No. A-5-1E

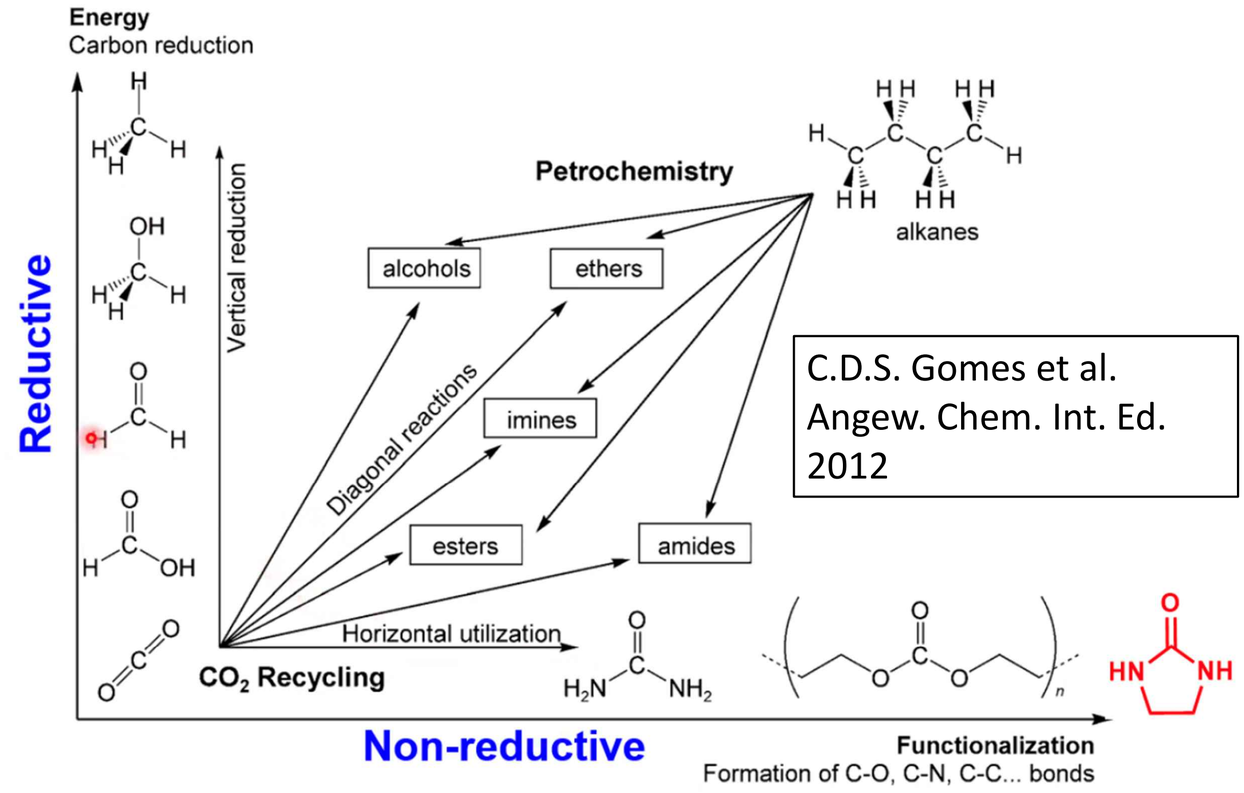
PJ : Development of Combined Carbon Capture and Conversion (quad-C) System for the Utilization of Atmospheric CO_2

Background and Strategies

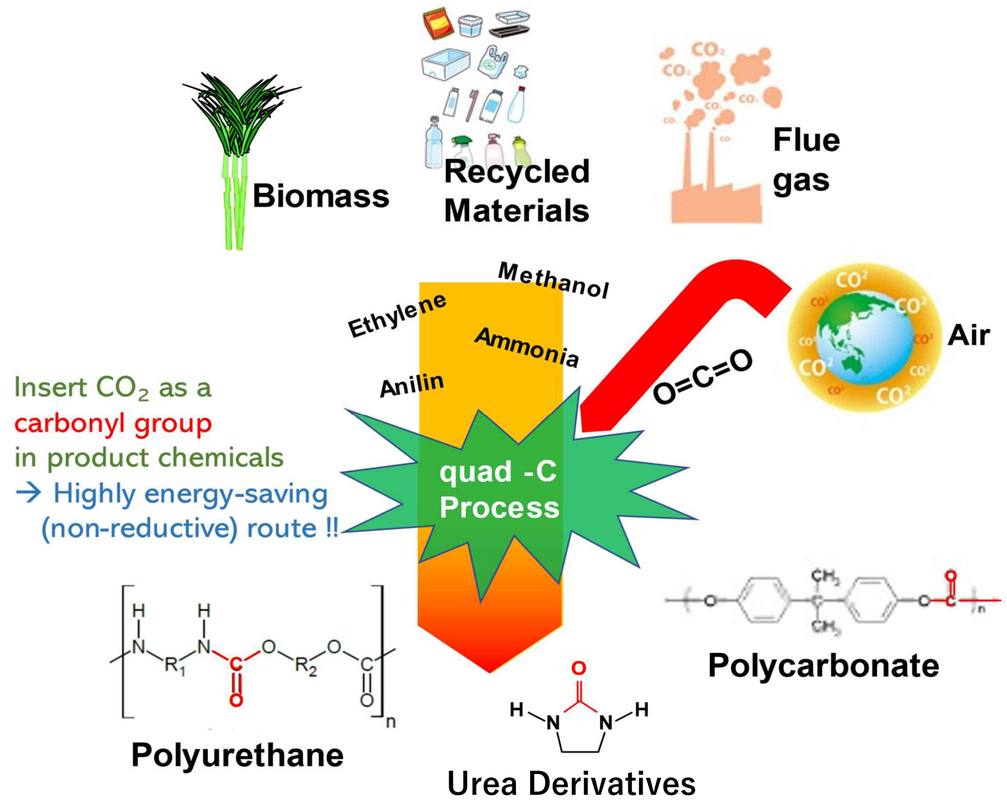
Organization: Tohoku University, Osaka Metropolitan University,
Renaissance Energy Research Corporation
Contact: Prof. Yasuhiro FUKUSHIMA fuku@tohoku.ac.jp (PM)

