Unique Nanotechnology Converts Carbon Dioxide to Valuable Products

(DOE Award #: DEFE0031707)

Bingyun Li, PhD (WVU)
Badie Morsi, PhD (Pitt)
Jingxin Wang, PhD (WVU)

(A). Previous Data

Computational analysis and lab studies identifying amino acids (AAs) that convert CO_2 into nanomaterials

(A)

❑ Solvent preparation

$$HOOC\text{-}R\text{-}NH_3^+ \;\; \underset{low\ pH}{} \;\; \xleftrightarrow{-H^+} \;\; {}^-OOC\text{-}R\text{-}NH_3^+ \;\; \xleftrightarrow{-H^+} \;\; {}^-OOC\text{-}R\text{-}NH_2$$

low pH — *neutral - mildly acid pH* — *high pH*

$${}^-OOC\text{-}R\text{-}\boxed{NH_3^+} + NaOH \longleftrightarrow Na^+ + {}^-OOC\text{-}R\text{-}\boxed{NH_2} + H_2O$$

❑ Reactions with CO_2

Carbamate formation

$$CO_2 + 2Na^+[{}^-OOC\text{-}R\text{-}NH_2] \longleftrightarrow \underbrace{[Na^+]_2[{}^-OOC\text{-}R\text{-}NH\text{-}COO^-]}_{Carbamate} + \underbrace{{}^-OOC\text{-}R\text{-}NH_3^+}_{Zwitterion}$$

Carbamate hydrolysis

$$[Na^+]_2[{}^-OOC\text{-}R\text{-}NH\text{-}COO^-] + H_2O \longleftrightarrow \underbrace{Na^+[{}^-OOC\text{-}R\text{-}NH_2]}_{Amino\ acid} + \underbrace{NaHCO_3}_{Bicarbonate}$$

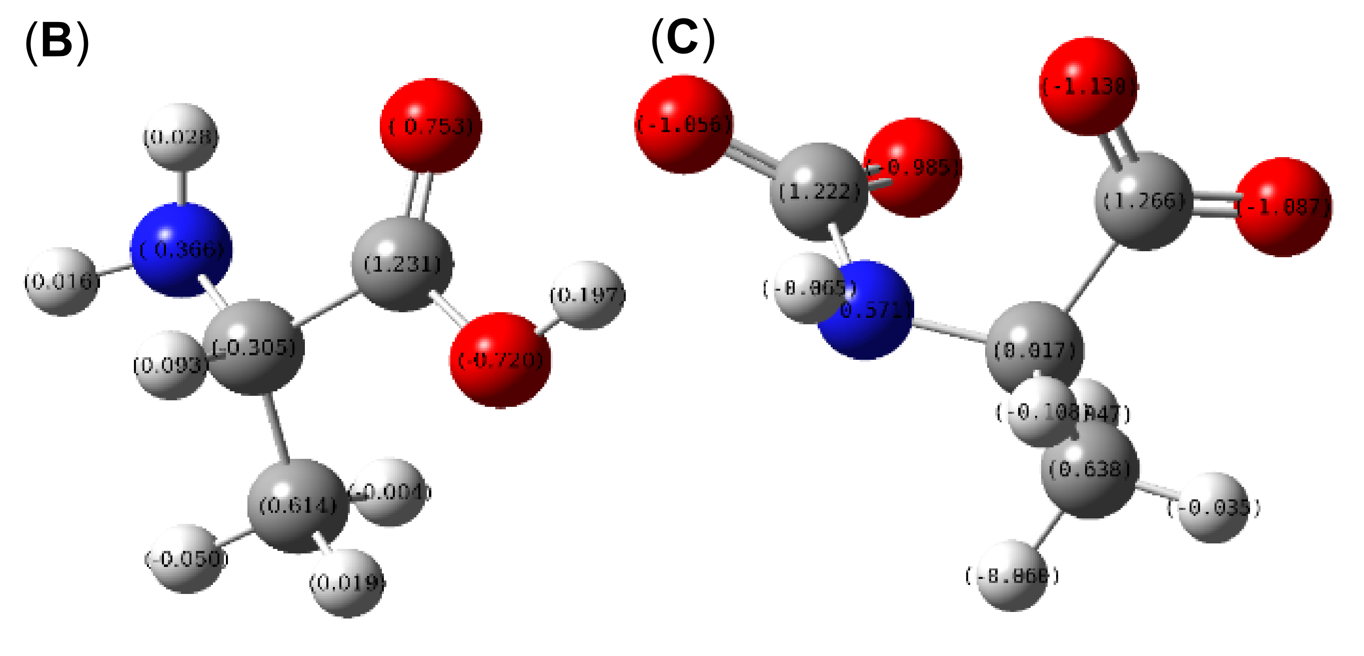


Fig. 1. (**A**) Reactions involved. Optimized structures of Alanine or Ala (**B**) and (**C**) its capturing of CO_2. The charge on each atom is indicated in the figure.

