FIELD CRYSTALLIZATION OF MEA-DITHIAZINE: IDENTIFYING MATERIALS, LEVERAGING H-BONDING SYNTHONS, AND OPPORTUNITIES FOR CRYSTALLIZATION INHIBITION

29 June 2023

Jeremy Holtsclaw, Pioneer Oil Company
Nathan Schultheiss, Pioneer Oil Company & Purdue University
Tom Everett, Purdue University

SPE-213831-MS

Introduction

Description of the challenge

Contributing factors

Identify possible solutions

Discovery phase

Summary

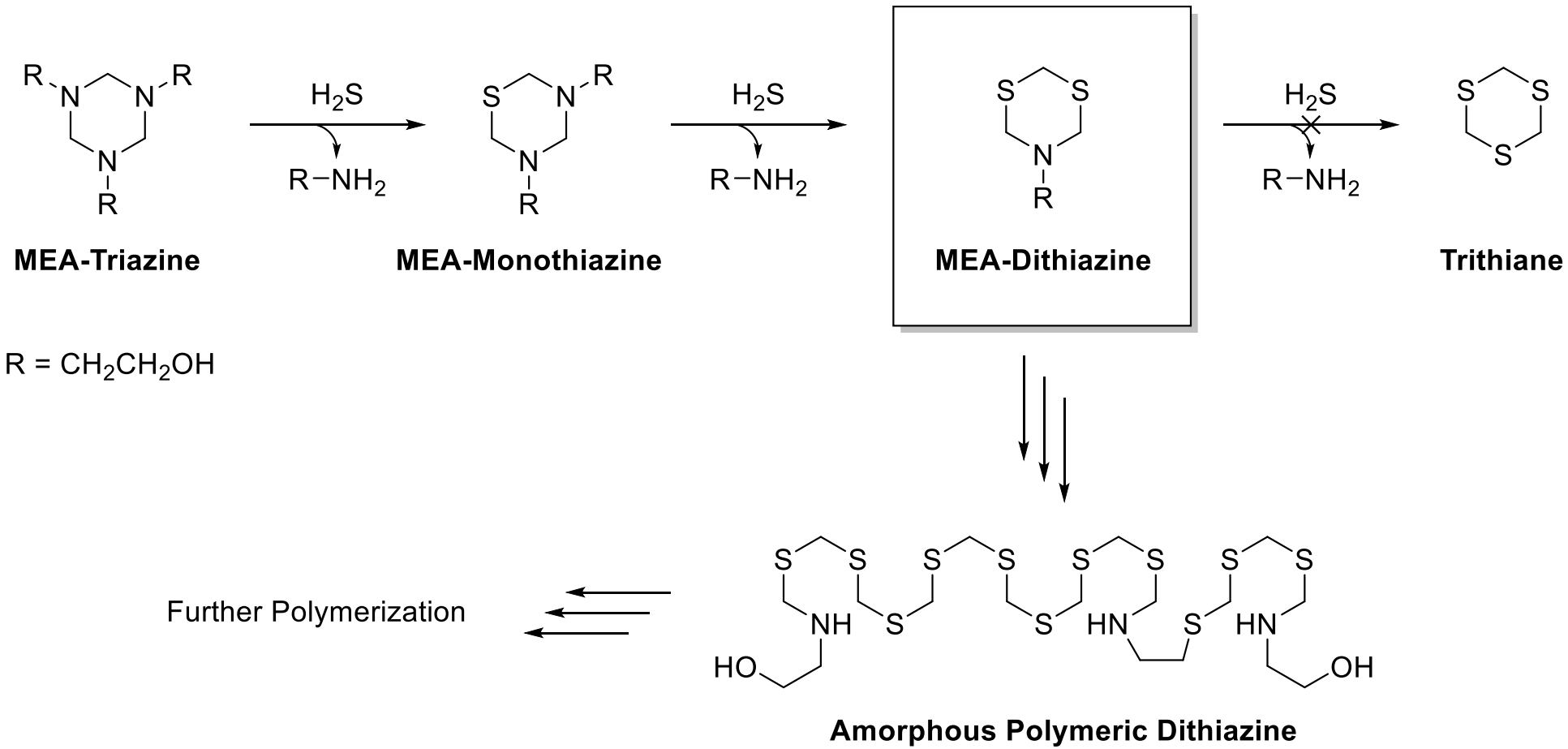
Continuation of work

SPE-213831-MS Field Crystallization of MEA-Dithiazine: Identifying Materials, Leveraging H-bonding Synthons, and Opportunities for Crystallization Inhibition, J Holtsclaw, N Schultheiss, T Everett

Opportunity – Cost Savings

- 47% MEA-Triazine scavenger at 15 gal/d ($12/gal, $1.33/lb)
- Treated at rate of 2.8x excess
- 5-6 gal/d (ideal treatment)
- 9.6 gal/d (supplier rec'd)
- Opportunity → $50k/y operational efficiency savings ($135/d of excess triazine)

