OXYIUM: Oxygen Integrated Unit for Modular Biomass Conversion to Hydrogen

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National Energy Technology Laboratory

Carbon Management Project Review Meeting

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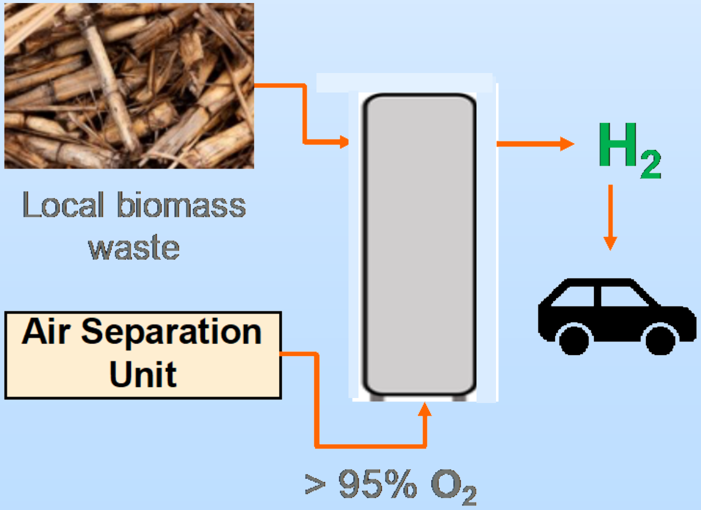
Project Goal

- Modular biomass gasification through modular oxygen production
- Biomass conversion enables low-emissions hydrogen production
- Distributed biomass waste requires localized gasification units
- Pure hydrogen production (> 99 %) from biomass conversion requires pure oxygen (> 95 %) to prevent formation of undesired byproducts and the need for downstream purification

Project Goal

- **Challenge:** SoA large-scale air separation technologies (e.g., cryogenic isolation) are either not economical or are infeasible at small, modular scale
- **Objective:** Develop a fast, high-capacity, reversible oxygen sorbent that enables efficient gasification of biomass, coal, waste, etc., in small, modular units

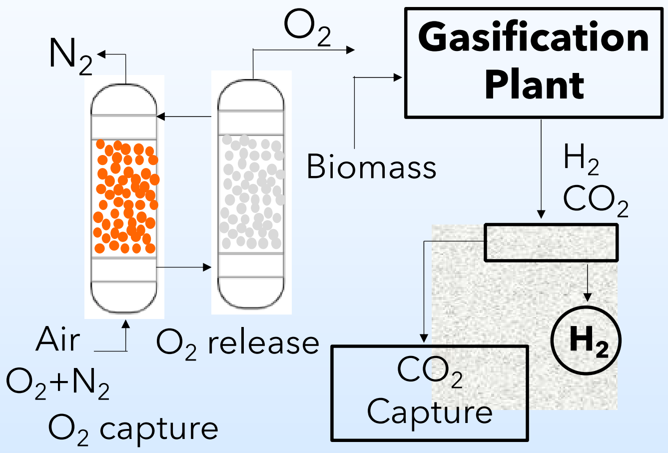


Project Overview

- Funding: \$1.6M total, \$1.25 federal share
- Period of performance: 24 months (Oct 2023 – Sept 2025)
- Objectives:
  - Demonstrate feasibility of reversible O_2 capture at > 6 wt-%
  - Technoeconomic analysis showing lower cost than SOA O_2 units for 5 – 50 MWe H_2 production plants
  - Start TRL 2; End TRL 3–4
- Distinctive features
  - Captures O_2 from air, not N_2, reducing energy and equipment needs
  - High reversible O_2 capacity
  - Long lifetime due to stability of polymer walls and room-temp operation
  - ~2-min cycle time due to sorbent mesoporosity

Project Overview

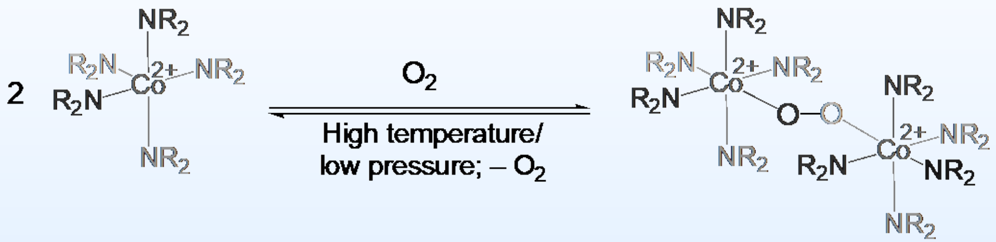
Integrated Air Separation Unit Biomass Gasifier