Gly salt solvent converted CO_2 to bicarbonate nanomaterials

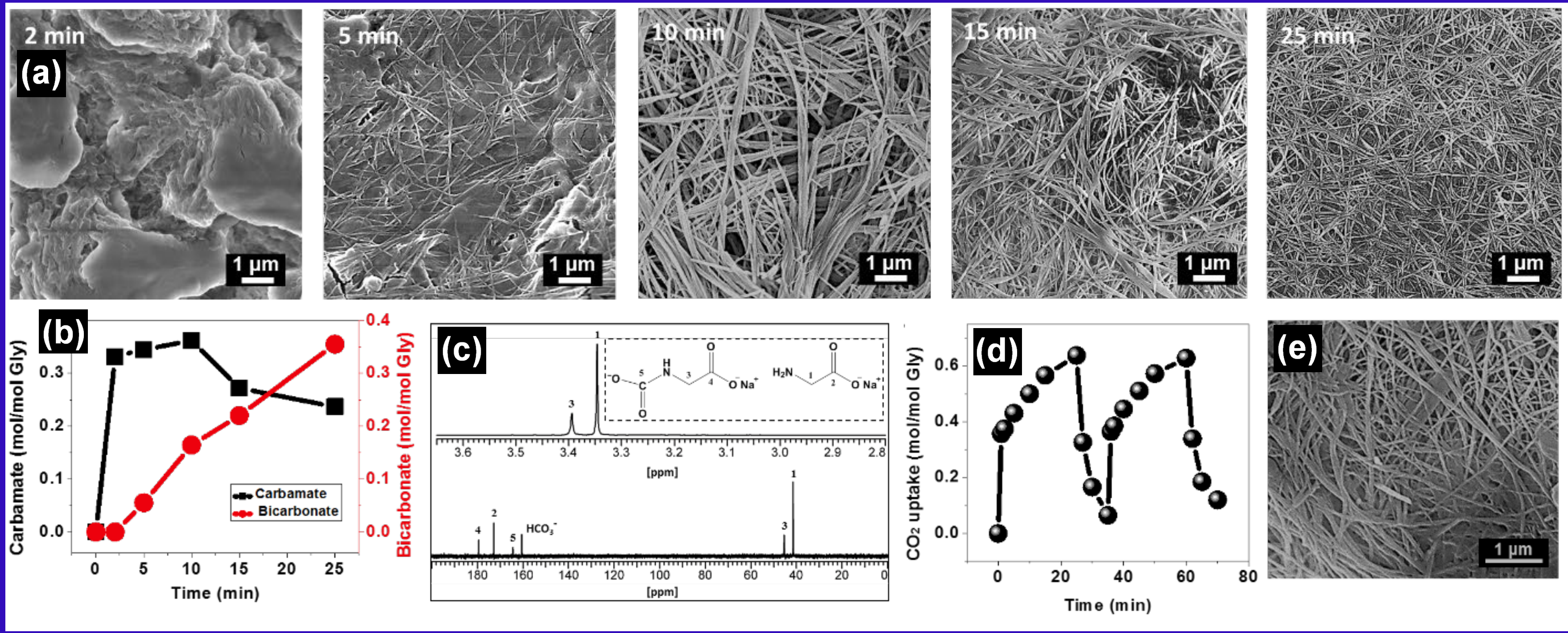


Fig. 2. Glycine (Gly) sodium salt solvent: (**a**) Nanofiber formation and (**b**) species changes in solvent vs. CO_2 absorption time. (**c**) ^{1}H (upper) and ^{13}C (lower) nuclear magnetic resonance (NMR) spectra after CO_2 absorption. (**d**) CO_2 absorption and desorption in two cycles. (**e**) Nanofiber re-formation after CO_2 absorption, desorption, and re-absorption. Gly was 25 wt%.

(B). Project Objective and Research Team

Overall Project Objective

- To develop and test an innovative nanotechnology that can utilize CO_2 from coal-based power systems or other industrial sources as the primary feedstock to produce commercially valuable products.

