Application of Raman spectroscopy for monitoring of hydrogen sulfide scavenging reactions using biomass-based chemicals

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APPLICATION OF RAMAN SPECTROSCOPY FOR MONITORING OF HYDROGEN SULFIDE SCAVENGING REACTIONS USING BIOMASS-BASED CHEMICALS

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INTRODUCTION

Hydrogen sulfide (H_2S) is a toxic and corrosive species which poses serious operating, health, safety and environmental problems to oil and gas production. Injection of chemicals, called H_2S scavengers, in offshore platforms is used to reduce H_2S concentration. H_2S scavengers, however, ends up in the water discharge into the sea and are associated to a high environmental impact. In recent years, research on the development of novel environmental-friendly H_2S scavengers has become relevant.

OBJECTIVE

Assess the feasibility of using Raman spectroscopy for monitoring gas-liquid as well as aqueous phase reactions between H_2S and biomass-based scavengers (BBS) and benchmarking them with MEA-triazine (HET), which is the most used H_2S scavenger.

EXPERIMENTS

Two types of experiments were carried out:

Gas-liquid reactions at 80 °C

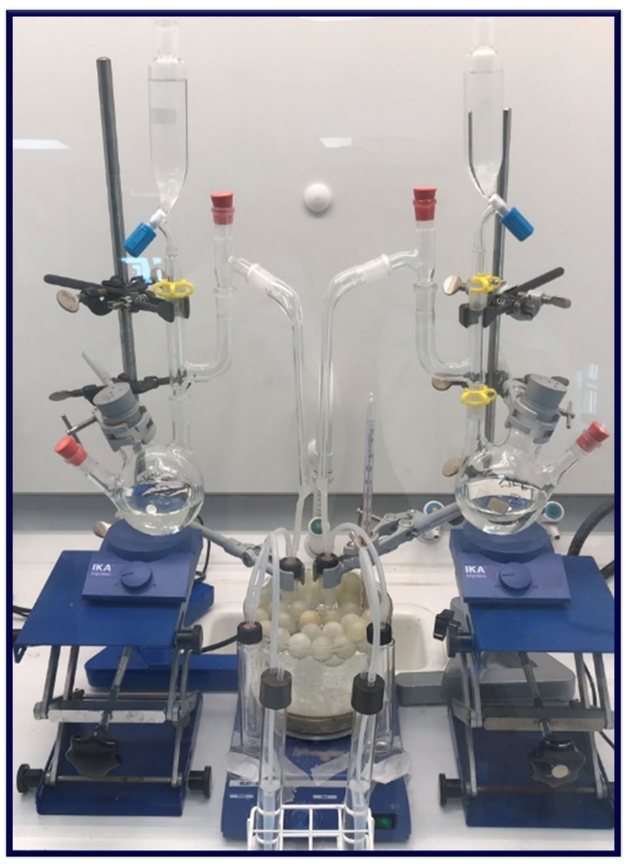
- Scavengers: BBS1, BBS2 and HET: 100 mM, 10 mL, initial pH: 10
- H_2S generation: $Na_2S{\bullet}3H_2O$: 200 mM, 100 mL and HCl: 1M, 50 mL
- Temperature of reaction: 80 °C
- Bubbling H_2S in scavenger solutions for 5 hours
- NaOH solution used to trap H_2S
- Offline monitoring: 2 spectra (3 acc x 5 sec) at beginning and end.

Aqueous phase reactions at 80 °C

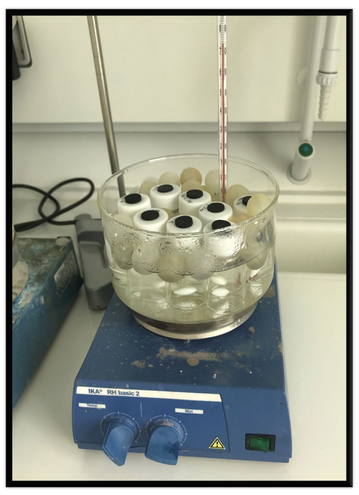
- Scavengers: BBS1, BBS2 and HET: 25 mL, initial pH: 10
- Initial concentration: 100 mM (Equimolar for scavenger and bisulfide)
- Temperatures: room and 80 °C
- Initial pH: 10
- Offline monitoring: 1 spectrum (3 acc x 5 sec) every 10 min for 1 hour

SETUP

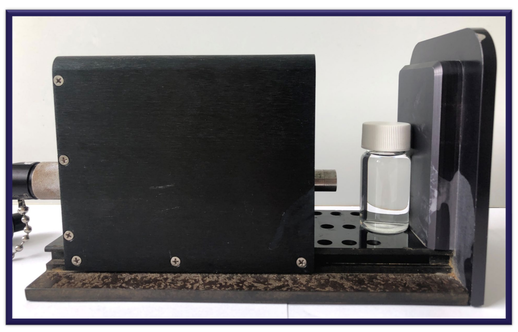
The setups allow offline monitoring for gas-liquid and aqueous phase reactions.



