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Amine screening for oxidation by bench-scale experiments

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Introduction

- Amine solvents are key to post-combustion carbon capture (PCCC) technologies due to fast kinetics, high CO_2 capacity, and well-established process infrastructure.

- Oxidative degradation, mainly driven by dissolved oxygen (DO), raise concerns about the environmental consequences of long-term solvent use.

- Oxidation is mainly caused by three factors
  - DO in the hotline to the stripper
  - Ferric ions (Fe^{3+}) in the absorber that catalyze oxidation
  - NO_2 in the flue gas

- Many of degradation products are toxic and difficult to manage.

- The ability to predict and mitigate oxidative degradation are critical for solvent development.

Previous screening studies

	Liu H. et al. (2015)	Buvik et al. (2021)	Liu Q. et al. (2024)
Number of amines	12	18	14
Duration (hours)	100	504	336
Amine (wt%)	30	30	4 or 5 mol/L
Volume (mL)	350	200	200
Gas flow rate (mL/min)	vortex	60	20

Common conditions; 60ºC, 2% CO_2, 98% O_2, measured loss of amine, 0.4-0.5 mM Fe^{3+}

Major findings

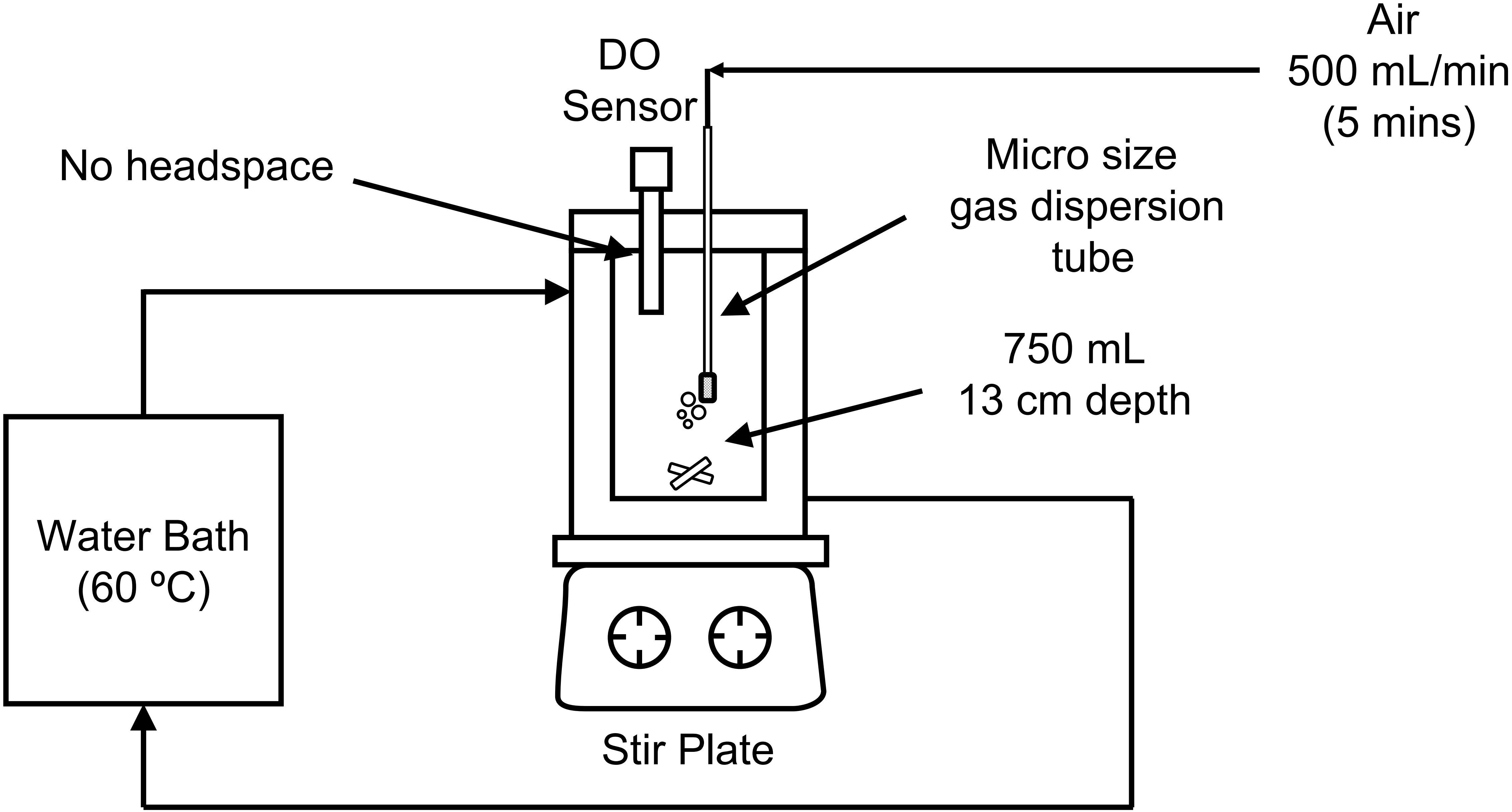
- Buvik: Strong structure–stability correlations: Limited conformational freedom, steric shielding, and reduced α-hydrogen availability decreased oxidation.
- Liu Q.: Oxidative stability increased with amine order and was further enhanced by steric hindrance.

