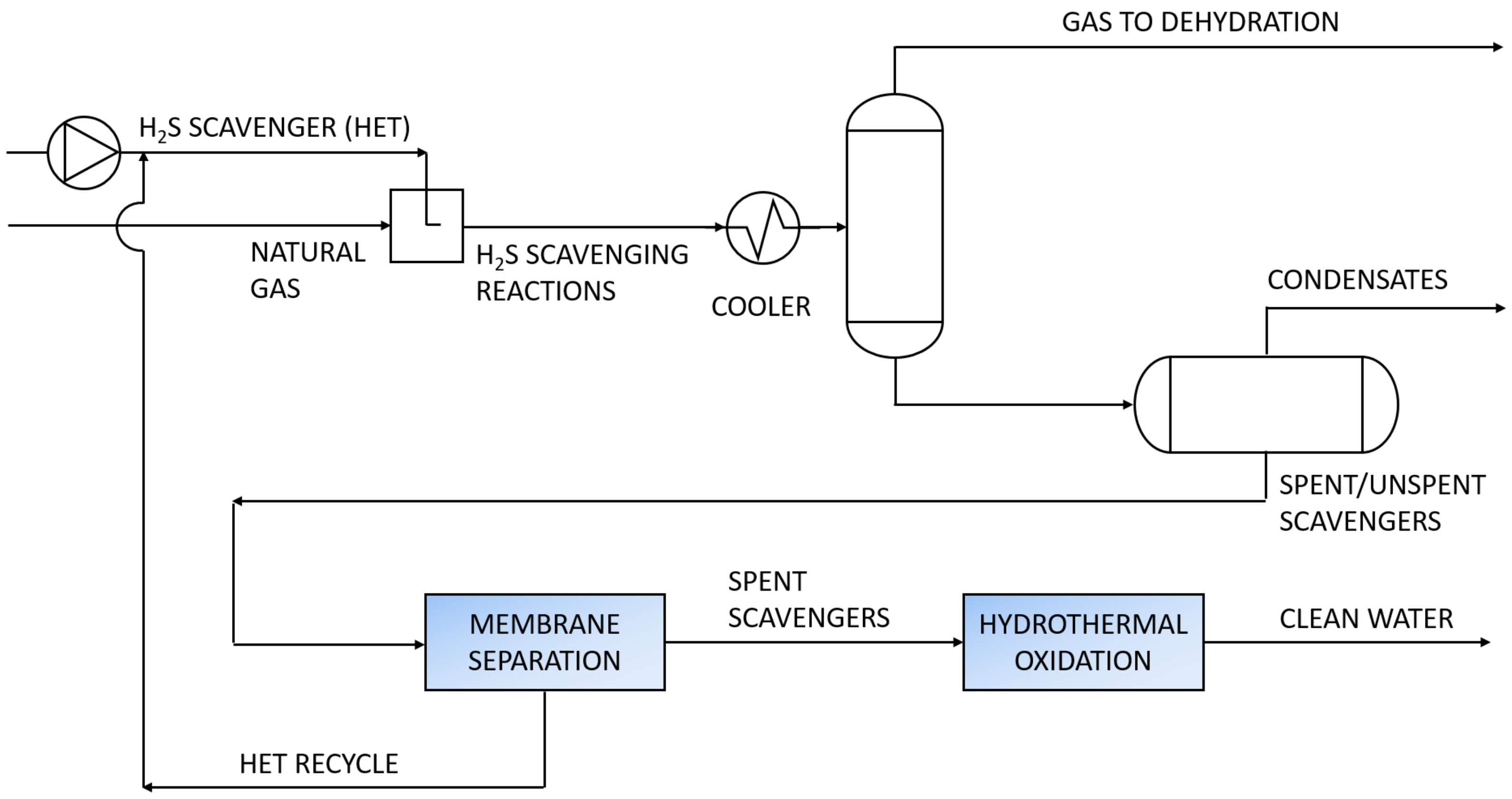
- High concentration of organics of moderate toxicity
- Large amount of unreacted triazine (HET)
- Problematic to re-inject due to fouling/scaling propensity