Project Tasks

- **Task 1:** Project management and planning (Li, Morsi, Wang)
- **Task 2:** Technology maturation plan (Li, Morsi, Wafle)
- **Task 3:** Lab-scale unit modification (Li)
- **Task 4:** Selection of best candidate amino acid solvent (Li)
- **Task 5:** Process optimization to produce high-purity nanomaterials (Li)
- **Task 6:** Life cycle assessment (LCA, Wang)
- **Task 7:** Process and techno-economic analysis (TEA, Morsi)

Project Funding, Team, and Industry Sponsor

Funding: DOE-NETL: $800,000; Cost-share: $218,205

- Bingyun Li, PhD (PI, WVU)
- Badie Morsi, PhD (Co-PI, Univ. of Pitt)
- Jingxin Wang, PhD (Co-PI, WVU)
- Trina Wafle (Co-I, WVU)
- Ron Rosinski (Longview Power, LLC)

- Naomi R. O’Neil (Project manger, NETL)
- (Andy Aurelio, Steven A. Mascaro; NETL)

Pitt

(C). Accomplishments (Task by Task)

Task 1: Project management and planning

Task 2: Technology maturation plan

A. TARGET COMMERCIAL APPLICATION

The proposed carbon capture and conversion technology encompasses addresses two market segments:

- Those who want to capture carbon
- Those who want to use the byproduct

B. CURRENT TECHNOLOGY READINESS LEVEL - BEGINNING OF PROJECT TRL

- AA salt solvent: TRL 2-3
- Process engineering system: TRL 1

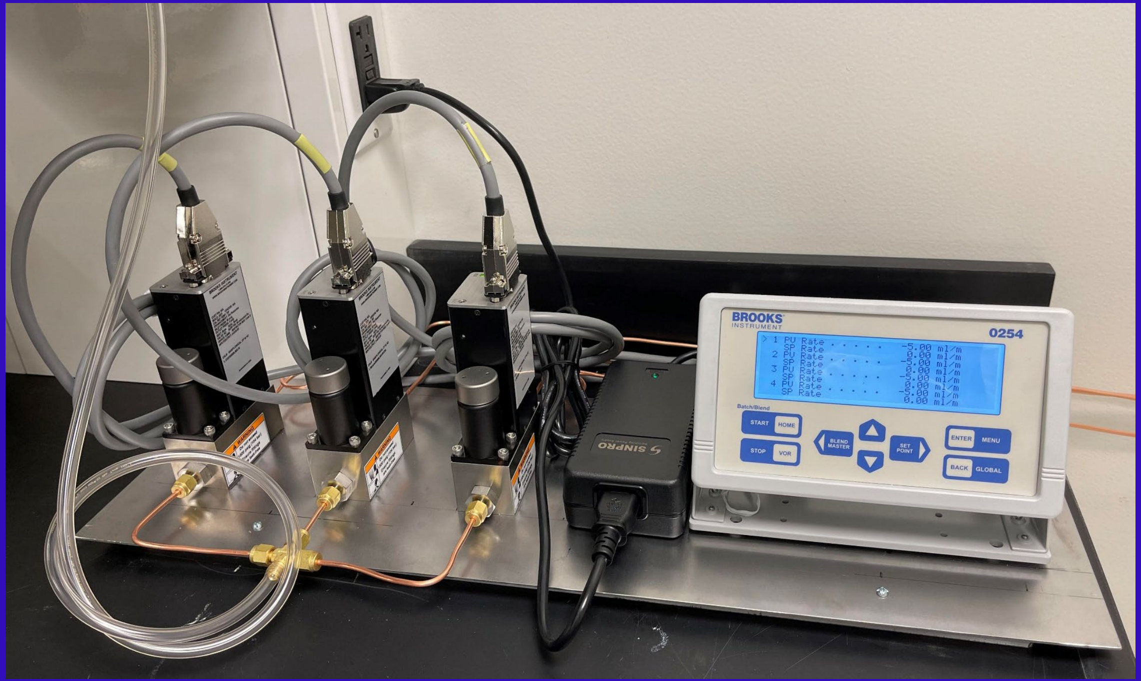
C. PROPOSED WORK – END OF PROJECT TRL

- AA salt solvent: TRL 4
- Process engineering system: TRL 4

D. POST-PROJECT PLANS

To seek funding to pursue the three switchable pathways for cost-effective carbon management under various conditions (flue gas, direct air capture, *etc.*)