Buvik V, Vevelstad SJ, Brakstad OG, Knuutila HK. Stability of Structurally Varied Aqueous Amines for CO_2 Capture. *Ind. Eng. Chem.* Res. 2021; 60 (15): 5627–5638.
Liu H, Hatchell D, Namjoshi AO, Rochell GT. *Oxidative Degradation of Amine Solvents for CO_2 Capture.* The University of Texas at Austin. 2015.
Liu, Q, Luo T, Yin Y, Ouyang Y, Xiao M, Gao H, Sema T, Liang Z. Oxidative Stability of Structurally Varied Amines for Post-Combustion CO_2 Capture. *Chemical Engineering Science.* 2024; 299: 120458.

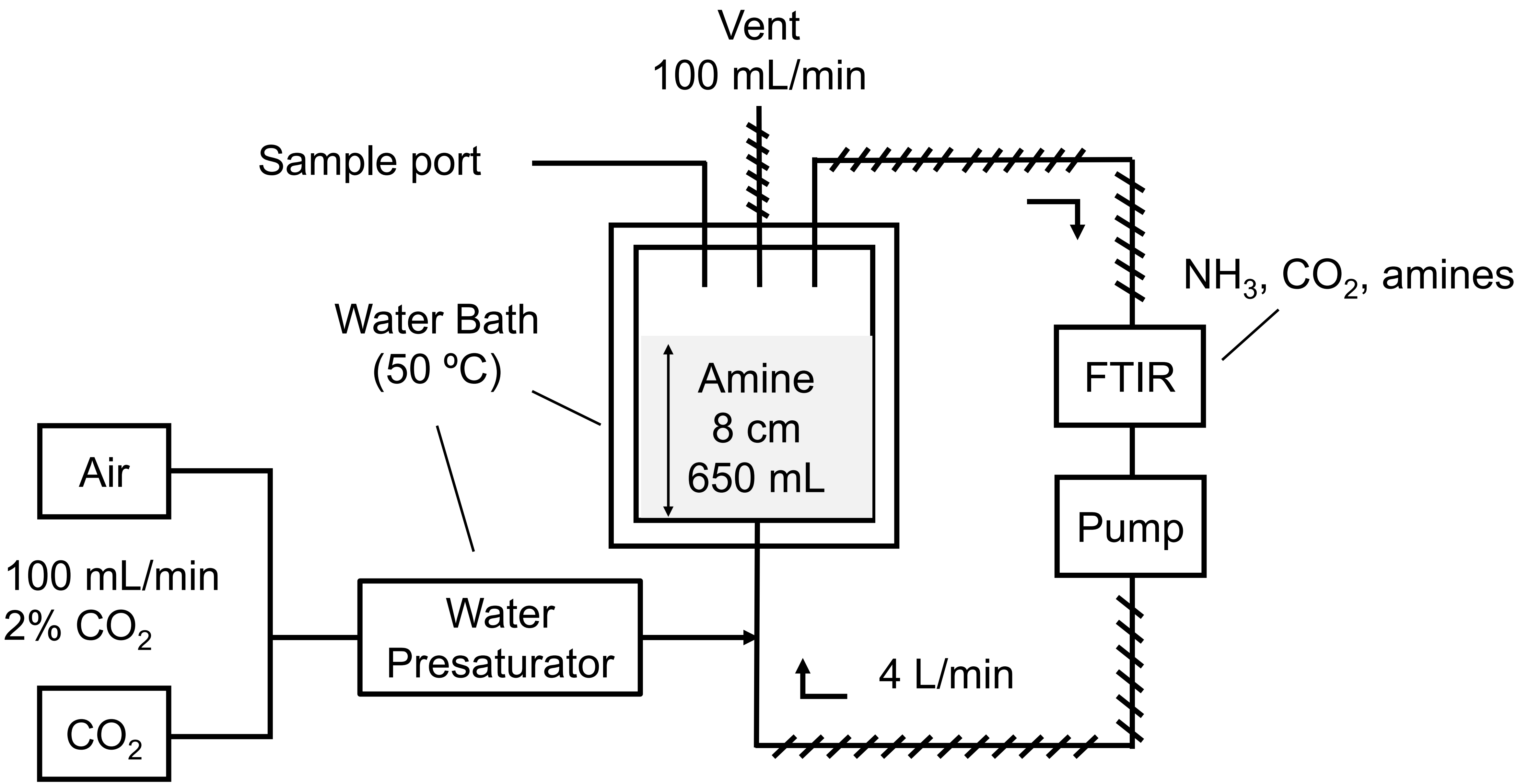
Research Objectives

- Measure degradation rate at absorber conditions with Fe^{3+}
- Based on two methods
  - Depletion of DO 5-60 minutes
  - NH_3 generation 5-10 days
- Measure 14 practical amines
- Compare results with previous work

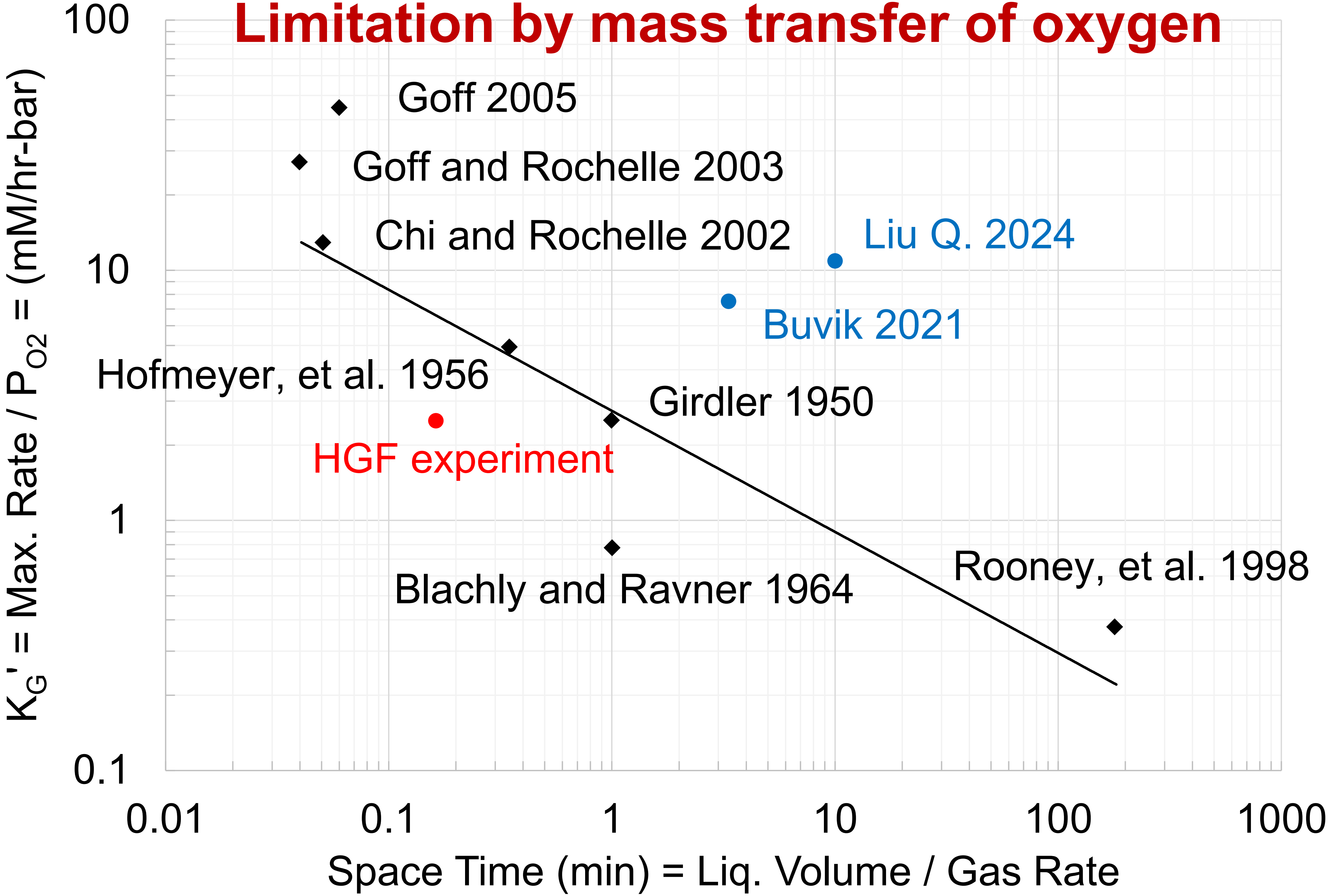
Oxygen Depletion Batch Reactor (ODBR)