COD	(120 – 320) g/L
pH	8.9 – 9.6
Triazine (HET)	(8 – 15) wt%
Monoethanolamine (MEA)	(2 – 5) wt%
Dithiazine (DTZ)	(1 – 4) wt%
Formaldehyde (FA)	(1 – 2) wt%

THE CHALLENGE

- Can HET be separated before discharge for recycling?
- Can the spent scavengers be treated in a compact unit for clean discharge?



ZEROH2S PROJECT: WORK DONE SO FAR (2020-2021)

- 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

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 *

- Experimental tests on hydrothermal oxidation of SUS

Chemical Engineering Journal 427 (2022) 131020

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Chemical Engineering Journal

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

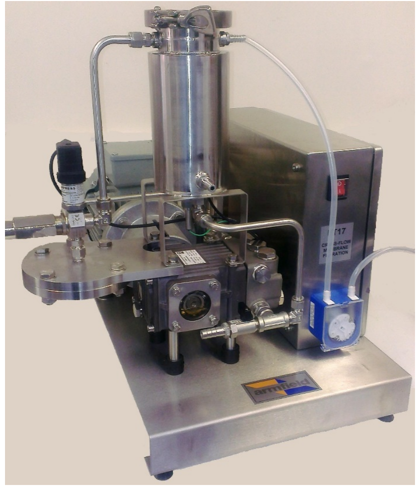
Proof of concept of hydrothermal oxidation for treatment of triazine-based spent and unspent H_2S scavengers from offshore oil and gas production

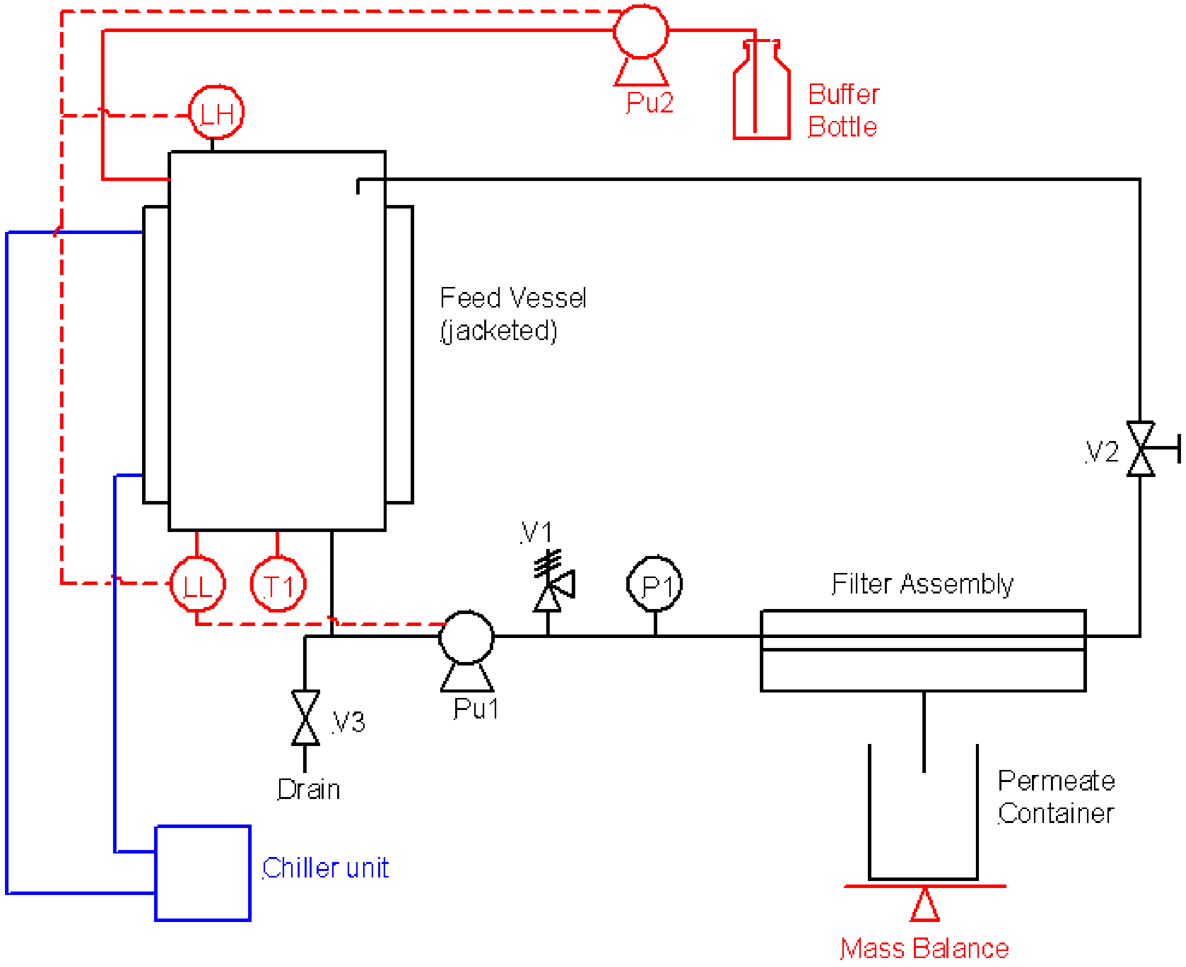
Nikolaos Montesantos, Mahdi Nikbakht Fini, Jens Muff, Marco Maschietti *