The Triazine Reaction Pathway*



*Energy Fuels **2020**, *34*, 9923-9931

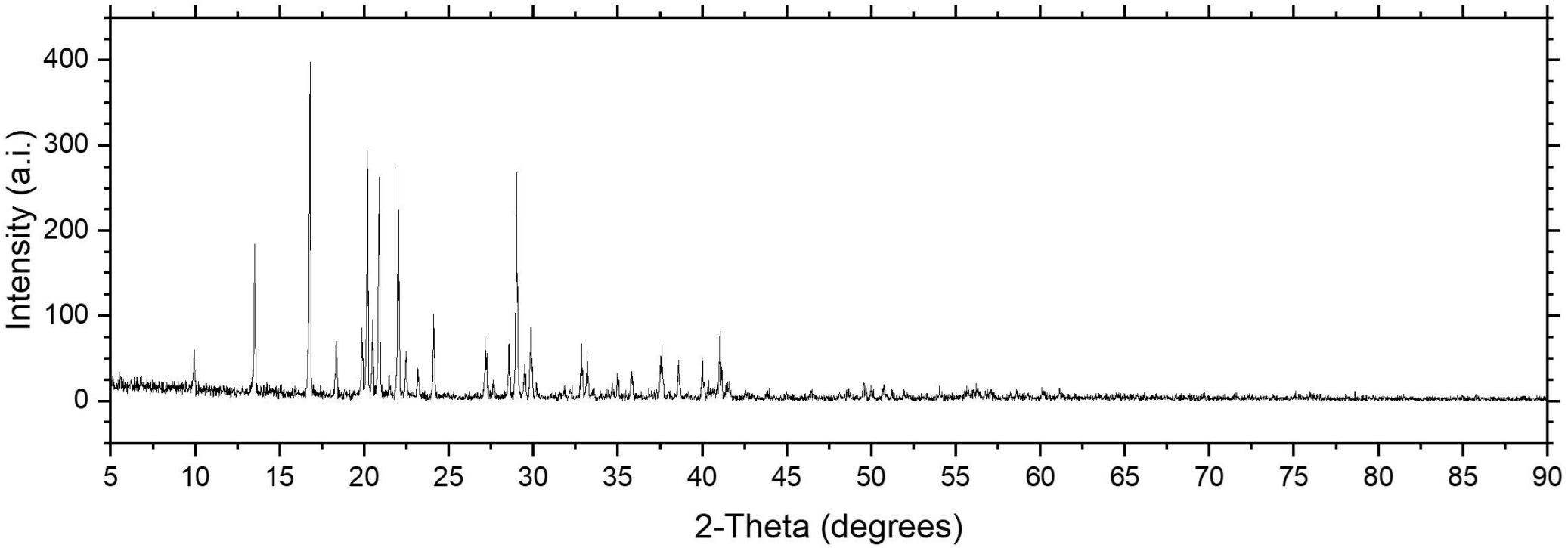
Location Conditions

- **Temperature and Humidity → Feb 23 °F – Mar 33 °F – Apr 43 °F**
- **Gas flow from the static mixers**
- **~10 gal/d of the 47% MEA-Triazine solution**

Challenge – Operational Issues

Typical remedy uses heat or hot water to melt or dissolve the physical blockage

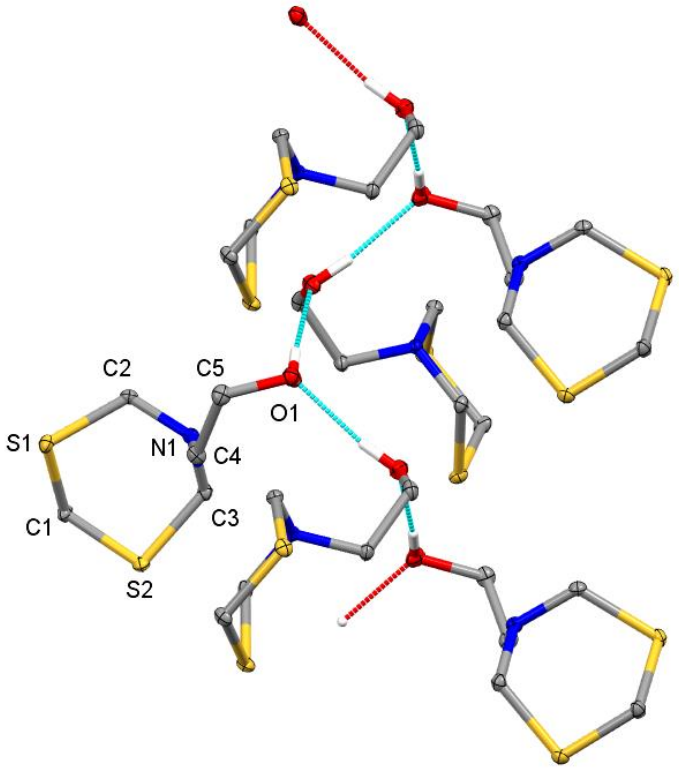
PXRD of Field Sample (not recrystallized)



Field crystals were of suitable quality for single crystal X-ray crystallography

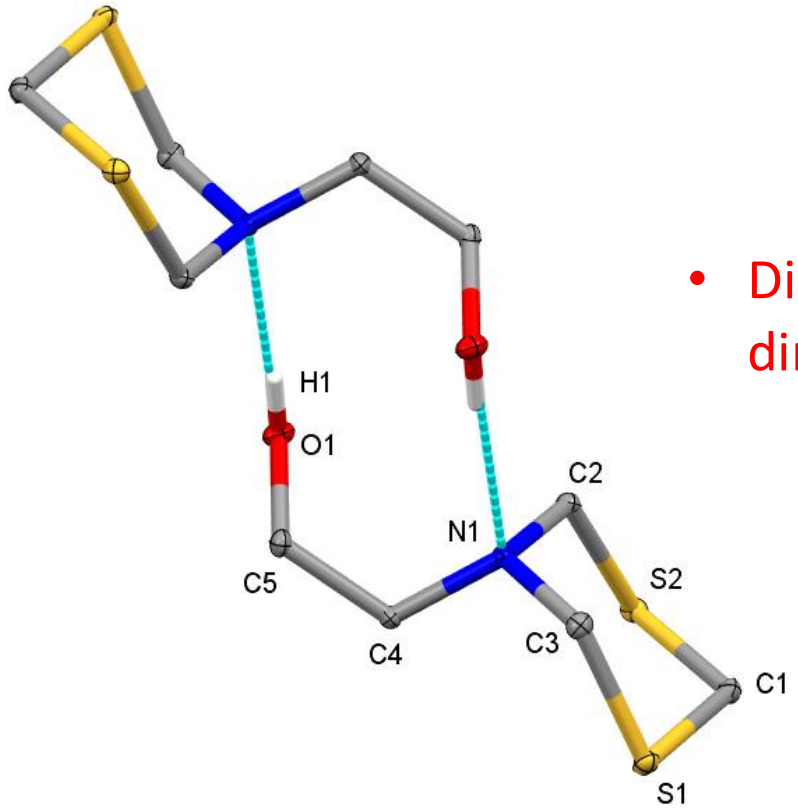
Polymorphic Crystal Structures of MEA-Dithiazine

- Helical one-dimensional strands



Form I

(Galvez-Ruiz et. al., 2004)