Gas-liquid reactions



Aqueous phase reactions



Raman box

CHARACTERISTIC RAMAN PEAKS

- Bisulfide (HS^-)
- Biomass-based scavenger (BBS)
- Triazine (HET)
- Thiadiazine (TDZ) – intermediate HET - H_2S by-product
- Dithiazine (DTZ) – final HET - H_2S by-product

Component	HS^- [1]	BBS [2]	HET [3]	TDZ [3]	DTZ [3]
Raman shift, cm^{-1}	2574	2260	923	634	675

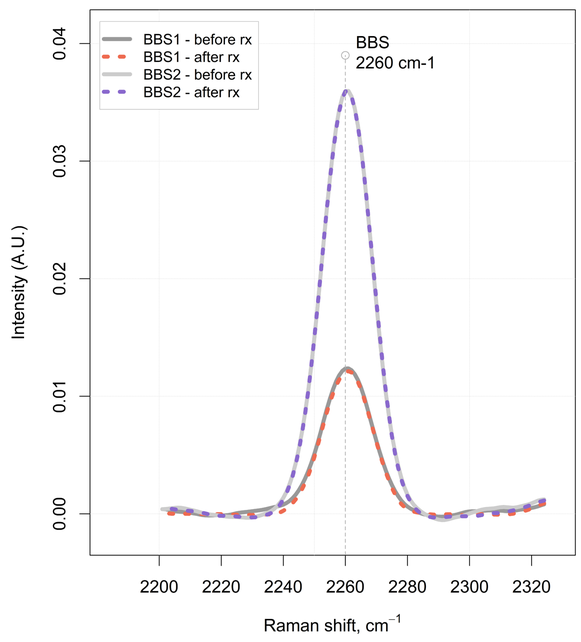
[1] Johansen et al, Chem. Eng. Trans., 74, (2019), 541-546.

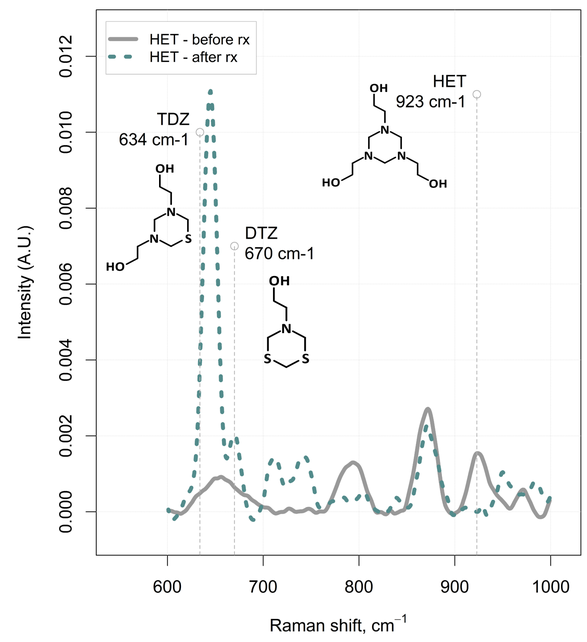
[2] Socrates, G. Infrared and Raman Characteristics Group Frequencies, third ed., Wiley, 2001.