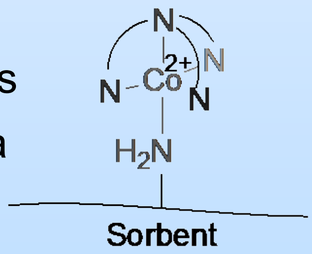
Enabled by:

- PARC/SRI's patented amine aerogel platform, demonstrating high and tunable porosity and amine content
- Chemical functionalization with reversible O_2 capturing groups

Foundational literature: Penta-amino Co(II) reversibly binds O_2 with 2:1 Co:O_2 stoichiometry



- Immobilization in a porous sorbent provides high specific surface area (>300 m^2/g)
- Pore tuning will enable rapid rates of gas transport, bulk diffusion, and high O_2 uptake
- **Key innovation:** Eliminate inert support material and chemically bind Co^{2+} to sorbent amine groups
- Co(II) center geometry will force a 1:1 Co:O_2 stoichiometry, rather than traditional 2:1 ratio, thereby *doubling* the potential O_2 capacity



Project Team

SRI

Aerogel development, Fixed bed testing, TEA & LCA

- Dr. Koyel Bhattacharyya
  - Principal investigator
  - Sorbent design & synthesis

- Dr. Gabriel Iftime
  - TEA & LCA support

- Dr. Ranjeet Rao
  - Sorbent synthesis & characterization

- Bishal Karki
  - Sorbent synthesis

- Dr. Jon Bachman
  - Sorbent characterization & testing

- Dr. Rahul Pandey
  - Sorbent characterization & testing

- Dr. Jin Ki Hong
  - Fixed bed design, build, & testing

Project Team

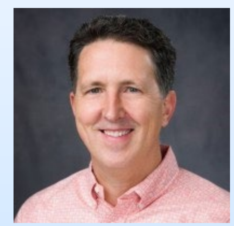
SIMACRO
SIMULATION PARTNER

Process design (Aspen)

PCI

Manufacturer of modular O_2 ASU

Design and simulation of Air Separation Unit (ASU)



Commercialization adviser

Project Tasks

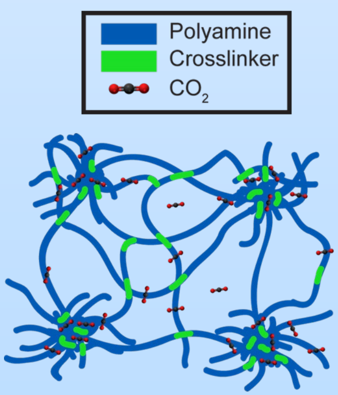
- Sorbent synthesis
- Analysis set-up
- O_2 capture/release demonstration
- Sorbent scale-up to > 25 g
- Bench-scale prototype system demonstrating capture
- Modeling of O_2 absorption module (Simacro)
- Technoeconomic analysis and commercialization outlook
- Key milestones: > 4.5 mmol N/g sorbent, > 2 mmol Co^{2+}/g, production at > 25 g scale