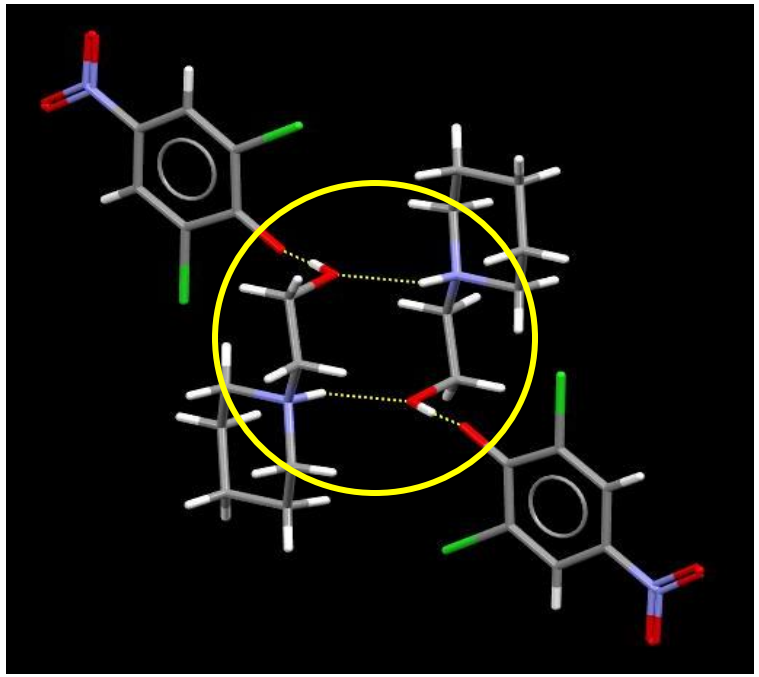


- Discrete dimers

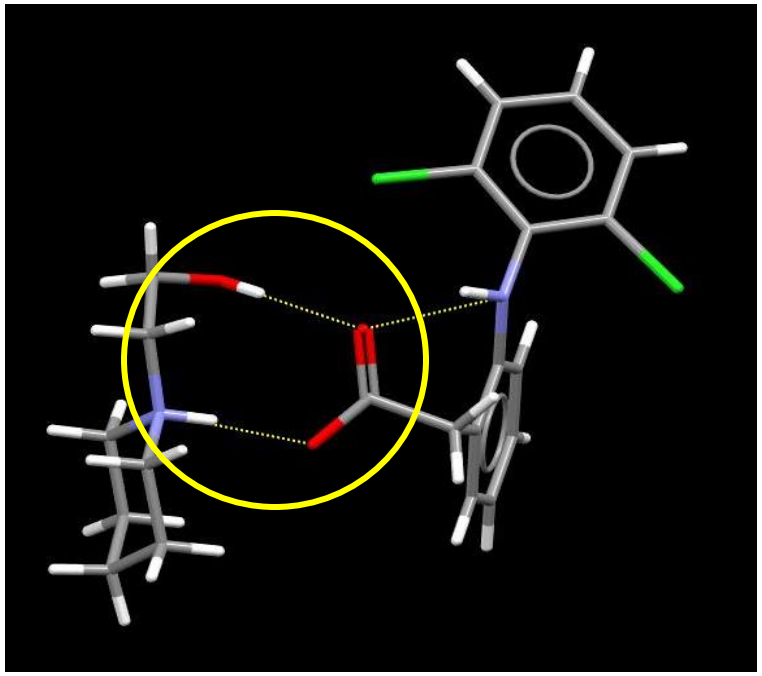
Form II

(Schultheiss et. al., 2022)

CSD Database Search Results



CSD refcode NIVJIO
(Szafran et. al. 2019)



CSD refcode WIRREU
(Sabatino et. al. 1996)

Insights from the CSD Database Search

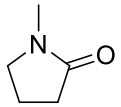
1) Avoid including molecules that contain proton-donating functional groups, e.g., carboxylic acids and hydroxyls, as salts are likely to recrystallize.

2) Introduce molecules containing hydrogen bonding functional groups but do not donate a proton, e.g., amides, oximes, pyrrolidones, and piperidones.

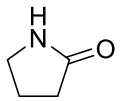
3) Introduce larger molecules (polymers) that contain hydrogen bonding functional groups but are not proton-donating.

Potential Inhibiting Molecules

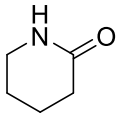
Small molecules



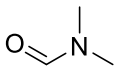
N-Methyl-2-pyrrolidone



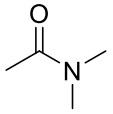
2-Pyrrolidone



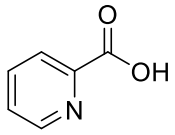
2-Piperidone



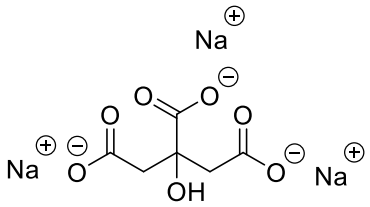
N,N-Dimethylformamide



N,N-Dimethylacetamide

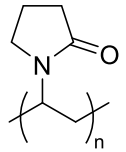


Picolinic acid

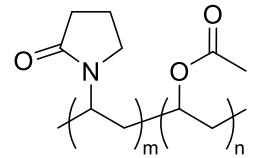


Sodium citrate

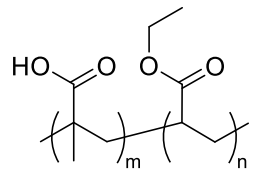
Polymers



poly(1-Vinyl-2-pyrrolidone)