CROSS-FLOW FILTRATION SETUP

Operating conditions:

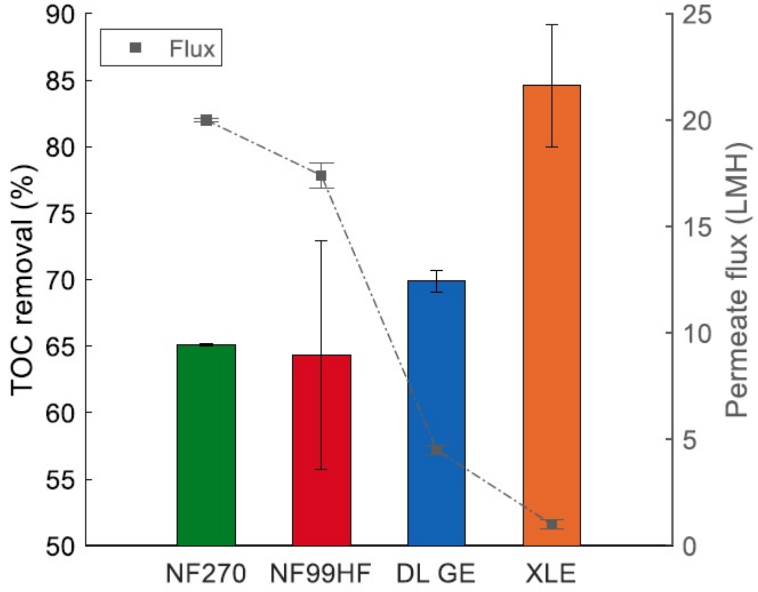
- 30 bar and 40°C
- Recovery of 250 mL of permeate out of 500 mL of feed or recycle of permeate for 24 h fouling tests
- Flow rate: 100 L/h
- Cross-flow velocity: 24.5 cm/s
- Duration: (2 – 10) hours