Technology Background

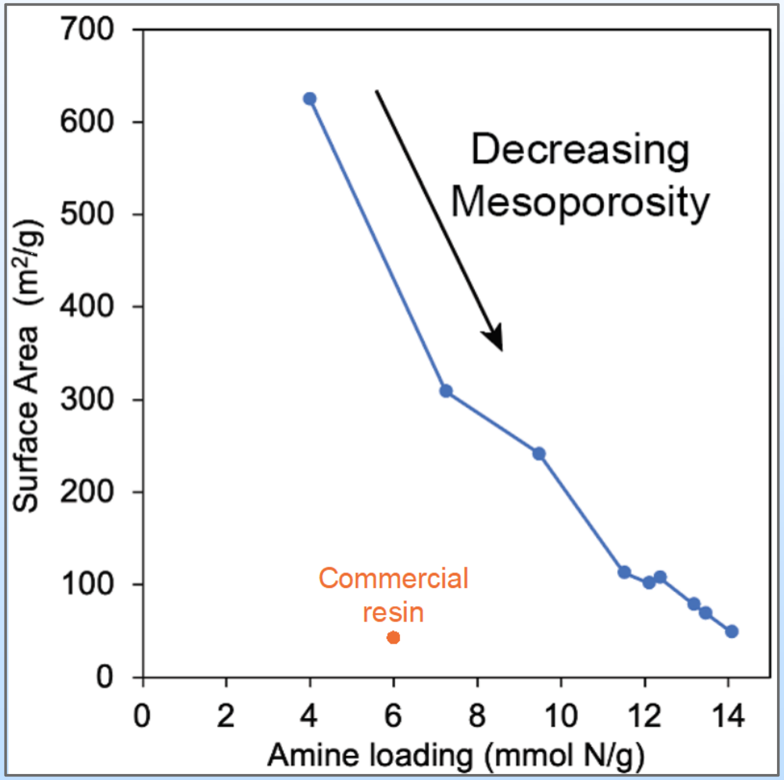
Pressure swing sorbent based on PARC's porous amine polymer synthesis platform

PARC polyamine aerogels synthesized for CO_2 capture:

- Moderate porosity
- Ambient drying
- Scalability
- High surface area
- Tunable chemistry
- Variety of form factors



High surface area polymers with Amine loading from 3 – 14 mmol N/g



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Project Scope

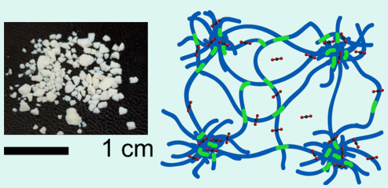
Envisioned operation:

Adsorption at ambient conditions

Desorption at 0% O_2 partial pressure (under N_2)

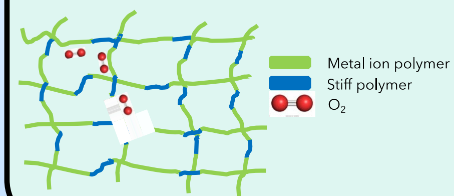
Prior work:

High surface area polymer amine aerogels



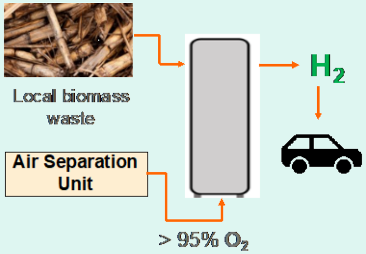
This project

Develop a high-capacity O_2 sorbent and demonstrate performance in fixed-bed reactor



Future development

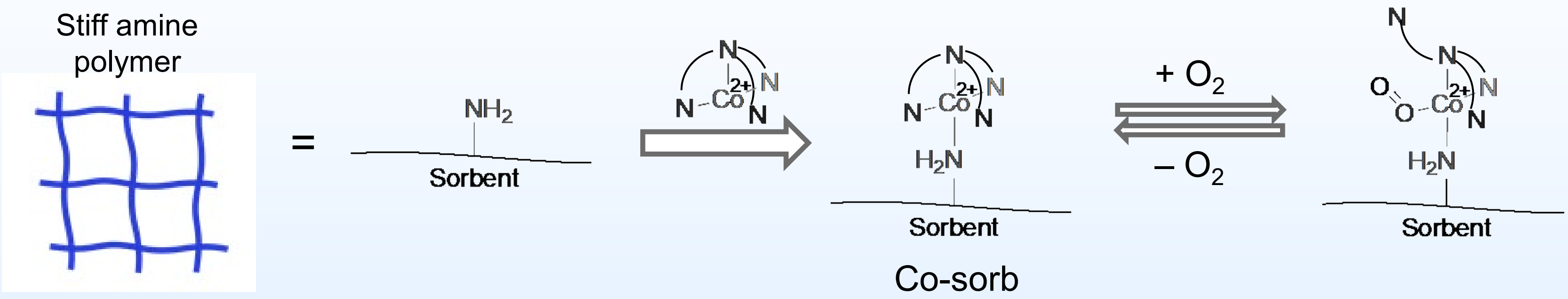
Integration into a small-scale biomass gasification system