Copolymer 1-vinyl-2-pyrrolidone and vinyl acetate

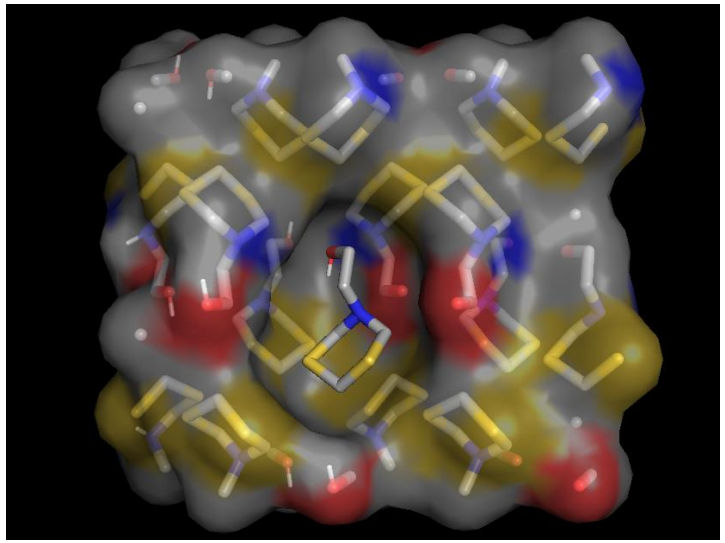


Copolymer methacrylate and ethyl acrylate

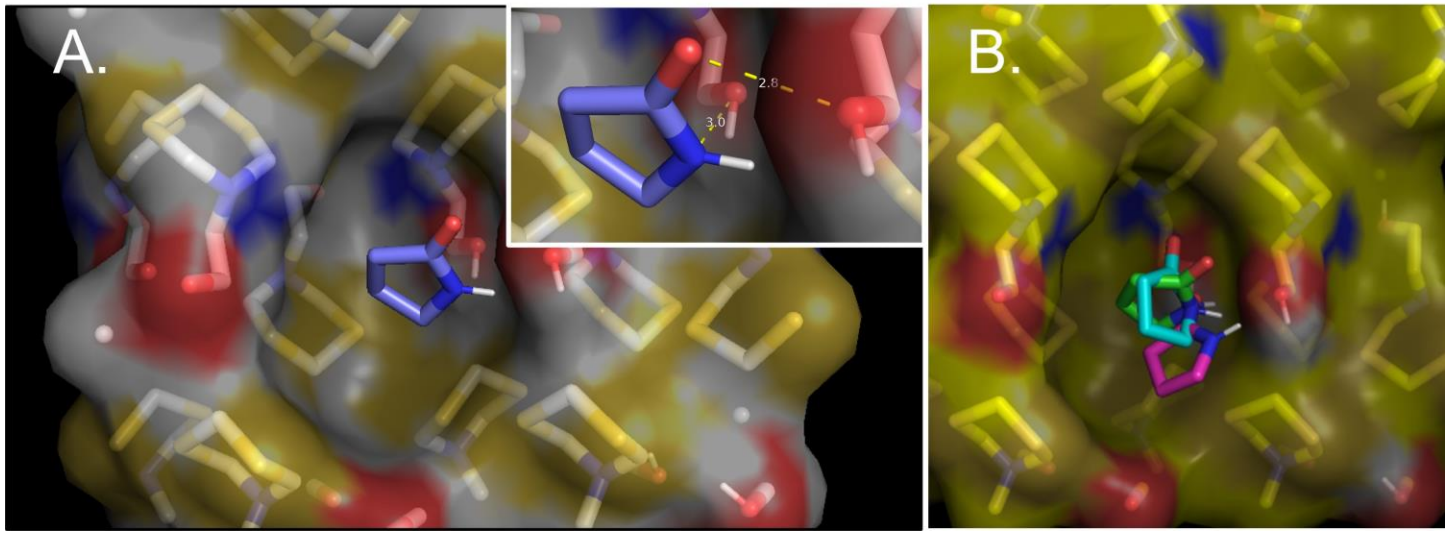
In Silico Screening

- Hypothesis: Higher binding energies would be better crystallization inhibitors
- Criteria to screen potential inhibitors:
  - A) Size
  - B) Shape
  - C) Intermolecular Interactions/Binding Energies
- Concept
  1. Utilize MEA-Dithiazine (Form II) XRD crystal structure with a vacancy in the lattice
  2. Insert inhibitor molecule into vacancy and calculate binding energy
  3. Adjust molecular orientation to give largest binding energy
- Binding energy is dependent on the size, shape, and strength of the intermolecular interactions

Computational Method-Autodock Vina



Crystal of MEA-Dithiazine (Form II) showing "binding pocket"



A. Optimized location of 2-pyrrolidone, B. Several conformations of 2-pyrolidone within the MEA-Dithiazine (Form II) crystal lattice

Calculated Binding Energies

	Molecular Weight	Density, g/cm³	Est. Free energy of binding, kcal/mol	OH---N (nearest neighbor), Å	OH---HO (nearest neighbor), Å
N,N-Dimethylformamide	73.09	0.944	-2.815	3.8	2.7
Dimethylacetamide	87.122	0.940	-3.195	4.0	2.7
MEA-Dithiazine	165.27	1.468	-3.211	4.3	2.7
1-(2-Hydroxyethyl)-1-piperidinium	130.21	0.973	-3.337	4.2	2.5
2-Piperidin-1-yl-ethan-1-ol	129.20	0.977	-3.340	3.7	2.8
N-Methyl-2-pyrrolidone	99.133	1.03	-3.437	4.2	2.8
Urea	60.06	1.32	-3.675	2.9	2.8
2-Pyrrolidone	85.106	1.12	-3.688	3.0	2.8
2-Piperidone	99.13	1.07	-3.994	3.2	3.9
Picolinic acid	123.111	1.31	-4.635	3.0	2.7
Poly(1-vinyl-2-pyrrolidone) (3 monomer units)	355.52	1.2	-4.654	---	2.2
Citrate	189.10	1.7	-5.251	4.1	2.7

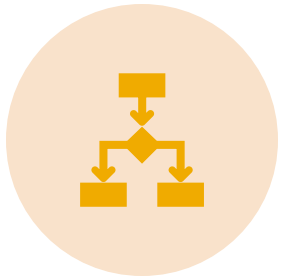
In Silico Lessons Learned

- All screened molecules had low-to-moderate binding energies
- Large negative biding energies could result in crystals and/or co-crystals
- Size is important. Larger molecules/polymers give larger binding energies
- Results should be taken as qualitative, not absolute
- Further effort is needed if inhibitor screening done solely with computational methods
- Compare computation results to lab observations

Initial Inhibitor Lab Screening

A 1:1 ratio (by mass) of MEA-Dithiazine and inhibitor were added to a vial with a suitable solvent.

Solvent was then evaporated. Spontaneous crystallization removed inhibitor from further consideration.



