

II. PROPOSAL NARRATIVE

Abstract.

Direct air capture (DAC)--the concentration of CO₂ from ambient air--is being widely investigated as a strategy for mitigation of the adverse effects of distributed sources of CO₂. Although the pursuit of novel materials and processes will inevitably lead to further reductions in DAC cost, the fact that a significant amount of process energy input is directed towards the delivery of a product that is not highly valuable from a chemical standpoint is inherent to the nature of DAC processes, and likely cannot be overcome through materials/process innovation. As part of this project, we seek to ask the following question, which, to the best of our knowledge, has not been explored previously in the carbon capture and conversion literature: ***rather than directing DAC energy input purely for the purposes of demixing CO₂ from N₂, can we instead use these energy inputs to overcome thermodynamic constraints limiting the steady state catalytic conversion of CO₂ to methanol under ambient conditions?*** Funds requested as part of this proposal will be directed towards an assessment of the scientific and techno-economic feasibility of the single-step direct capture and conversion of CO₂ from ambient air to fuels and chemicals.

Introduction.

Although strategies for reducing direct air capture (DAC) cost are being widely explored,¹⁻³ significant energy inputs, the lower bounds of which are determined by second law efficiencies,⁴ are needed to extract CO₂ from low-

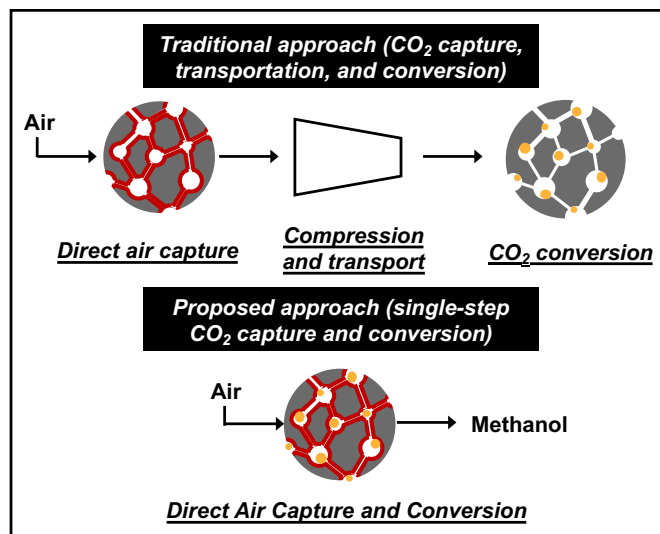


Fig. 1: Traditional approach to capturing and converting CO₂ from ambient air to fuels and chemicals (top) versus proposed single-step approach (bottom)

concentration sources. In the absence of significant cost incentives for capturing CO₂, the relatively large energy input required to capture CO₂ will need to be

recovered through the value of the product—in this case pure CO₂. Rather than producing a pure CO₂ stream that has negligible chemical and/or fuel value, we seek to direct this energy input towards converting CO₂ to methanol at ambient pressures (Fig. 1). This single step process can be carried out by replacing steam during the regeneration step with H₂ (Fig. 2), and will help circumvent thermodynamic constraints that render the direct, steady state conversion of CO₂ at 400 ppm to methanol infeasible.^{5,6} ***The project is aligned with the goals of CCME, which include the enabling of novel, broadly deployable approaches to climate change mitigation, and will foster the creation of technical leadership, research infrastructure, and a graduate workforce in two critical areas of CCME research- carbon capture from distributed and point sources, and the conversion of CO₂ to fuels and chemicals.***

Objectives.

- 1. Demonstrate feasibility of the conversion of CO₂ from ambient air to methanol.*
- 2. Evidence methanol production through temperature swing adsorption-reaction.*
- 3. Conduct preliminary techno-economic assessment calculations.*
- 4. Identify key technological and scientific knowledge gaps.*

Approach.

First, non-noble metal catalysts that convert CO₂ at ambient pressures to methanol will be developed.⁷ Catalyst performance will be evaluated on an existing fixed-bed flow reactor setup equipped with an online gas chromatograph. Catalyst formulations identified as part of aim 1 will be combined with supported amine adsorbents that

concentrate CO₂.
Temperature swing
adsorption-reaction
studies will be
conducted using
hydrogen co-feeds
at atmospheric
pressure facilitating