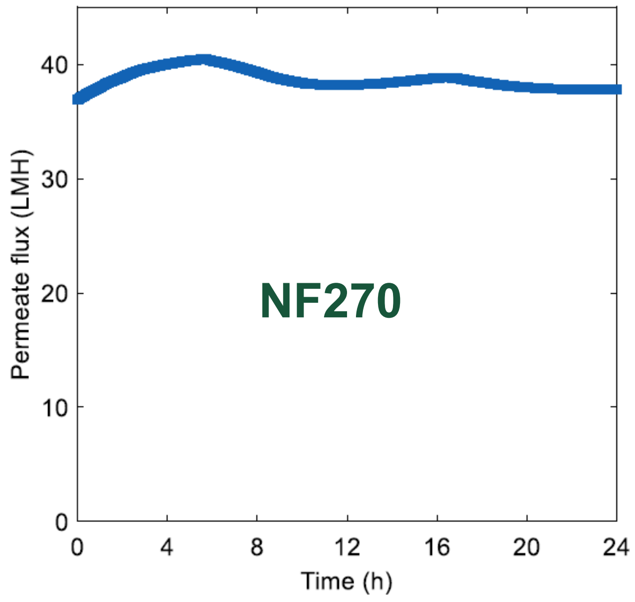


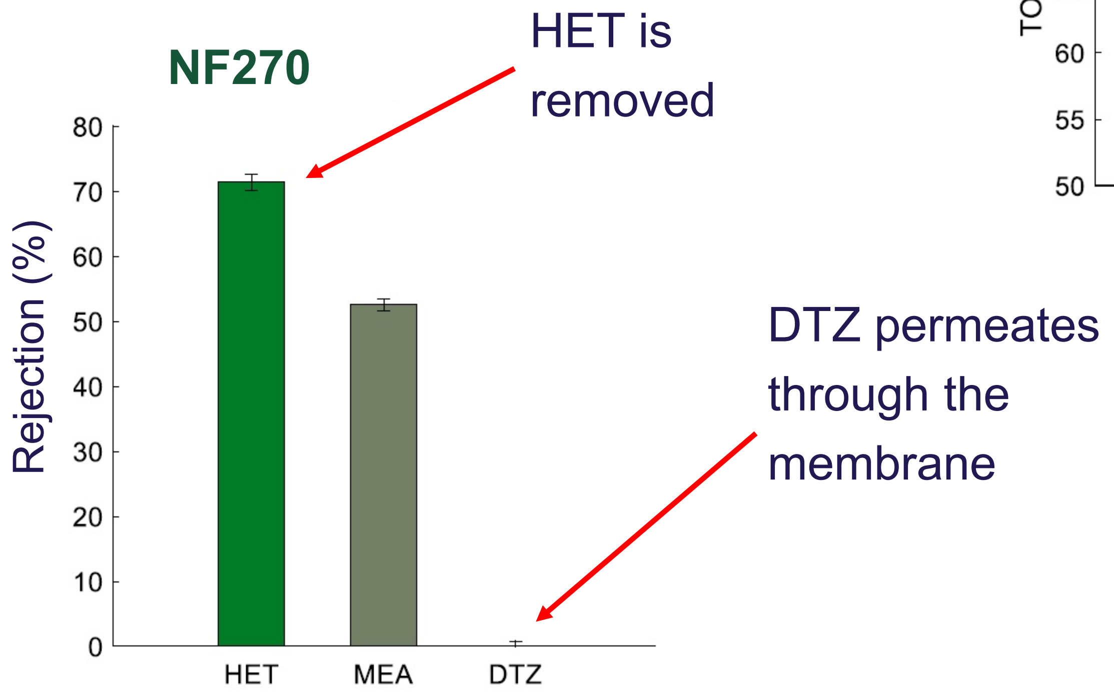


KEY RESULTS FROM THE MEMBRANE TESTS

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

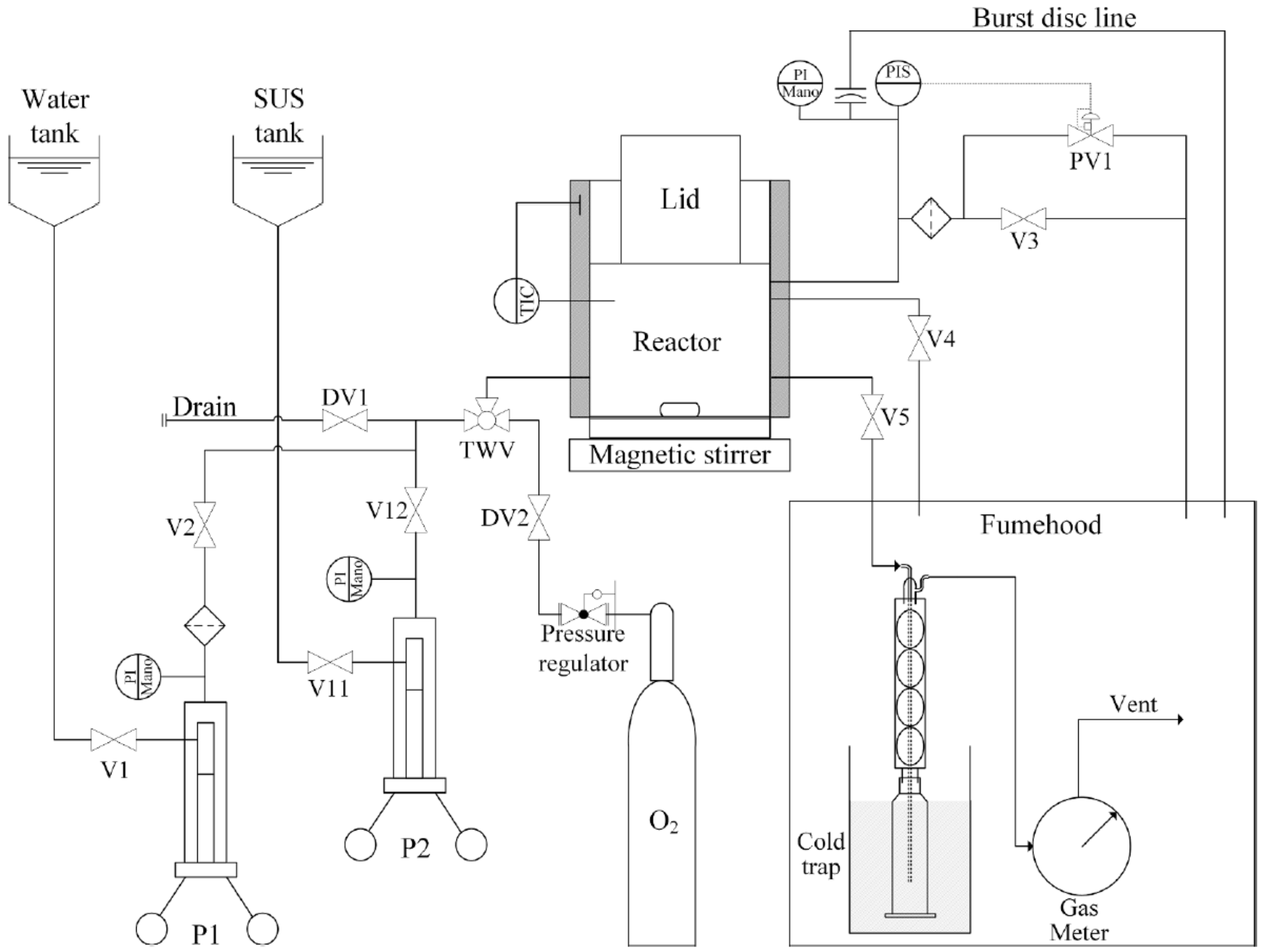






- The separation HET/DTZ is possible!
- Membrane separation cannot be explained on the basis of molecular size only
- The permeation of DTZ can be explained by its high polarity and hydrophobicity