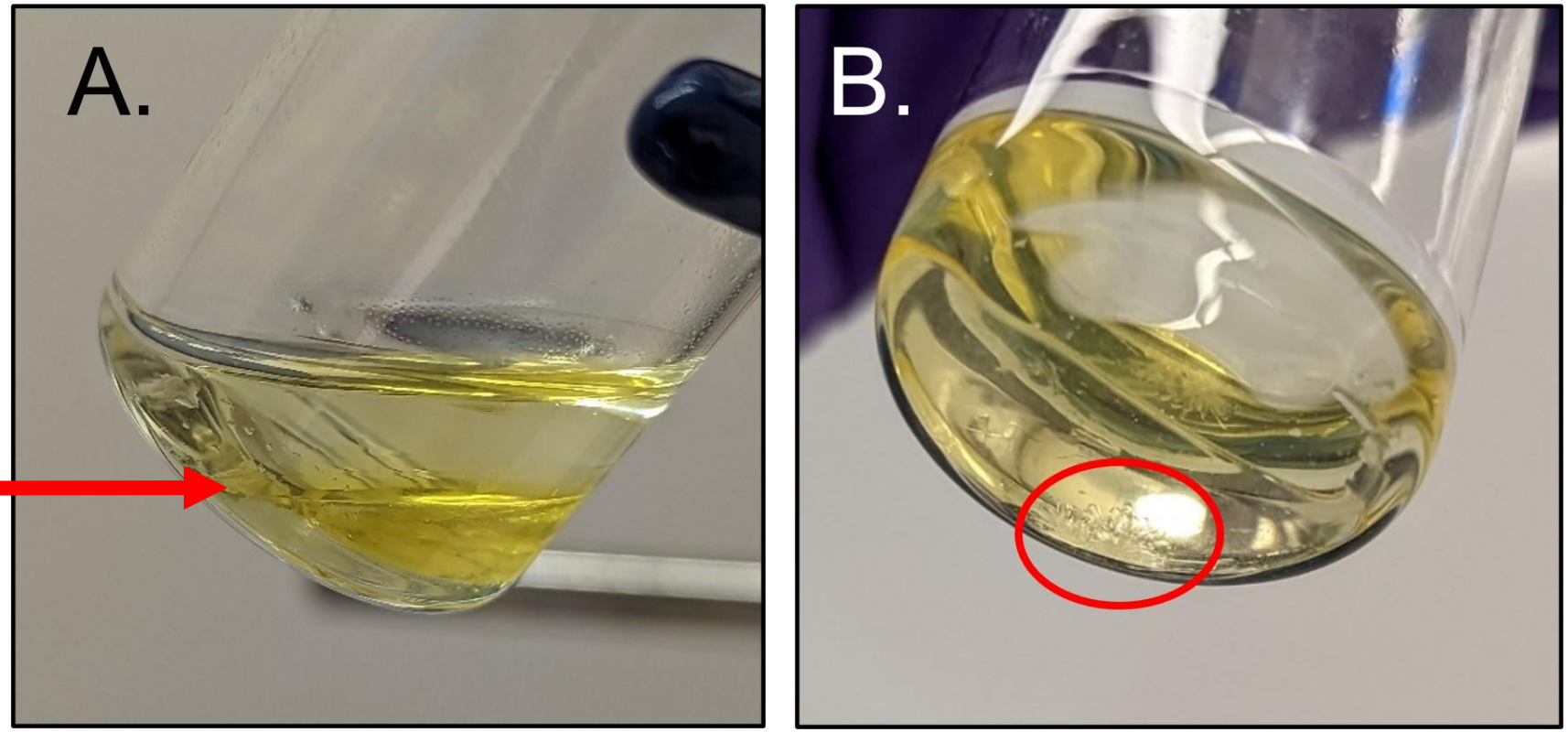
Crystallization was induced by scratching. If crystals formed, candidate was removed from trial.

Repeated for low temperature (37 °F).

Titrate inhibitor concentration.