High Gas Flow reactor (HGF)



Limitation by mass transfer of oxygen



Comparison of methods

	ODBR	HGF	Liu H., 2015	Buvik, 2021	Liu Q., 2024
Criteria for oxidation	DO	NH_3	Amine loss	Amine loss	Amine loss
Number of amines	14	14	12	18	14
Duration (hours)	3	50	100	504	336
O_2 (vol%)	18	18	98	98	98
Fe^{3+} (mM)	1	1	0.4	0.5	0.5 Fe^{2+}

Common conditions: 60ºC, 30 wt% amine, 2% CO_2
Exceptions: Liu H. vortexed, Liu Q. 4 or 5 M, HGF 50ºC
ODBR and HGF include 6 amines not in previous work

Selection of amines

- 6 amines unreported for oxidation screening
  - CESAR1,
    1-Methylpiperazine (1-MPZ), Hydroxyethylpiperazine (HEP)
    Diethylenetriamine (DETA), 1,3-Propanediamine (PDA)
    1,6-Hexamethylenediamine (HMDA)

- 6 amines reported in one paper
  - Monoethanolamine (MEA), Piperazine (PZ)
    Aminomethylpropanol (AMP), Aminoethylpiperazine (AEP)
    Ethylenediamine (EDA), Methylaminopropylamine (MAPA)

- 2 amines reported in more than two papers
  - Monopropanolamine (MPA), Methyldiethanolamine (MDEA)