HYDROTHERMAL OXIDATION SETUP



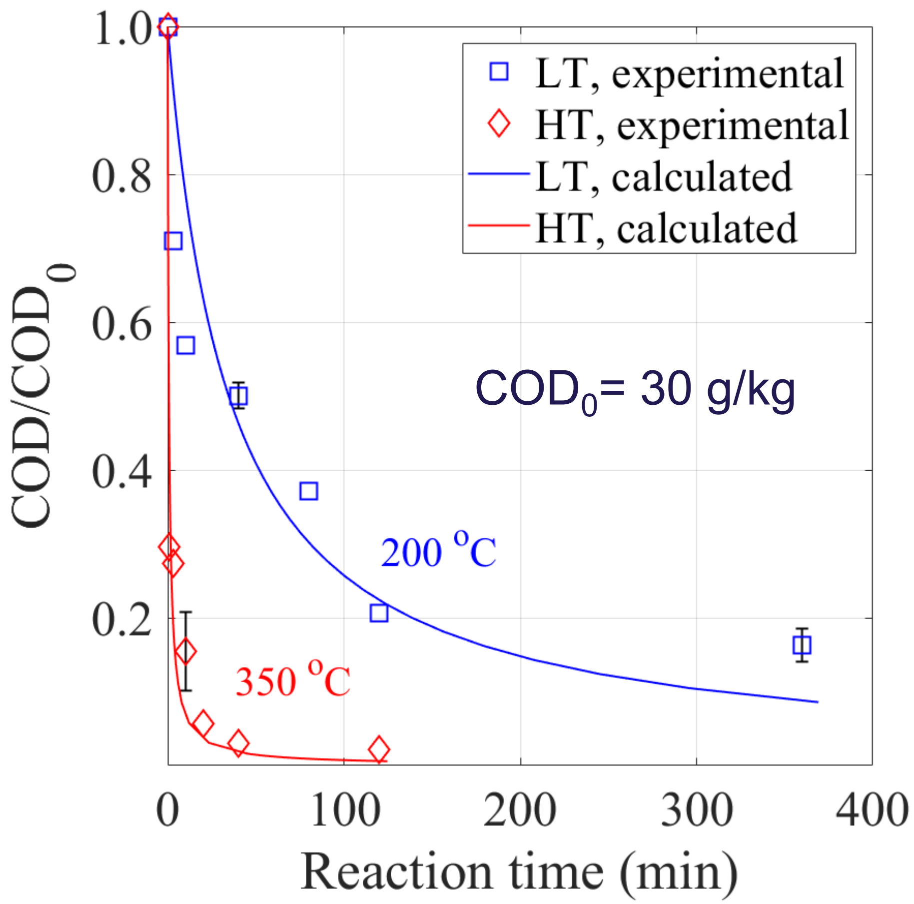
Customized HPHT injection reactor:

- Quick heating and product quenching
- Accurate P, T control
- Accurate results supporting the scale-up to continuous-flow reactors

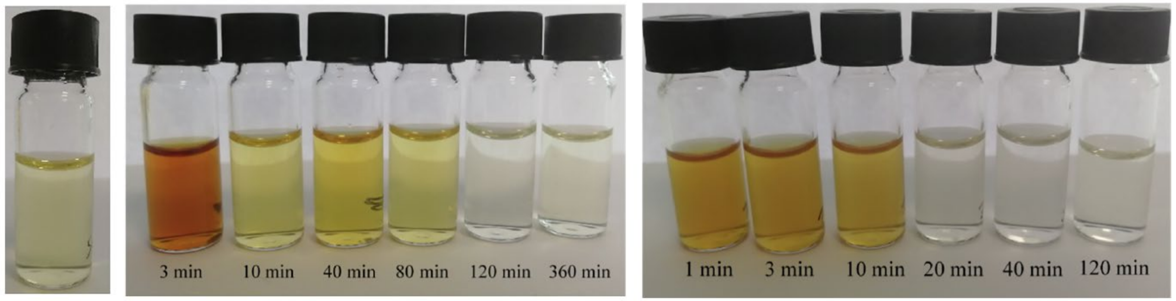
Operating conditions:

- 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

COD REDUCTION AND REMOVAL OF KEY POLLUTANTS

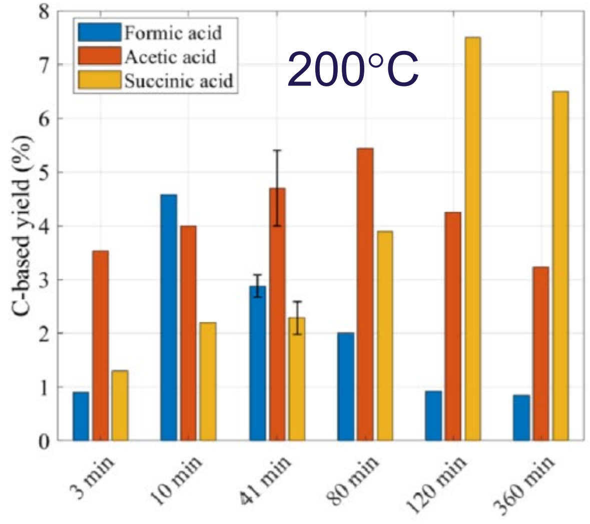


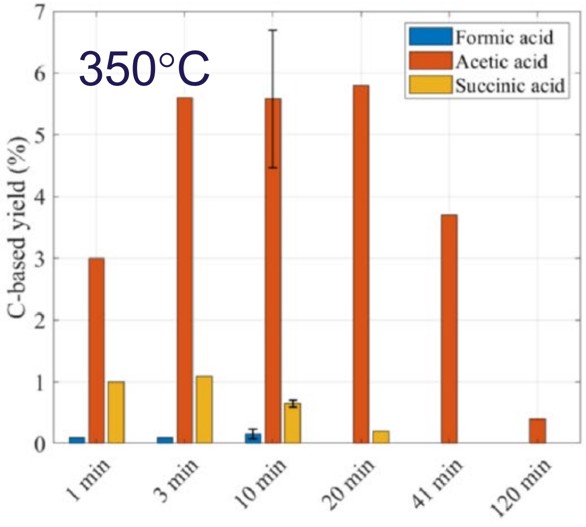
- HET, MEA, and DTZ rapidly decompose
- FA: >98% reduction in 10 min at 350°C or 30 min at 200°C
- COD reduction ca. 70 times faster at 350°C
- C, N, S converted into CO_2, ammonium, nitrate, and sulfate