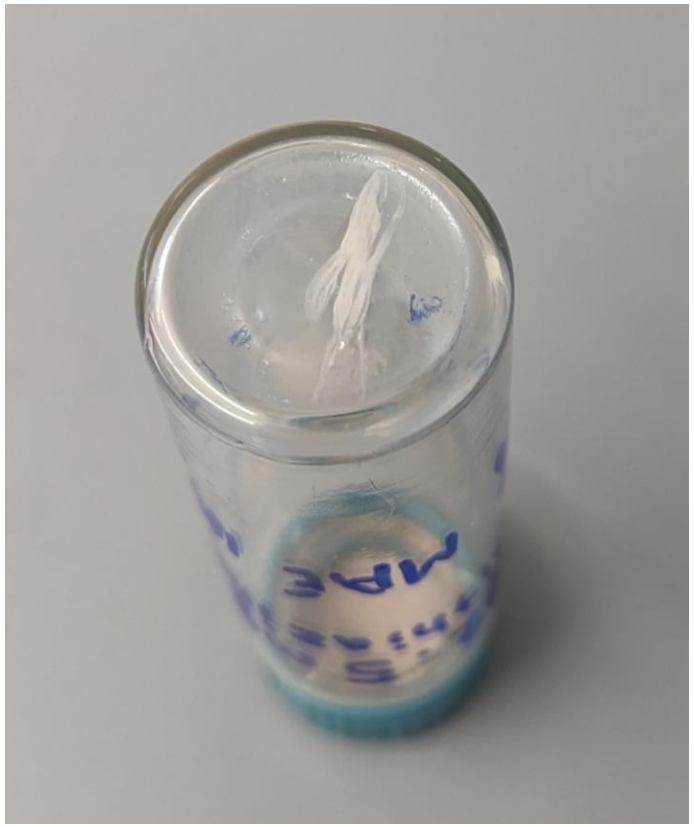
MEA-Dithiazine Crystals

Phase Separation



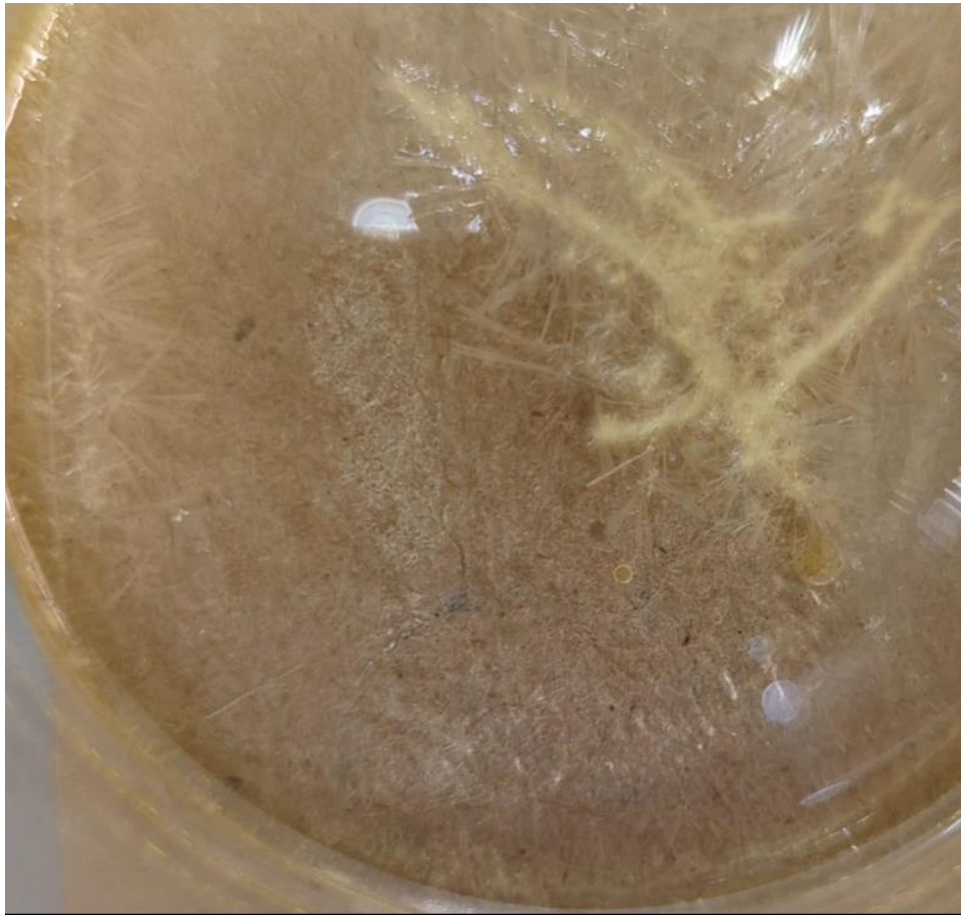
Scratch Testing-Negative Results

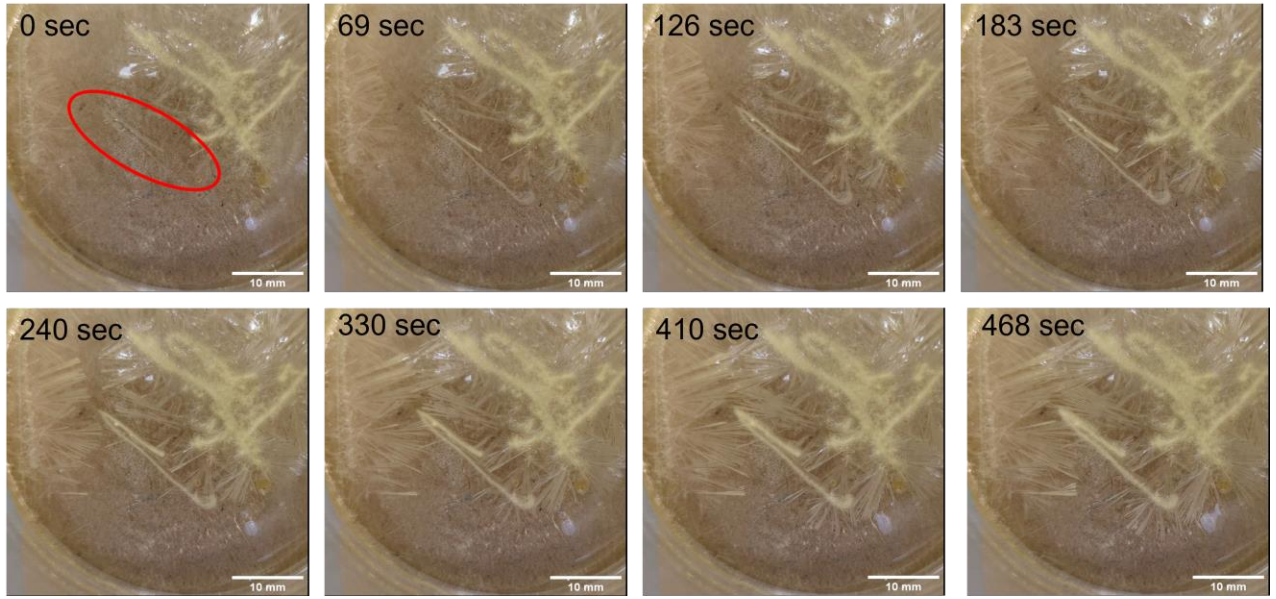
40% (w/w) 90F to MEA-Dithiazine



40% (w/w) MAE 100-55 (copolymer of methacrylic acid and ethyl acrylate with surfactants)