Rate constant for DO and NH_3

$$\frac{d[O_2]}{dt} = k_{DO}\,[O_2] \qquad (1)$$

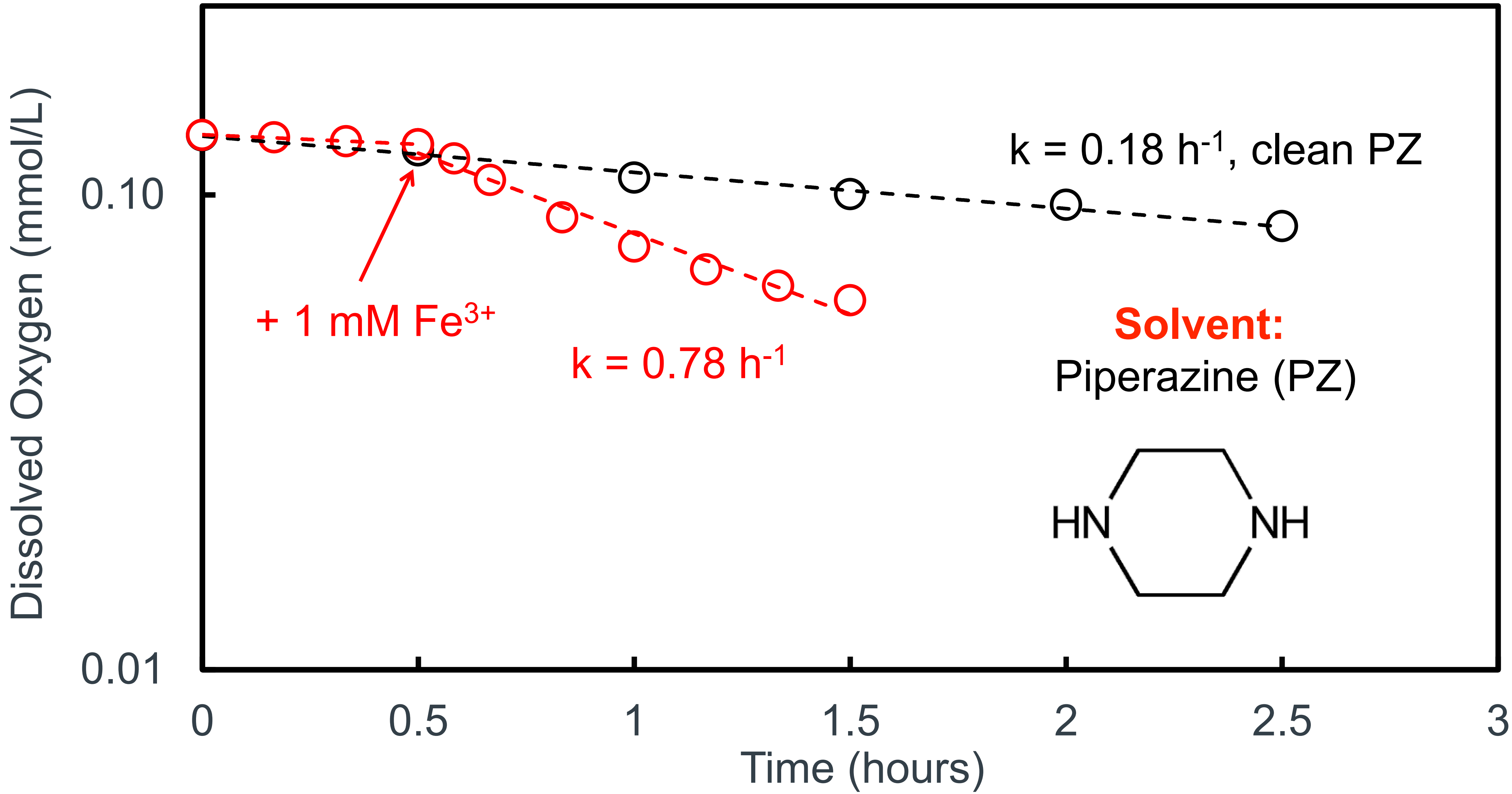
- 1 mol of NH_3 will be generated during 3 mol of DO is consumed
- The DO concentration in HGF experiment is relatively constant at 4.8 mg/L