Background

- CO_2 utilization can be more energy saving (horizontal utilization)
  … , but needs to target variety of downstream chemicals with smaller market size



C.D.S. Gomes et al. Angew. Chem. Int. Ed. 2012



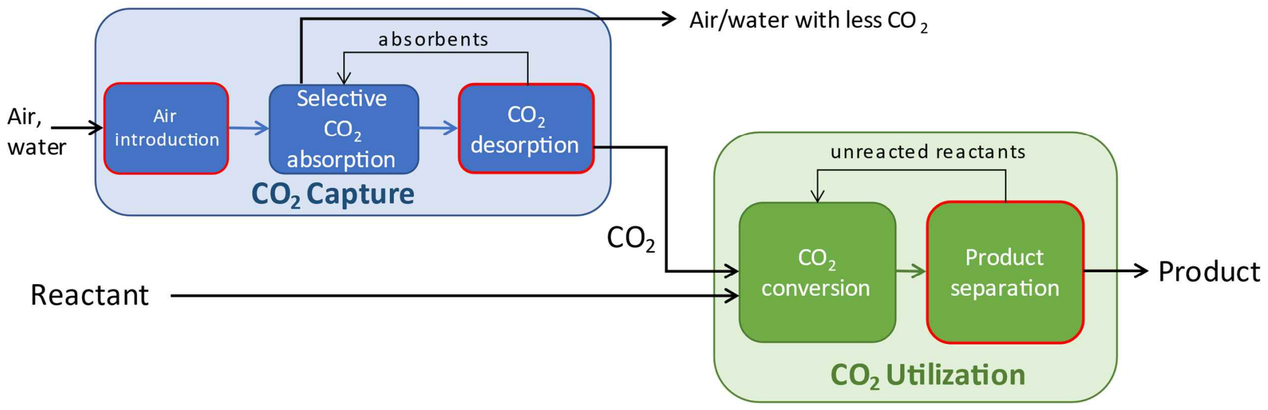
Our strategy for atmospheric CO_2 utilization:

Energy Saving Strategy

Common challenge for DAC-U:
Energy requirements in:
1) Air introduction
2) CO_2 desorption.
3) Product separation

→ Use of **Dual Function Materials (DFMs)** for capturing CO_2 from the atmosphere

→ Eliminate need of 2) CO_2 desorption



Catalyst

$$A + CO_2 \rightarrow P + B$$

A: Reactant, P: Product, B: Byproduct

Please visit Poster A-5-4E for more details

quad-C Type I process:

DFM: Reactant × Absorbent of CO_2
with aid of CO_2 selective membrane
to avoid loss of reactant by evaporation

Please visit Poster A-5-3E for more details

quad-C Type II process:

DFM: Catalyst × Adsorbent of CO_2
Cerium oxide (CeO_2) is a known potential adsorbent AND catalyst, in independent works. No previous report of use as DFM. **Our project not only explored possibilities of DFMs, but also identified other potential materials with similar characteristics.**

Please visit Poster A-5-2E for more details

International Collaborations:

Institut des Sciences Moléculaires, University of Bordeaux, France

Principal Investigators:
Prof. Guido Sonnemann (CyVi), Prof. Dario Bassani (NEO)

- Synthesis of Nanoparticles with High CO_2 Adsorption Capacity (NEO)
- Ex-Ante Technoeconomic and Environmental Assessment of Emerging Technologies (CyVi)

National Taiwan University, Taiwan

Dr. Tsai-Wei Wu will be a visiting scholar (April. 2023 – Dec. 2023)
Expertise: "Assessment of CO_2 utilization processes"
- Rigorous process simulation
- Technoeconomic assessment

Workshop @ U Bordeaux
Yagihara (TU), Guzman (TU),
with Prof. Bassani (U Bordeaux)

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PJ : Development of Combined Carbon Capture and Conversion (quad-C) System for the Utilization of Atmospheric CO_2