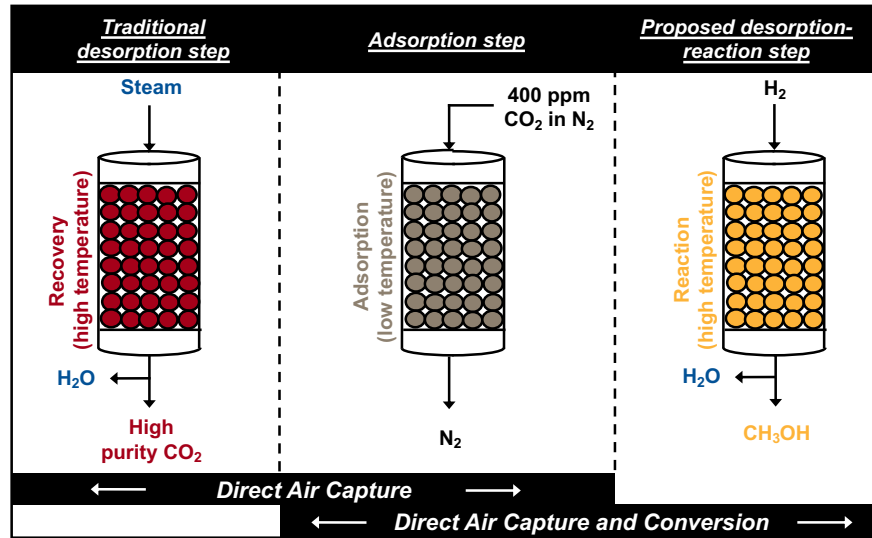


Fig. 2: Process steps for the direct capture and conversion of CO₂, involving replacement of the desorption step (left) with a hydrogenation step (right).

desorption and catalytic conversion to methanol. Temperature swing adsorption-reaction performance data collected in aim 3 will be used to develop energy consumption and cost estimates for the one-step conversion of CO₂ from ambient air to methanol (see attached letter of collaboration). The results of aims 1-3 will be used to identify key scientific and technological gaps in the area of one-step capture and conversion of CO₂ to chemicals and energy carriers.

Outcomes and Time Frame.

		Task	Outcome	Q1	Q2	Q3	Q4	Q5	Q6
Year 2	1a	Procure materials and set up low-pressure hydrogenation reactor	Identification of promising catalysts for sub-ambient pressure CO ₂ hydrogenation						
	1b	Test catalyst CO ₂ hydrogenation performance							
	2a	Synthesize and characterize supported amine CO ₂ adsorbents	Proof-of concept of single-step capture and conversion of low-pressure CO ₂						
	2b	Test temperature swing adsorption-reaction performance							
Year 1	3a	Conduct preliminary techno-economic assessments	Techno-economic assessment of optimized capture-conversion process						
	3c	Optimize sorbent-catalyst compositions and configurations							
		Submit project report and recommendations for future work	Final deliverable: An experimental and economic assessment of the single-step capture and conversion of CO ₂ from ambient air						

Progress and Management Reporting.

Project progress will be communicated through quarterly written progress reports and biannual oral presentations. A project report summarizing the major findings of the study will be submitted at the end of the project term.

Equipment and Facilities.

Resources that will be directed towards this project are all currently available either in the PI's laboratory or through user facilities at UH, and include the following: 2 benchtop fume hoods and stir plates with heating, and a vacuum oven for material pre-treatment. Materials characterization facilities at UH, especially those at TcSUH will be used on the project. A reactor unit having 6 mass flow controllers, one high-temperature furnace, and an online GC and mass spectrometer can be dedicated to the project. Technoeconomic analyses will be carried out using Matlab and AspenPlus. Input from industrial partners will help guide these technoeconomic evaluations (see attached letter of collaboration).

Internal and External Funding.

The PI has received no prior funding in this area over the past 48 months.

Future Proposal Submissions.

Department of Energy (Early Career Award)- March-April 2021, Scialog Conference on Negative Emissions Science- Nov-Dec 2020, National Science Foundation (Interfacial Engineering Program)- Rolling deadline, Industry whitepapers- including ExxonMobil Chemical Company and Shell.

III. Curriculum Vitae

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(a) Professional Preparation

Institute of Chemical Technology	Mumbai, India	Chemical Engineering	B.E., 2008
Georgia Institute of Technology	Atlanta, GA	Chemical Engineering	Ph.D., 2013
University of Minnesota	Minneapolis, MN	Chemical Engineering	Postdoc, 2017

(b) Appointments

2017- Present Assistant Professor, Chemical and Biomolecular Engineering, University of Houston
 2015- 2017 Postdoctoral Researcher, Chemical Engineering & Materials Science,
 University of Minnesota