$$\frac{d[O_2]}{dt} = 3\,\frac{d[NH_3]}{dt} \qquad (2)$$

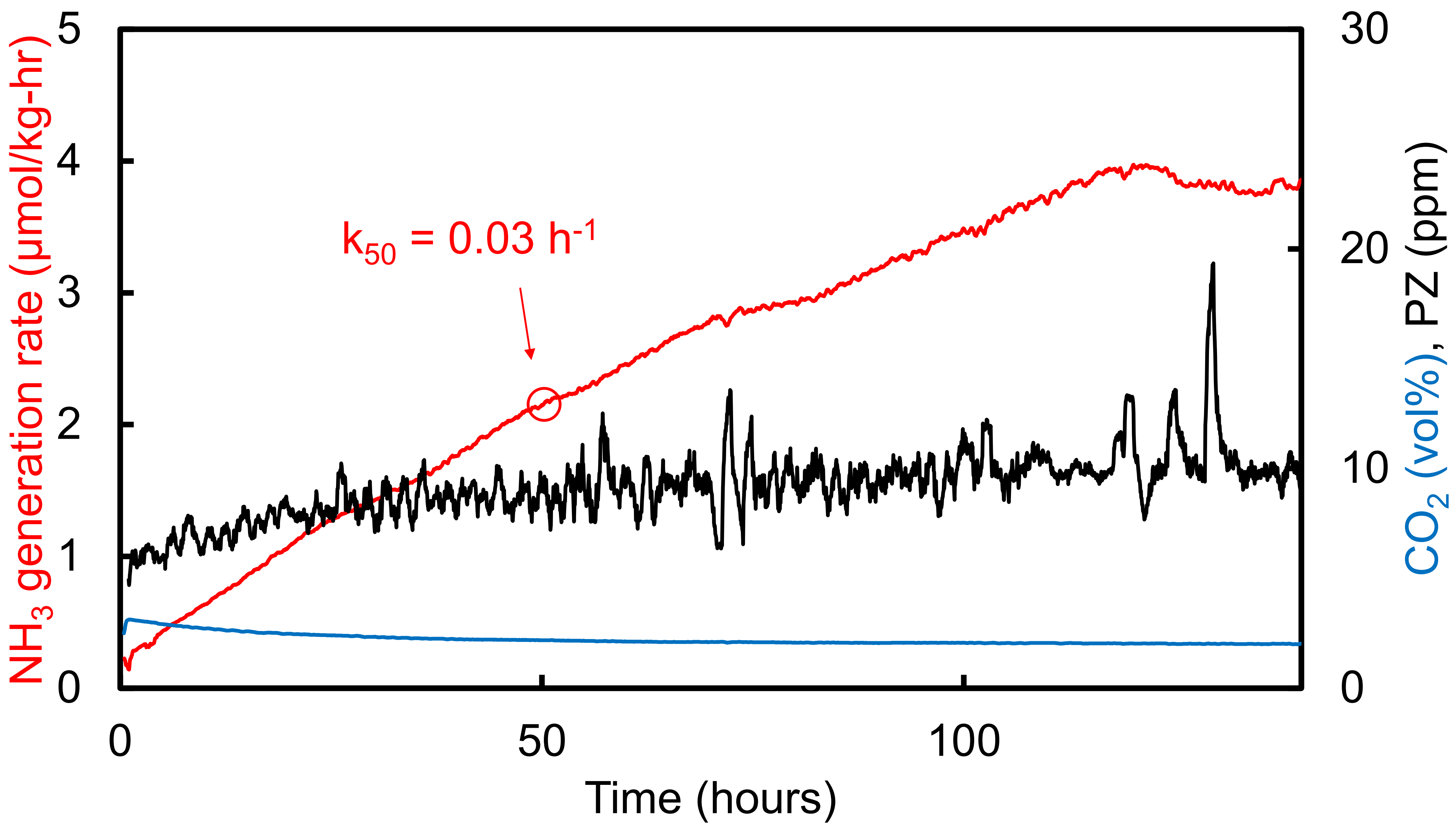
$$3\,\frac{d[NH_3]}{dt} = k\,[O_2] \qquad (3)$$

$$k_{50} = \frac{3\,\frac{d[NH_3]}{dt}_{50}}{[O_2]} \qquad (4)$$

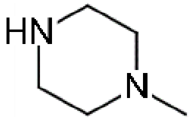
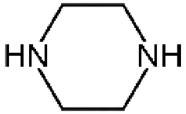
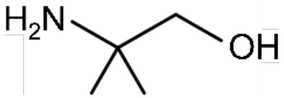
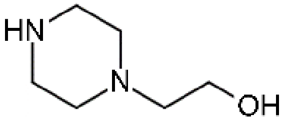
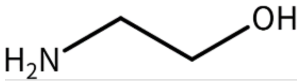
DO consumption in 5 m PZ (α=0.4) at 60 ºC



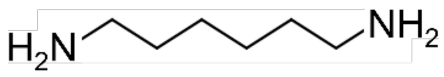
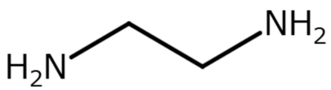
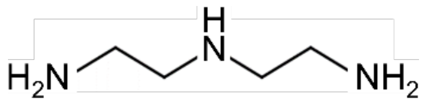
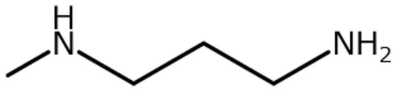
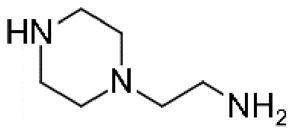
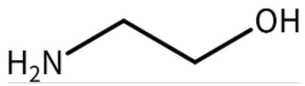
NH_3 generation in 5 m PZ (α=0.34) at 50 ºC