Exploration of Reaction Systems and Catalysts

Organization: Tohoku University, Osaka Metropolitan University,
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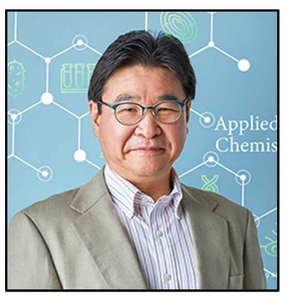
Contact: Prof. Yasuhiro FUKUSHIMA fuku@tohoku.ac.jp (PM)

Members



Dr. Keiichi Tomishige
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Dr. Mizuho Yabushita
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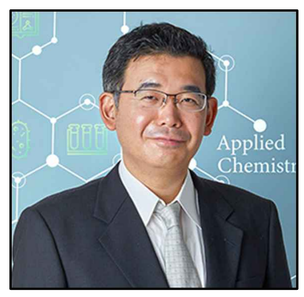
Tohoku University

Dr. Masazumi Tamura
Associate Professor,
Osaka Metropolitan University



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Dr. Miho Uchida
Adjunct Professor,
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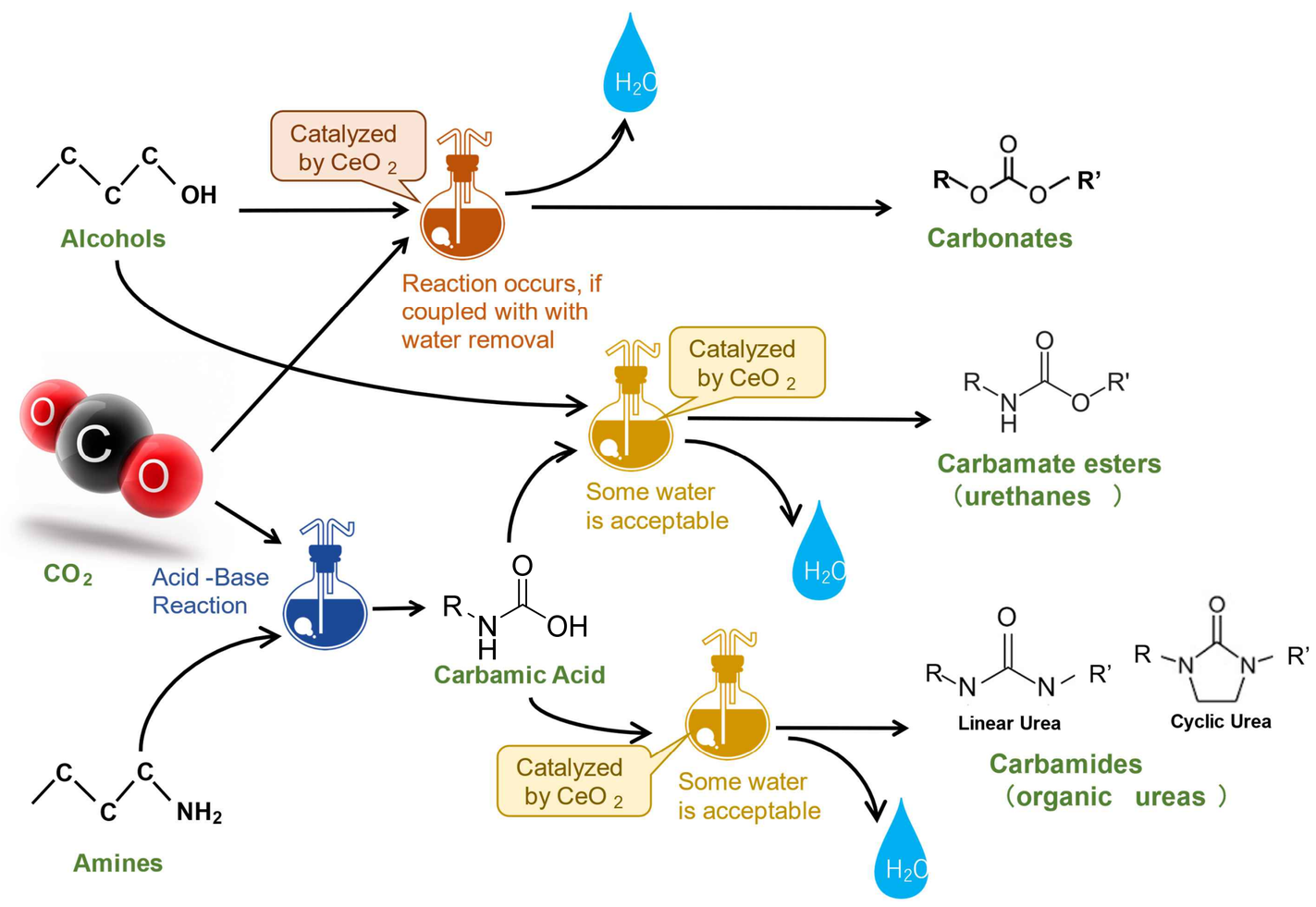
Reaction Systems