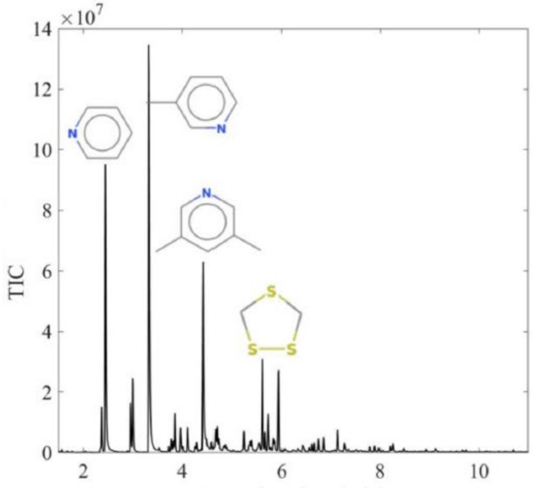


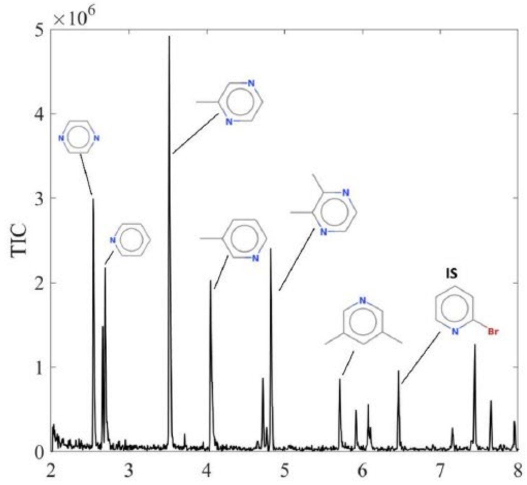
Feed 200°C 350°C

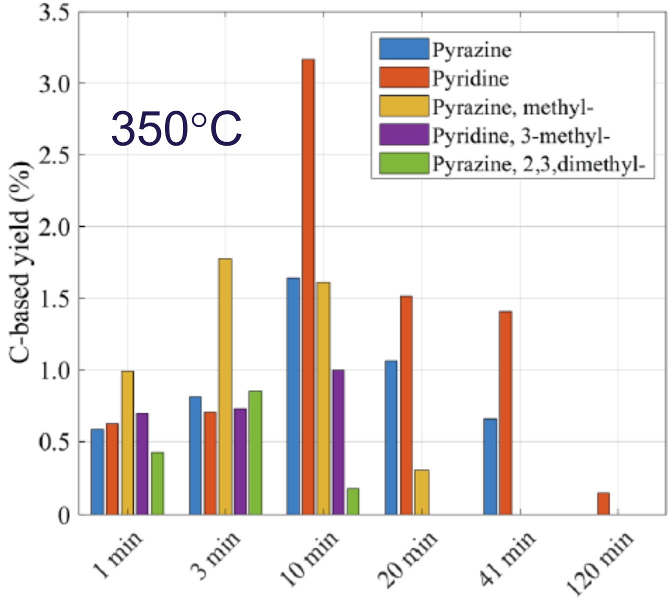
INTERMEDIATE OXIDATION PRODUCTS











- C1-C4 acids show a maximum and then decreases over time
- Same happens for pyridines and pyrazines, with pyridine being slowly degraded
- Toxicity substantially reduced anyway (e.g., 74% reduction with 20 min at 350°C)

LESSON LEARNED SO FAR (2020-2021)

- Unreacted HET can be recovered through nanofiltration.
- The COD of SUS samples can be drastically reduced via hydrothermal oxidation.
- Preliminary results (end of 2021) show substantial toxicity reduction as well.
- Preliminary basic design calculations show reactor volumes compatible with offshore installation (e.g,. hydrothermal oxidation reactor in the order of 1 m^3). In addition, excess heat is produced.

NEXT STEPS

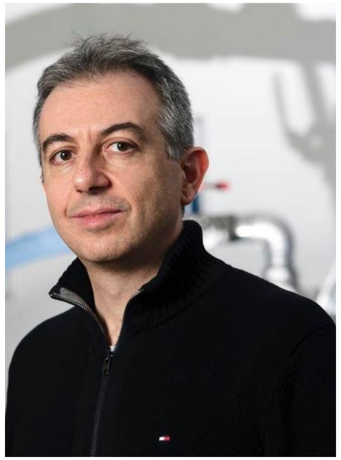
Next steps on this project (2022-2024):

- Improve the membrane separation by optmizing membrane thickness or incorporating naoparticles (e.g., carbon nanotubes, graphene oxide, graphene nanosheets, etc.) via interfacial polymerization in order to increase the HET/DTZ separation selectivity, while keeping a high permeability.
- Connect hydrothermal oxidation results to toxicity, instead of to COD only (collaboration on-going with DTU Environment).
- Process design and integration.

Future project:

- Scale-up and continuous-flow testing.

PROJECT TEAM



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Collaboration with DTU Environment (Lars Michael Skjolding, Anders Baun) on determination of toxicity of SUS derived water samples

DTU