Comparison to State of the Art

Material	Leading Zeolite (LiX)	Co(II)-Salen in binder	Leading-MOF sorbent	PARC OXYIUM sorbent
Status	Commercialized	R&D	R&D	R&D
Equilibrium O_2 loading [wt-%/g]	N/A (N_2 selective)	1.2%	< 7%	> 6% (10.5% theoretical)
O_2/N_2 selectivity	< 6 (N_2/O_2)	N/A	20	~ 20
Cycle time [min/cycle]	< 1	10	30	~2
Sorbent durability [years]	3-10	Unknown	Poor	> 1
Sorbent cost [$/kg]	40 - 60	45	50-100	25-30
O_2 cost [$/kg O_2]	0.115 (PSA)	0.268	High (no data)	~ 0.05
Pore size [nm]	< 0.9	< 1	< 1	10-100's
Moisture sensitivity	High	High	High	Low
Bed size factor [lbs sorbent/tonnes O_2/day]	100-200	12,600	No data	102 (sum of two beds)
Air Unit emissions [kg CO_2/tonne O_2]	159	N/A	N/A	27

Synthetic Pathway



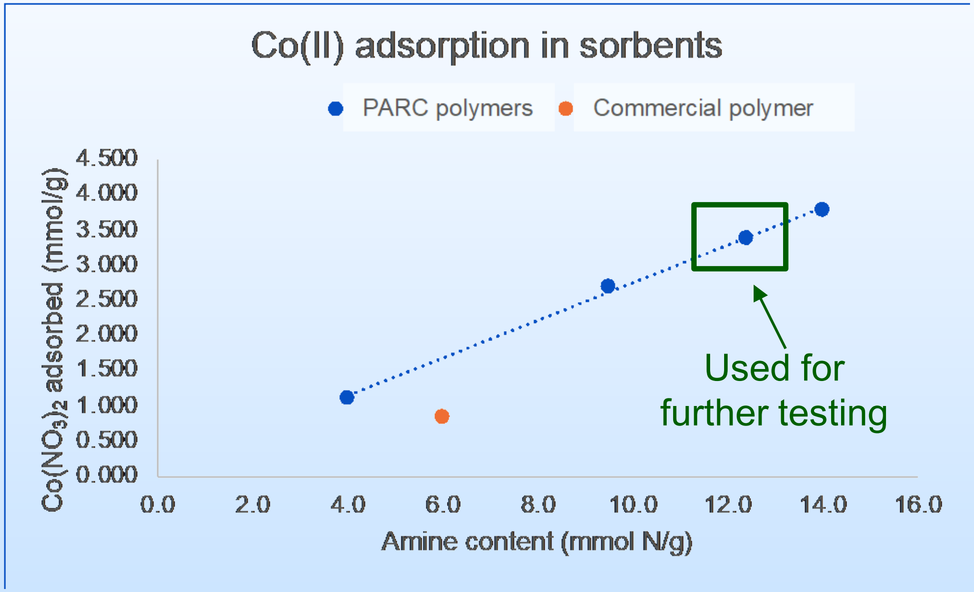
1. Modify existing high-porosity, high-amine polymers for Co(II) chelation
2. Incorporate Co(II) into polymer to form Co-sorb
3. Reversibly incorporate oxygen into Co-sorb

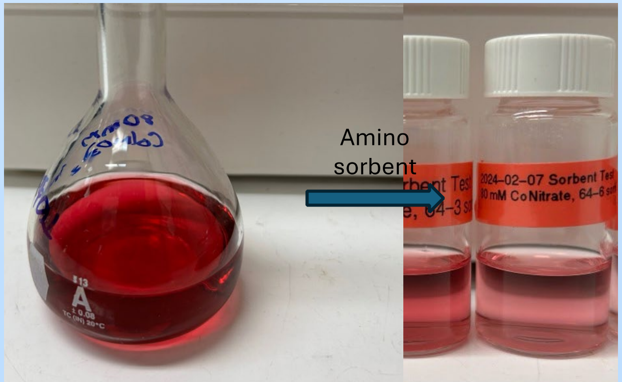
1. Amine polymer synthesis

Polymer ID	Amine content (mmol N/g)
T641	4.0
T643	9.5
T646	12.4
T6410	14.0
Lewatit VPOC 1065 (commercial)	6.0