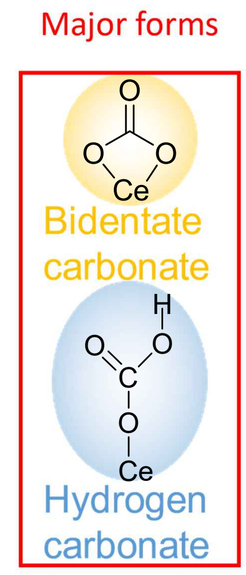
Overview

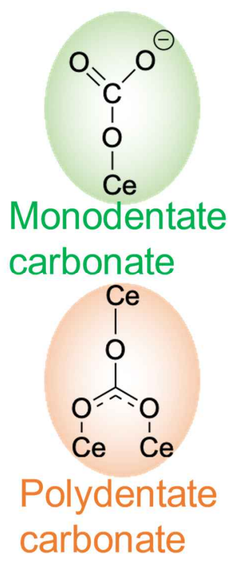
Carbamate esters and carbamides are main targets of this project



Adsorption characteristics

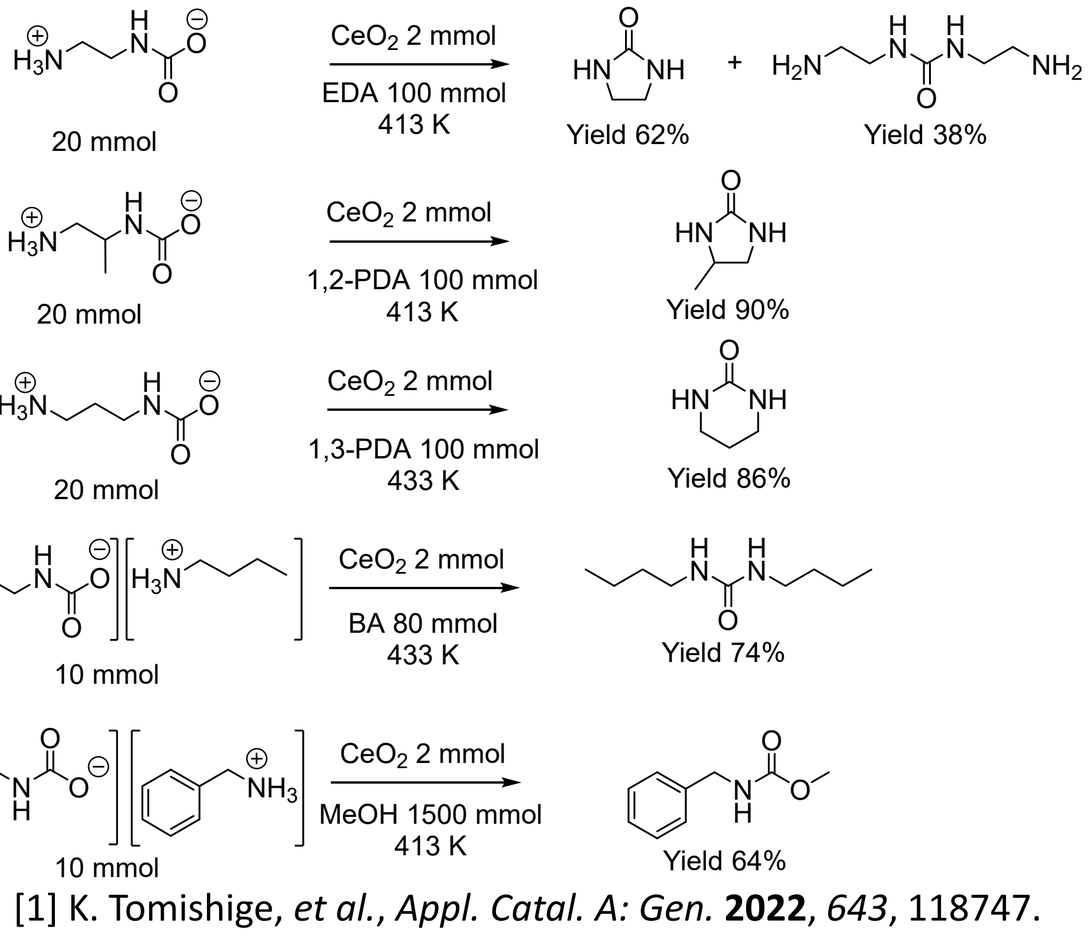
Apparatus:
FT-IR, modified for this project





- Sufficient adsorption with CO_2 at 0.04% (400 ppm) was confirmed on CeO_2
- Main adspecies on CeO_2 were bidentate and hydrogen carbonates
- Influence of water content in the gas on the CO_2 adsorption states and amounts was investigated

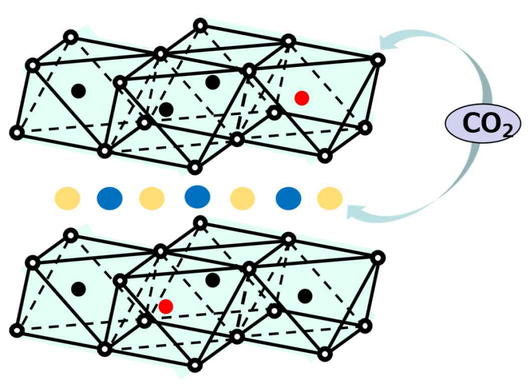
Using various amines[1] and alcohols, reaction systems for Type I process have been explored.