(c) Products

(i) Most Closely Related Products

1. Jacklyn N. Hall, & **P. Bollini**; Structure, characterization, and catalytic properties of open-metal sites in metal organic frameworks, *React. Chem. Eng.* 4, 207-222 (2019). <https://pubs-rsc-org.ezproxy.lib.uh.edu/en/content/articlepdf/2019/re/c8re00228b>
2. **P. Bollini**, & Aditya Bhan; Improving HSAPO-34 Methanol-to-Olefin Turnover Capacity by Seeding the Hydrocarbon Pool, *ChemPhysChem* 19, 479-483 (2018). <https://onlinelibrary.wiley.com/doi/abs/10.1002/cphc.201701027>
3. **P. Bollini**, & Aditya Bhan; Deactivation mechanisms in methanol-to-hydrocarbons chemistry, *Catalysis* 30, 146-156 (2018). <http://pubs.rsc.org/bookshop/collections/series?issn=0140-0568>
4. **P. Bollini**, M. A. Alkhabbaz, & C.W. Jones; Important roles of enthalpic and entropic contributions to CO₂ capture from flue gas and ambient air using mesoporous silica grafted amines, *J. Am. Chem. Soc.* 136, 13170-13173 (2014). <https://pubs.acs.org/doi/abs/10.1021/ja507655x>
5. **P. Bollini**, N. Brunelli, S. Didas, & C.W. Jones; Dynamics of CO₂ adsorption onto Amine Adsorbents. 1. Impact of Heat Effects, *Ind. Eng. Chem. Res.* 51, 15145-15152, (2012). <https://pubs.acs.org/doi/abs/10.1021/ie301790a>

(ii) *Other Significant Products*

6. Y. Kuwahara, D. Kang, J. Copeland, **P. Bollini**, C. Sievers, T. Kamegawa, H. Yamashita, & C. W. Jones; Enhanced CO₂ Adsorption over Polymeric Amines Supported on Heteroatom-incorporated SBA-15 Silica: Impact of Heteroatom Type and Loading, *Chem. Eur. J.* 18, 16649-16664, (2012). <https://onlinelibrary.wiley.com/doi/full/10.1002/chem.201203144>
7. Y. Kuwahara, D. Kang, J. Copeland, N. Brunelli, S. Didas, **P. Bollini**, C. Sievers, T. Kamegawa, H. Yamashita, & C. W. Jones; Dramatic Enhancement of CO₂ Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports, *J. Am. Chem. Soc.* 134, 10757-10760, (2012). <https://pubs.acs.org/doi/abs/10.1021/ja303136e>
8. J. Drese, S. Choi, S. Didas, **P. Bollini**, M.L. Gray, & C.W. Jones; Effect of Support Structure on CO₂ Adsorption Properties of Pore-Expanded Hyperbranched Aminosilicas, *Micropor. Mesopor. Mater.*, 151, 231-240, (2012). <https://www.sciencedirect.com/science/article/abs/pii/S1387181111005129>
9. **P. Bollini**, S. Choi, J. Drese, & C.W. Jones; Oxidative Degradation of Aminosilica Adsorbents Relevant to Post-combustion CO₂ Capture, *Energy Fuels*, 25, 2416-2425, (2011). <https://pubs.acs.org/doi/abs/10.1021/ef200140z>
10. W. Li, **P. Bollini**, S. Didas, S. Choi, J. Drese, & C.W. Jones; Structural Changes of Silica Mesocellular Foam Supported Amine-functionalized CO₂ Adsorbents Upon Exposure to Steam, *ACS Appl. Mater. Interfaces*, 2, 3363-3372, (2010). <https://pubs.acs.org/doi/abs/10.1021/am100786z>

(d) Synergistic Activities

- Conference Organizer: Chair, Fundamentals of Experimental and Theoretical Catalysis, AIChE National Meeting, Orlando, FL, November 2019
- Director, Southwest Catalysis Society, 2018-present
- Participant, Chevron Girls Engineering the Future, 2018-present
- Project Mentor, ACS Seed Project
- Reviewer for the Journal of Catalysis

IV. REFERENCES

- (1) Jones, C. W. *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 31.
- (2) Kulkarni, A. R.; Sholl, D. S. *Ind. Eng. Chem. Res.* **2012**, *51*, 8631.
- (3) House, K. Z.; Baclig, A. C.; Ranjan, M.; Van Nierop, E. A.; Wilcox, J.; Herzog, H. J. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (51), 20428–20433.
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- (5) Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. *Chem. Rev.* **2020**, *In Press*.
- (6) Chen, P.; Zhao, G.; Liu, Y.; Lu, Y. *Appl. Catal. A Gen.* **2018**, *562* (June), 234–240.
- (7) Studt, F.; Sharafutdinov, I.; Abild-Pedersen, F.; Elkjær, C. F.; Hummelshøj, J. S.; Dahl, S.; Chorkendorff, I.; Nørskov, J. K. *Nat. Chem.* **2014**, *6* (4), 320–324.