MEA-Dithiazine Rapid Crystal Growth



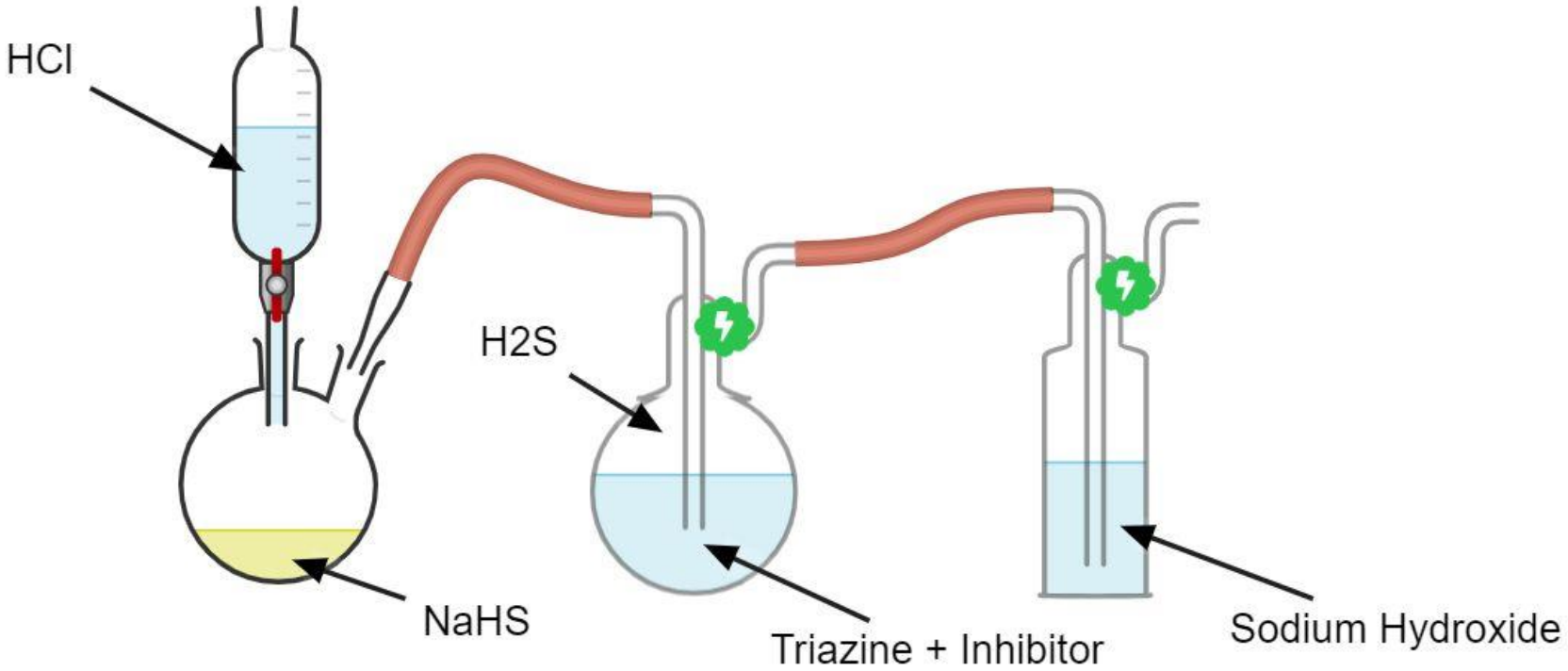


0.1- 0.2 mm/s crystal growth rate

Lab Screening Summary

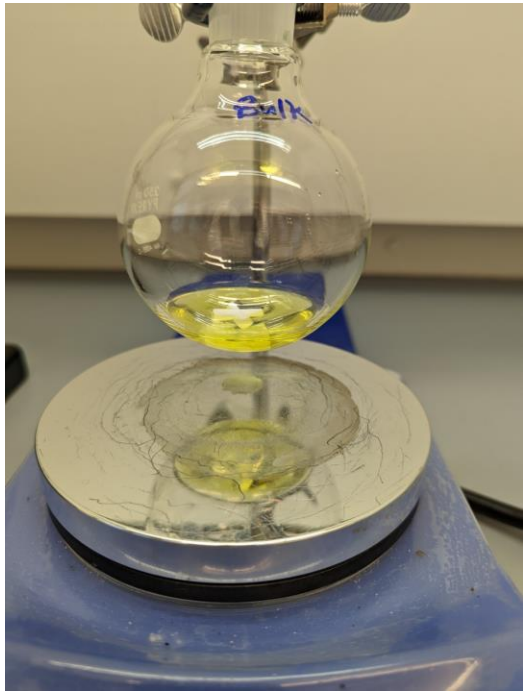
- Kollidon 30, 2-pyrrolidone, and 2-piperidone were effective at the lowest concentrations and lowest temperatures
- 2-Piperidone was the overall the most efficient with respect to concentration (25% w/w with respect to MEA-Dithiazine)
- Kollidon 30 needed 35-40% to be effective
- 2-Pyrrolidone needed 35%
- All three showed good low temperature tolerance at these concentrations

Reproducing Field Conditions in Lab

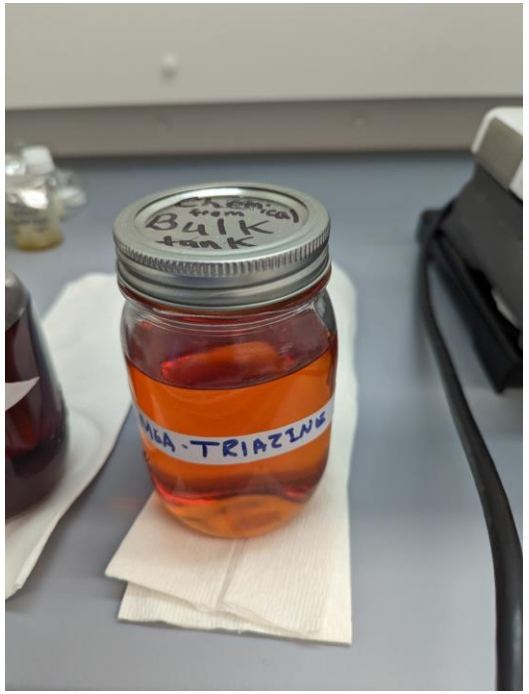


Example: H_2S scavenger after bubbling hydrogen sulfide gas.

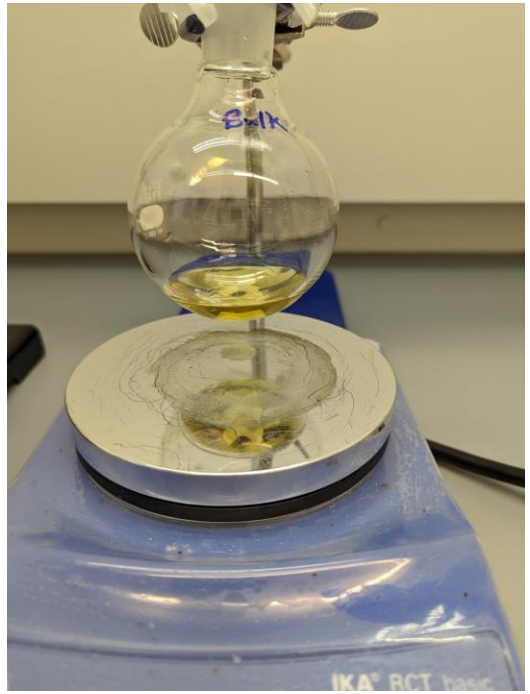
Reproducing Crystals in Lab-Reaction with HS^-