[1] K. Tomishige, *et al.*, *Appl. Catal. A: Gen.* **2022**, *643*, 118747.

New potential materials were found for Type I and Type II processes.

LDH
Layered
Double
Hydroxides



- LDH performs as DFM-assisting material (CO_2 carrier) for Type I process.
- By doping other metals, LDH may work as DFM for Type II process.

Patent application: PCT/JP2022/36820
the concept of Type II process with various DFMs

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Type II process: Use of metal oxides and LDH as DFMs

Organization: Tohoku University, Osaka Metropolitan University,
Renaissance Energy Research Corporation
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Members

Column Modules Development

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Process Simulation

Dr. Yasuhiro Fukushima
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Tohoku University

Mr. Koki Yagihara
Research fellow (D2)
Tohoku University

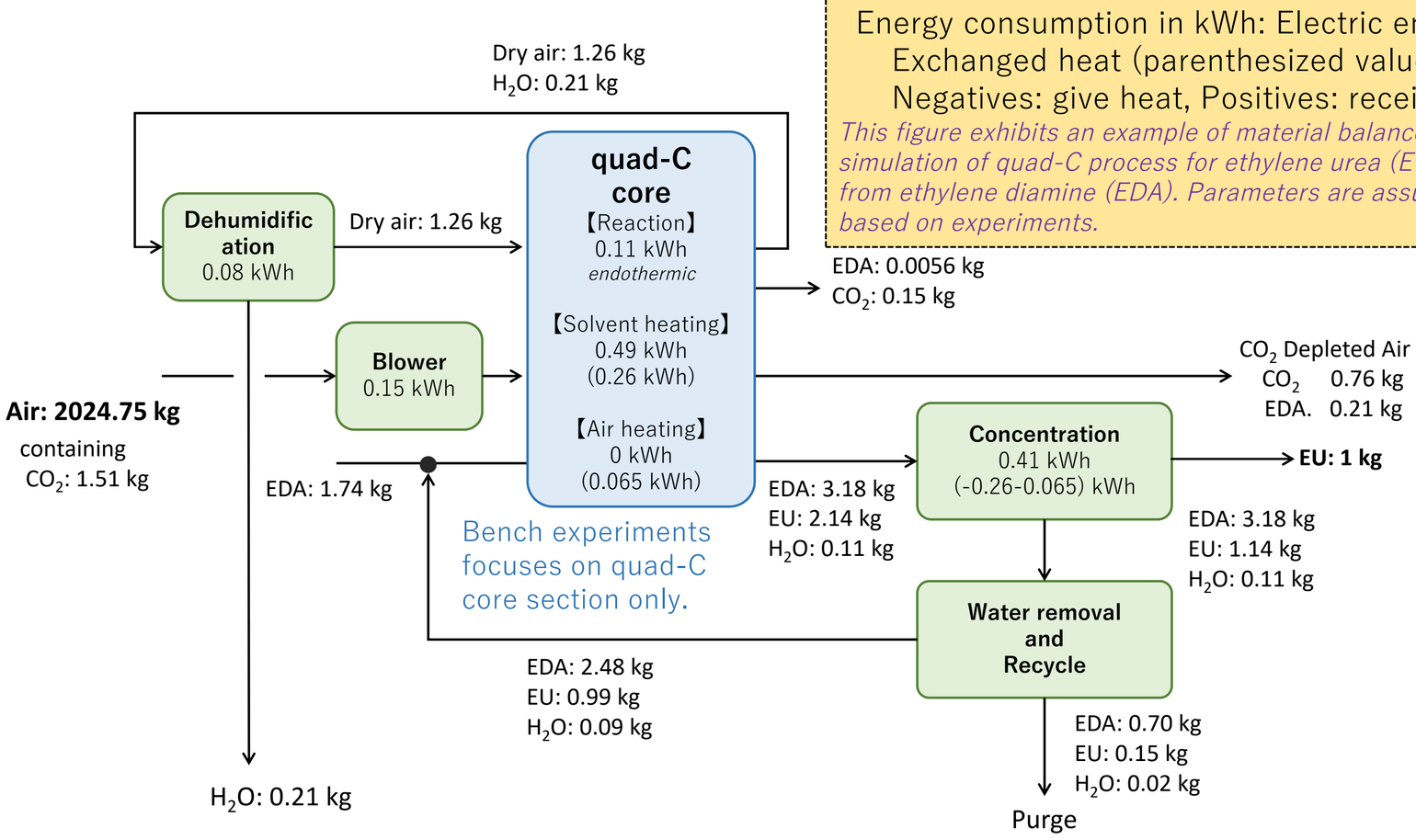
Type II quad-C process

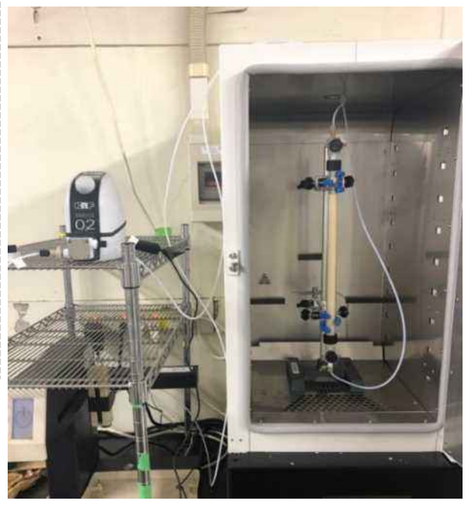
Material Balance Estimates

Model-based estimation of material balances
→ Updating parameters through experiments