2. Co(II) incorporation

UV-Vis determination of Co(II) uptake by polymer

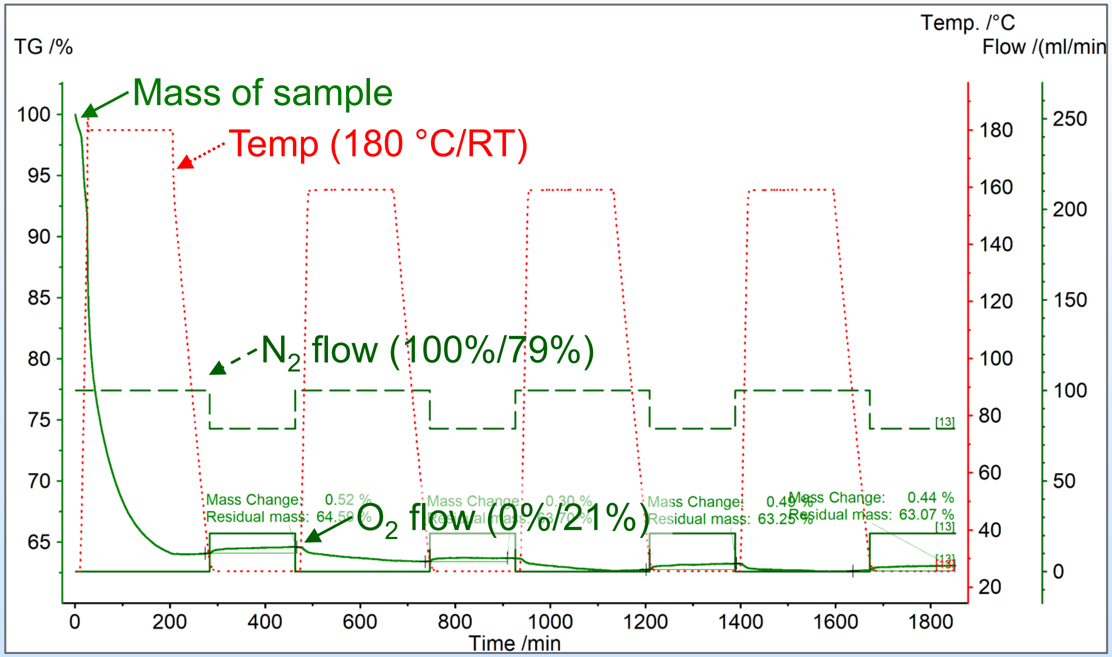


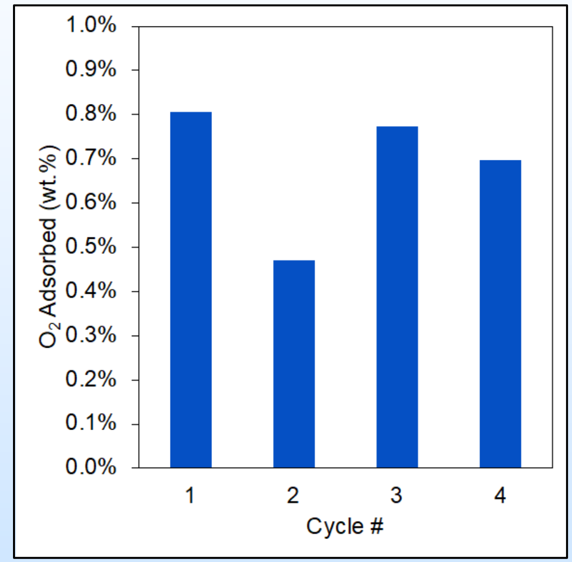


- Preliminary testing showing ability of sorbent to adsorb Co(II) and of UV-Vis to quantify adsorption performed with commercial Co(II) compound
- Significant Co(II) adsorption observed, up to 3.7 mmol Co(II)/g
- PARC polymers showed linear correlation between amine content and Co(II) adsorption
- PARC polymers adsorbed ~2x more Co(II) than commercial resin for the same amine content, indicating superior, open porosity of PARC material