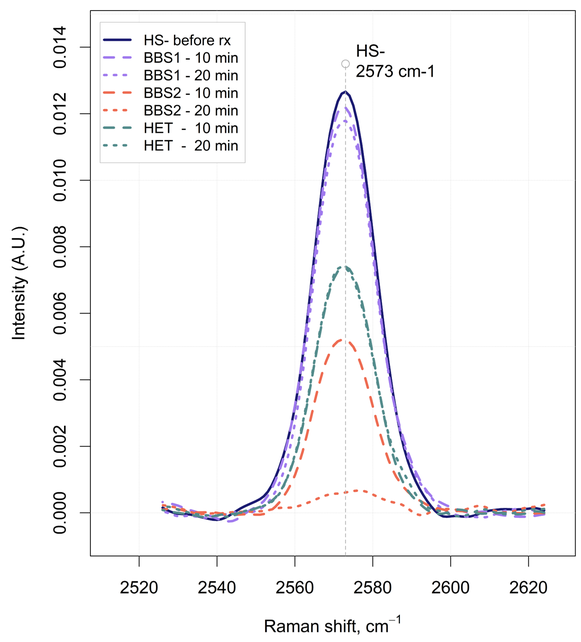
[3] Perez Pineiro et al, Ind. Eng. Chem. Res., 60, (2021), 5394-5402.

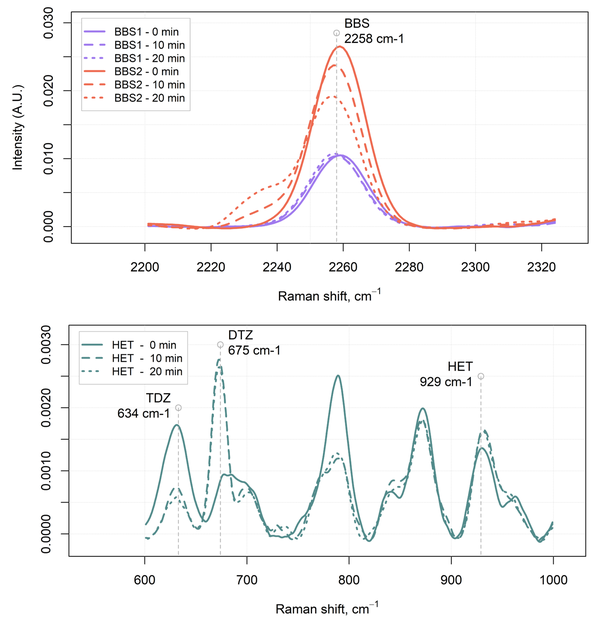
RESULTS

Gas-liquid reactions at 80 °C







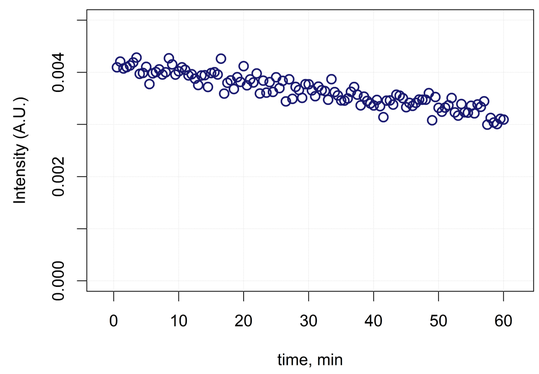


PERSPECTIVE

- Develop setups and procedures for quantitative on-line monitoring H_2S scavenging reactions.
- Acquire kinetic data regarding HET and H_2S scavenging reaction to use as benchmark for BBS scavenging reactions.

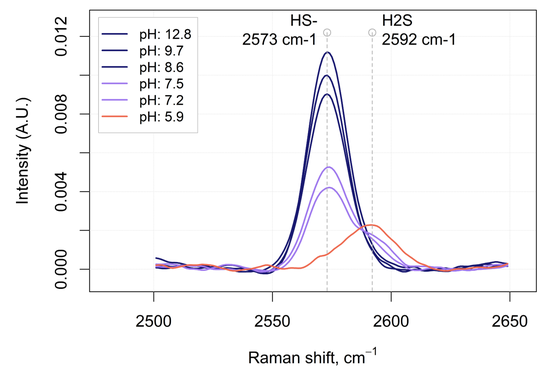
CHALLENGES

- Find a suitable internal standard for HET and HS^- reactions at 80 °C.



Acetonitrile lack of stability at 80 °C

- Changes of H_2S characteristic peak with different pH values.



HS^- and H_2S characteristic peaks

ACKNOWLEDGEMENTS

- The project “Reaction Kinetics of Green H_2S Scavengers”, run in collaboration with Copenhagen University, is financially supported by the Danish Hydrocarbon Research and Technology Centre.
- Christian Marcus Pedersen and Asger Røikjær Koue, from Copenhagen University, are acknowledged for the synthesis of the biomass-based scavengers.

AALBORG UNIVERSITY

Center for Olie og Gas - DTU
The Danish Hydrocarbon Research and Technology Centre