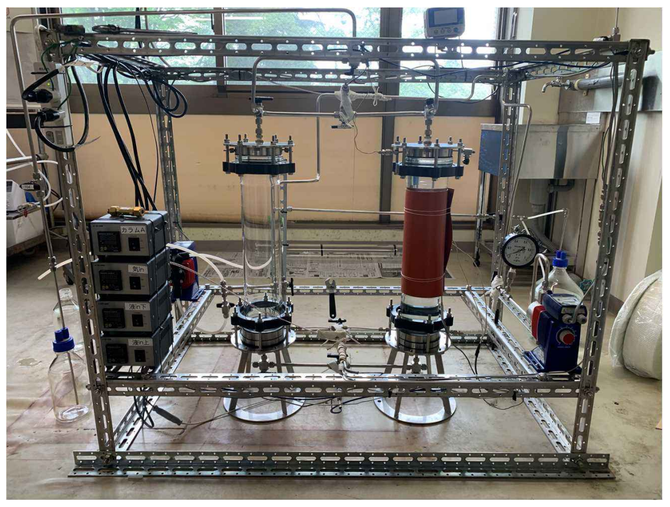
Energy consumption in kWh: Electric energy
Exchanged heat (parenthesized values):
Negatives: give heat, Positives: receive heat

This figure exhibits an example of material balance based on simulation of quad-C process for ethylene urea (EU) production from ethylene diamine (EDA). Parameters are assumed: not yet based on experiments.