3. Reversible oxygen uptake

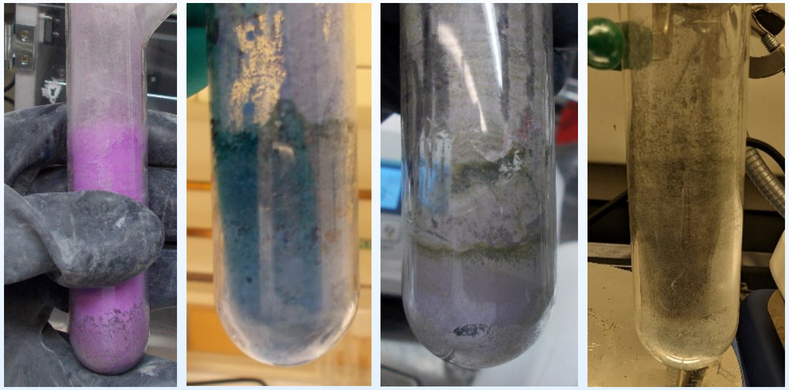
TGA determination of reversible oxygen adsorption/desorption





- Preliminary testing shows ability of Co-sorb to adsorb/desorb O_2 and of TGA to quantify O_2 uptake
- Testing performed with dry 21 % O_2 in N_2 gas
- Mass increase with oxygen addition, mass loss with heat/absence of oxygen, as expected

Next steps



- Adsorption of tetra-amino Co(II) into amine sorbent
  - Concurrent synthesis of tetra-amino Co(II) complexes
- Increase Co(II) loading in Co-sorb
  - Currently < 30% of amines occupied by Co(II), many of which are buried away from pores, but some of which are likely available with better pore swelling
- Reduce hygroscopicity of Co-sorb
  - Current Co-sorb requires heating to release water, but goal is to reduce water-sensitivity to permit intake of ambient air for O_2 separation regardless of humidity

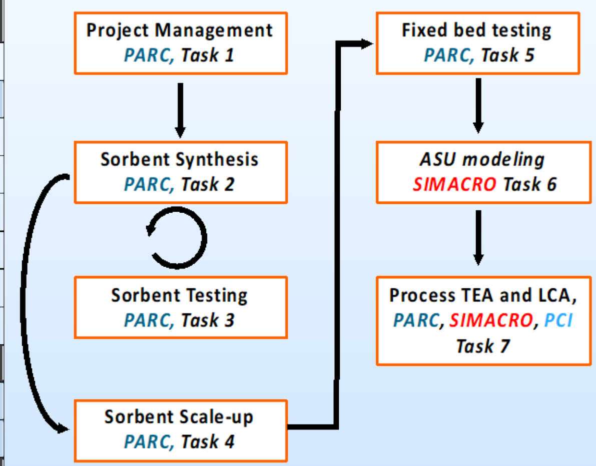
Conclusions

- Amine sorbent synthesized with up to 14 mmol N/g
- Co(II)-containing Co-sorb synthesized with at least 3.7 mmol Co/g sorbent
- Reversible oxygen adsorption/desorption demonstrated for at least four cycles
- Characterization methods verified:
  - Elemental analysis for amine content of sorbent
  - UV-Vis for Co(II) uptake by sorbent
  - TGA for O_2 uptake by Co-sorb
- Fixed-bed reactor planning and building underway