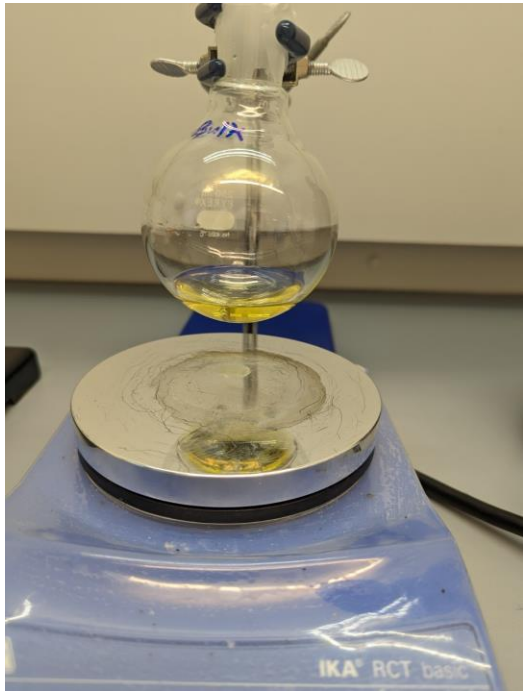
Sodium hydrosulfide in water



47% triazine solution

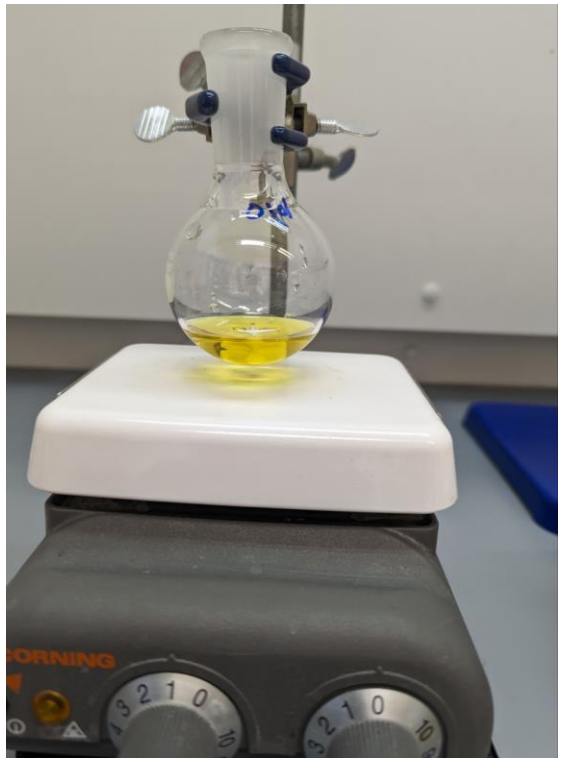


NaSH solution after adding 47% triazine solution



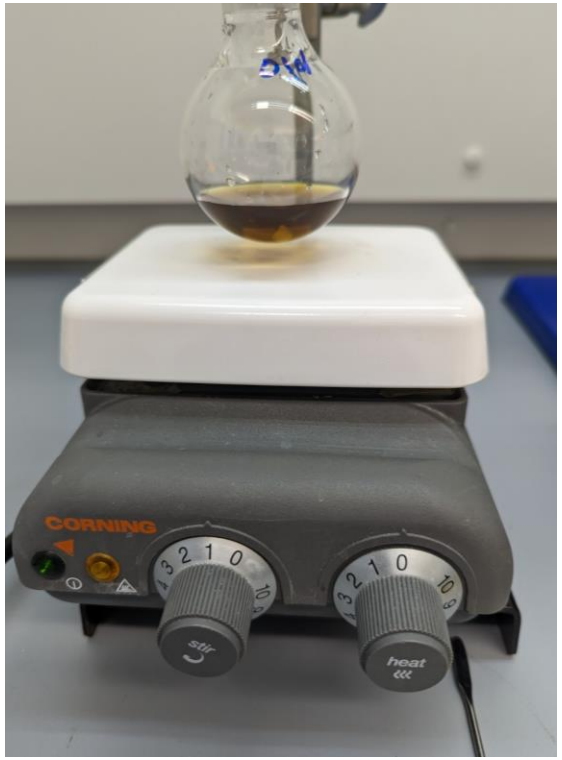
NaSH solution after adding 47% triazine solution after 4 days

Reproducing Crystals in Lab-Reaction with HS^-

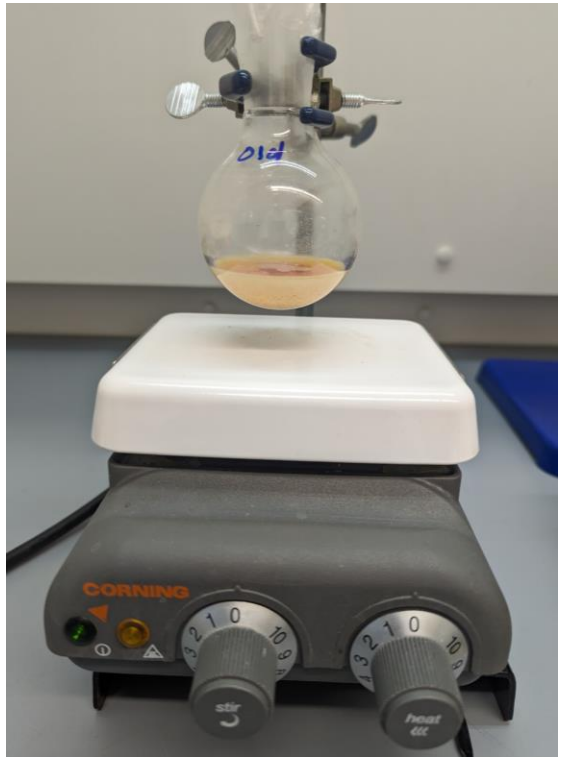


Sodium hydrosulfide in water

Spent 47% triazine solution



NaSH solution after adding spent 47% triazine solution



NaSH - triazine solution after 4 days

Conclusions

- Low vapor pressure, hydrogen bonding capable molecules (2-pyrrolidone, 2-piperidone and poly(1-vinyl-2-pyrrolidone)) successfully inhibited the crystallization of MEA-Dithiazine (Form II) in laboratory experiments.
- Computational tool Autodock Vina was used as a preliminary screening tool to explore molecular docking affinities between molecules, providing insights into suitable experimental candidates.
- The Cambridge Structural Database (CSD) was used to examine reported solid-state structures of dithiazine-like molecules and their propensity to crystallize as multi-component materials.
- Additionally, the CSD revealed that if proton-transfer (charge-assisted hydrogen bonding) occurs, a crystalline salt will likely result, so these functional group moieties should be avoided.
- Economics: 25% 2-piperidone (+$0.55/lb, 11.8 wt%); 35% 2-pyrrolidone (+$0.25/lb, 16.5 wt%) for finished product

Thank you!

Acknowledgements

- Tim Hall
- Pioneer Oil Company
- Purdue University
  - Davidson School of Chemical Engineering
  - The Enhanced Oil Recovery Lab