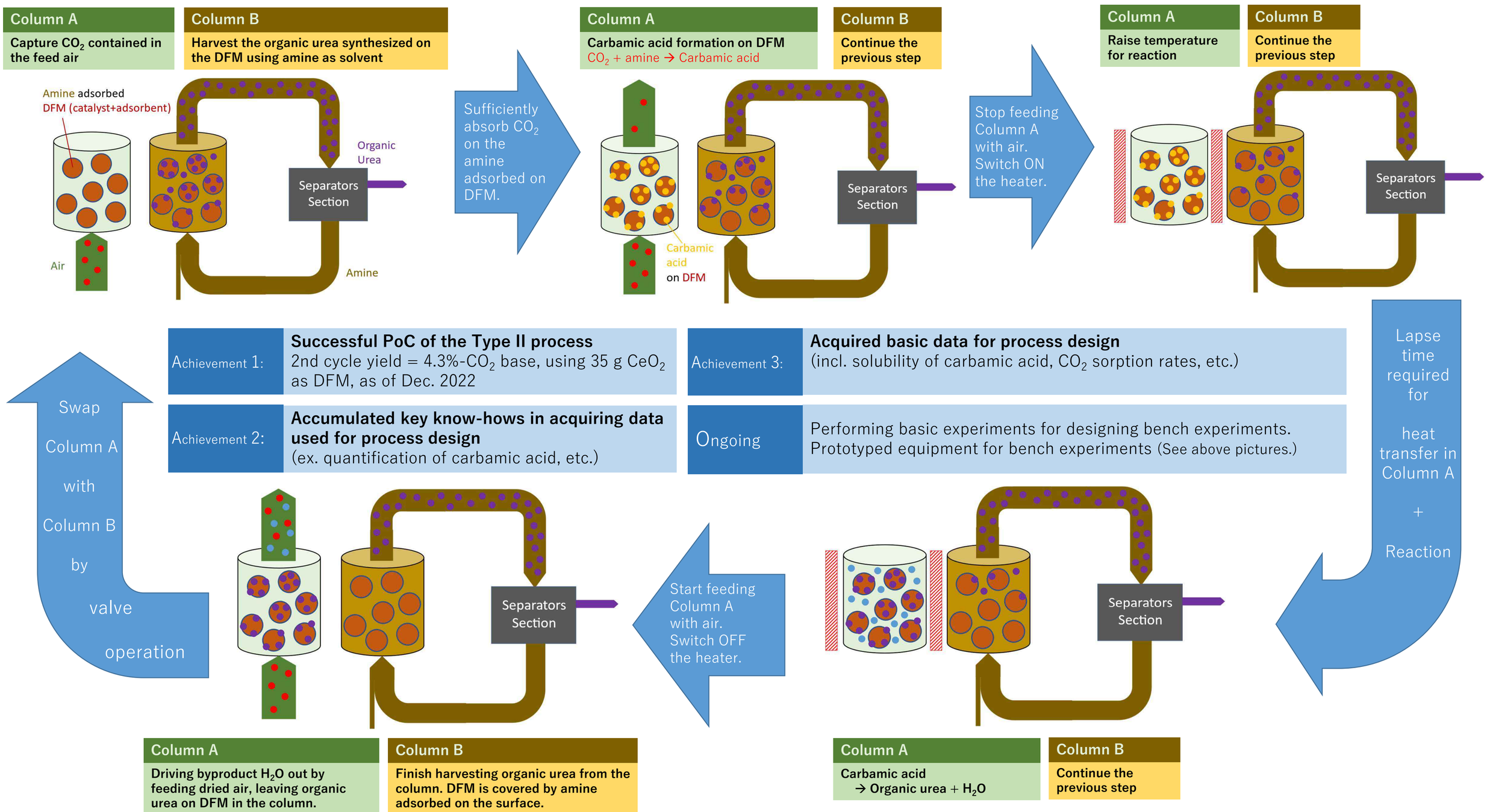


Basic experiments



Bench experiments

Design and Proof of Concept: quad-C core



Achievement 1:	**Successful PoC of the Type II process** 2nd cycle yield = 4.3%-CO_2 base, using 35 g CeO_2 as DFM, as of Dec. 2022
Achievement 2:	**Accumulated key know-hows in acquiring data used for process design** (ex. quantification of carbamic acid, etc.)
Achievement 3:	**Acquired basic data for process design** (incl. solubility of carbamic acid, CO_2 sorption rates, etc.)
Ongoing	Performing basic experiments for designing bench experiments. Prototyped equipment for bench experiments (See above pictures.)

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PJ : Development of Combined Carbon Capture and Conversion (quad-C) System for the Utilization of Atmospheric CO_2

Type I process: Membrane-enabled use of amines as DFMs

Organization: Tohoku University, Osaka Metropolitan University,
Renaissance Energy Research Corporation
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Members

Membrane Module Development

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Process Simulation

Dr. Yasuhiro Fukushima
Professor,
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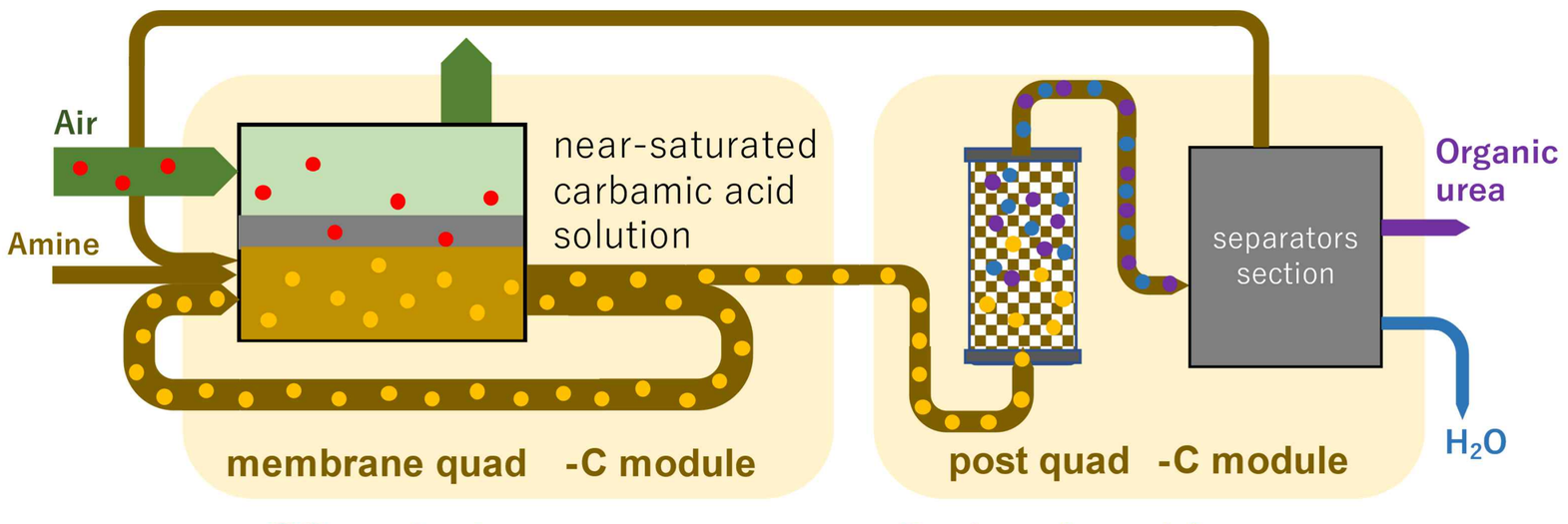
Dr. Jialing Ni
Project Assistant Professor,
Tohoku University