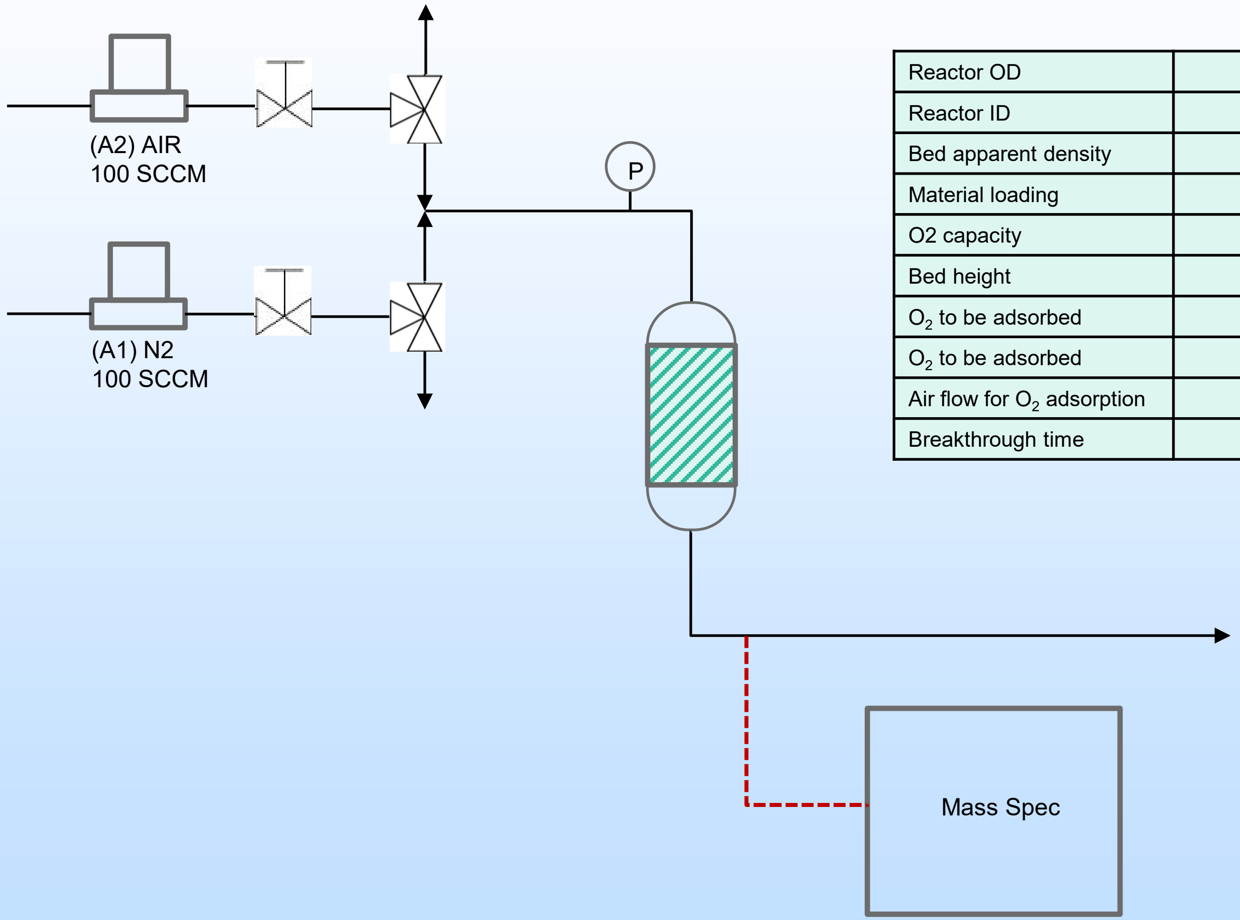
Thank you!

Gantt Chart and Work Structure

Task/Subtask Name	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 5	Qtr 6	Qtr 7	Qtr 8
Task 1.0 - Project Management and Planning								
Subtask 1.1 – Project Management Plan	D							
Subtask 1.2 – Project Maturation Plan	D							D
Task 2.0 - Sorbent synthesis								
Subtask 2.1 – Synthesis of amino polymer		D						
Subtask 2.2 – Synthesis of Co^{2+} sorbent				D		D		
Task 3.0 - Sorbent characterization								
Subtask 3.1 – Develop and validate testing procedures			D					
Subtask 3.2 – Detailed testing of Co^{2+} sorbents						D		
Task 4.0 - Sorbent scale-up and characterization								
Subtask 4.1 – Scale-up selected formulations								D
Subtask 4.2 – Measure sorbent physical properties								D
Task 5.0 – Fixed bed testing								
Subtask 5.1 – Building fixed-bed column					D			
Subtask 5.2 – Fixed-bed column testing of sorbents							D	
Subtask 5.3 – Optimization of fixed-bed process								D
Task 6.0 – Air separation unit (ASU) modeling							D	
Task 7.0 – Technoeconomic and life cycle analysis				D				D



OXYIUM Breakthrough Measurement P&ID



Reactor OD	25.4	mm
Reactor ID	23	mm
Bed apparent density	0.23	gram/mL
Material loading	5	grams
O2 capacity	0.5	mmol/gram
Bed height	5.2	cm
O_2 to be adsorbed	2.5	mmol O_2
O_2 to be adsorbed	56	mL O_2 at STP
Air flow for O_2 adsorption	100	mL at STP
Breakthrough time	160	sec