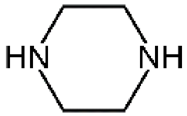
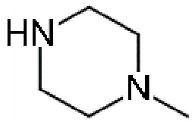
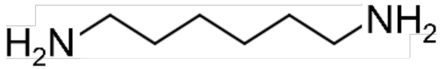
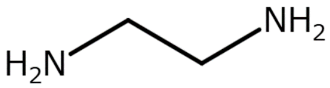
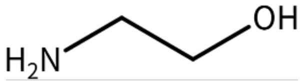


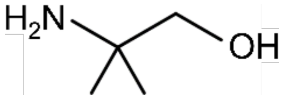
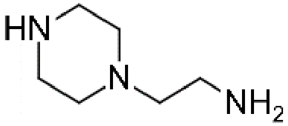
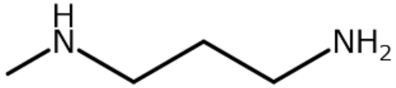
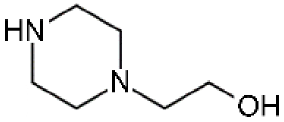
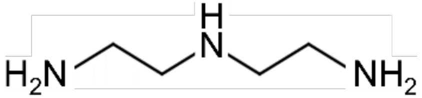
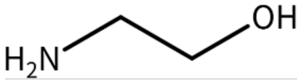
Summary of rates (1/2)

Amine	Structure	k_{DO} [h^{-1}] No Fe^{3+}	NH_3 generation k_{50} [h^{-1}]	Ratio $\frac{k_{DO,\ No\ iron}}{k_{50,\ HGF}}$
CESAR1	-	0.03	0.15	0.2
MPA		0.12	0.35	0.3
1-MPZ		0.16	0.14	1.2
PZ		0.18	0.03	6.0
AMP		0.18	0.10	1.8
HEP		0.28	0.28	1.0
MEA		2.04	2.20	0.9

Summary of rates (2/2)

Amine	Structure	k_{DO} [h^{-1}] No Fe^{3+}	NH_3 generation k_{50} [h^{-1}]	Ratio $\frac{k_{DO,\ No\ iron}}{k_{50,\ HGF}}$
HMDA		0.28	2.21	0.1
PDA		0.5	0.53	0.9
EDA		0.63	1.39	0.5
DETA		1.13	2.61	0.4
MAPA		1.59	3.54	0.4
AEP		1.65	0.28	5.9
MEA		2.04	2.20	0.9

Criteria for oxidation		$k_{DO,\ +\ 1\ mM\ Fe3+}$	k_{50}	Amine loss	Amine loss	Amine loss
Amine	Structure	ODBR	HGF	Liu, 2015	Buvik, 2021	Liu, 2024
CESAR1	-	11	7	-	-	-
PZ		17	1	-	2	-
MPA		18	16	0	17	17
1-MPZ		19	6	-	-	-
HMDA		24	100	54	-	-
EDA		43	63	45	-	-
MEA		100	100	100	100	100

Criteria for oxidation		$k_{DO, + 1 mM Fe3+}$	k_{50}	Amine loss	Amine loss	Amine loss
Amine	Structure	ODBR	HGF	Liu, 2015	Buvik, 2021	Liu, 2024
AMP		47	4	-	6	8
AEP		51	13	-	0	-
MAPA		60	161	-	60	-
HEP		62	13	-	-	-
DETA		68	119	-	-	-
PDA		70	24	0	-	-
MEA		100	100	100	100	100

Conclusion

- What amines are resistant to oxidation?
  - Unreported
    - Good: CESAR1, 1-MPZ
    - Bad: HEP, DETA
  - Reported
    - Good: PZ, MPA, AMP
    - Bad: MAPA, PDA, MEA
    - Unclear: HMDA, EDA

- The results of ODBR method are consistent with previous research, thereby demonstrating a high level of reliability

- Although the results focusing on the NH_3 generation may not be optimal for evaluating general oxidation resistance, quantifying NH_3 production is critical for technical design. In this regard, the HGF method offers a distinct advantage by enabling accurate measurement of NH_3 output.

Thank You

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