Type I quad-C process

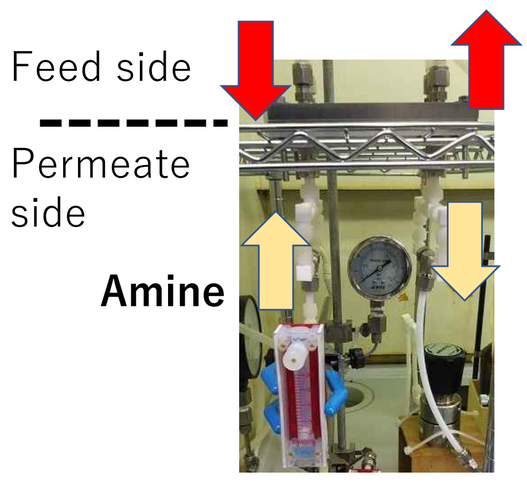
The Conceptual Design



CO_2 + Amine → Carbamic acid

Carbamic acid → Organic urea + H_2O

Platelike membrane module



Catalytic flow reactor

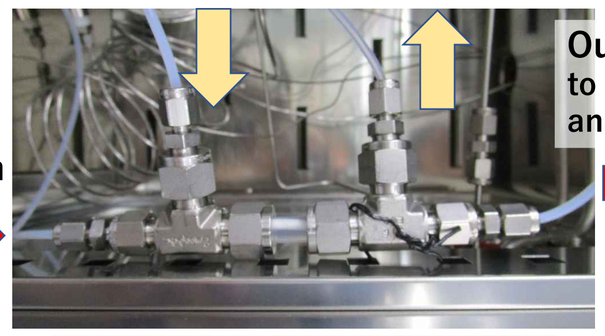
Performed by catalyst team → see A-5-2E

With ethylene diamine, T= 90℃ was found to be the best condition, achieving an yield of >90% for organic urea.

Hollow fiber membrane module

Aqueous solution
(permeate side stream)

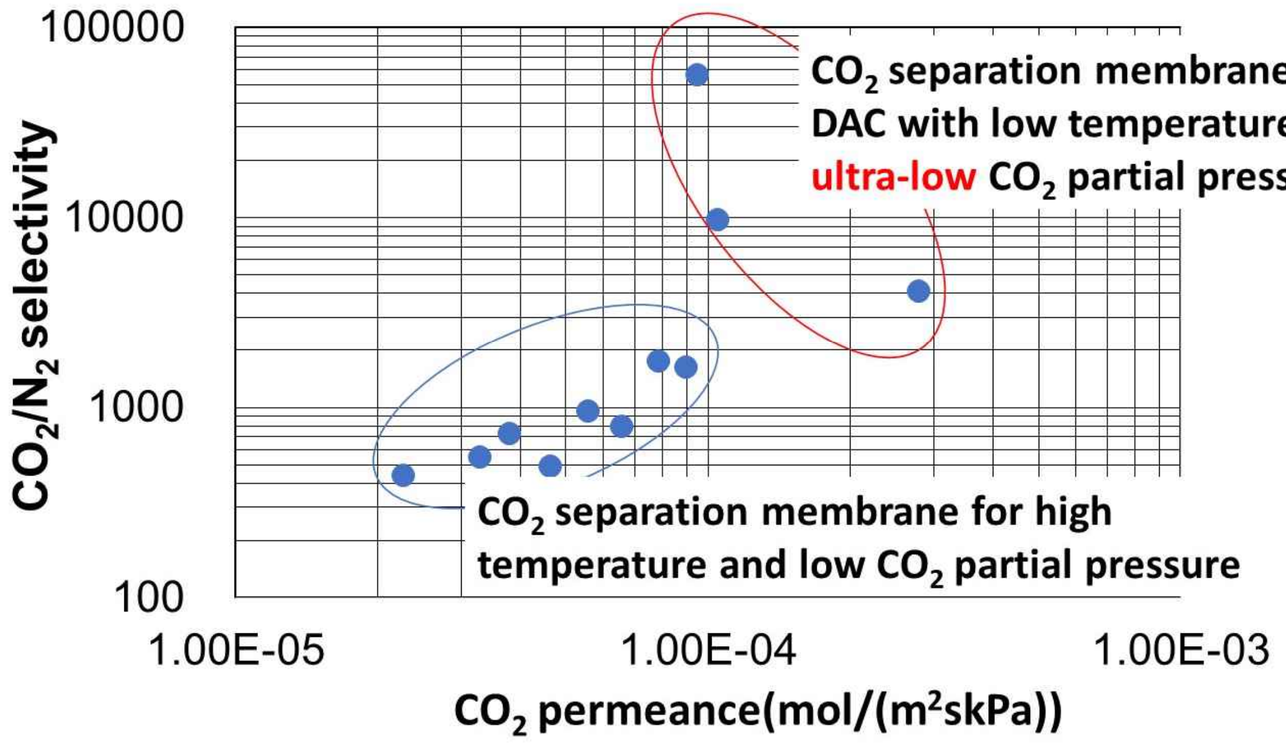
Feed gas
26 ml/min
CO_2 413ppm



Outlet gas to GC gas analysis

CO_2 gas recovery 9%

Successfully prototyped facilitated transport membranes with excellent CO_2/N_2 selectivity and sufficient permeance



✓ Prototyped hollow fiber membrane module with many support materials with various *d*, and pore size

D = 1.2 mm:
CO_2 permeance：2.7×10^{-4} mol/m²skPa
CO_2/ N_2 Selectivity: 4,000

D = 3 mm
CO_2 permeance：9.5×10^{-5} mol/m²skPa,
CO_2/ N_2 Selectivity: 55,000

Development of membrane modules with ionic liquids

✓Exploring the optimal ionic liquid using novel in-situ Raman spectroscopy
✓Numerical simulation and experimental investigation of mass transfer of CO_2