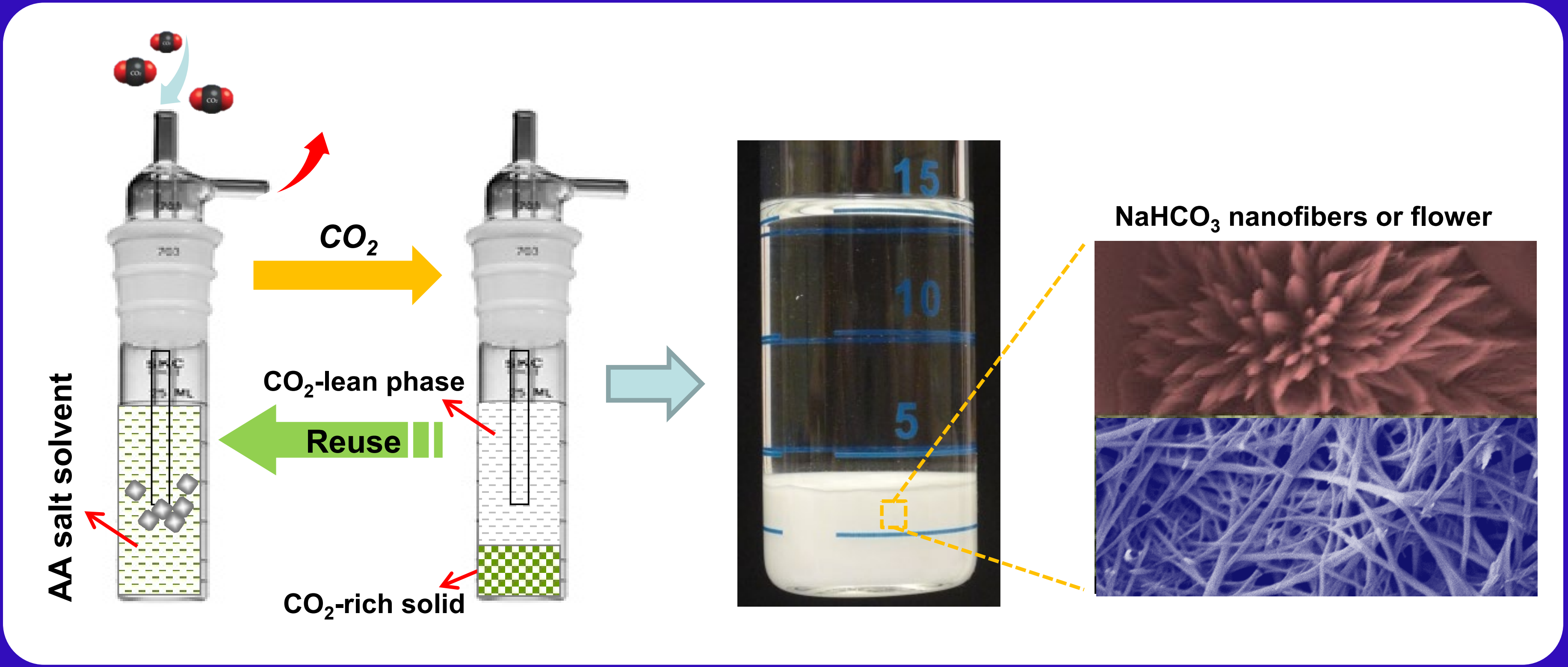
Task 3: Lab-scale unit modification



<u>Fig. 3.</u> Three mass flow meters were purchased and assembled.

Task 4: Selection of best candidate AA solvent

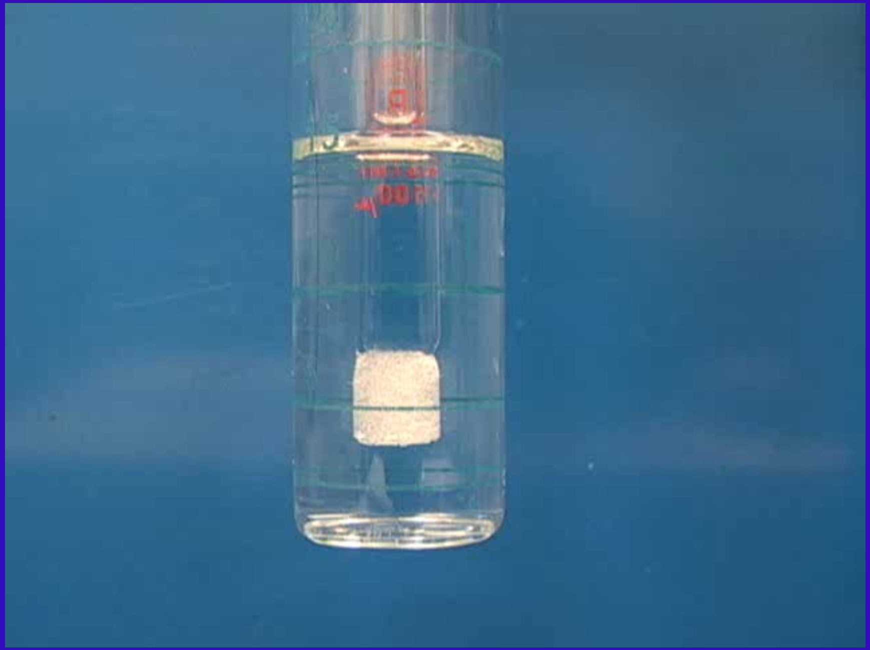
➢ **Technology development — Phase-change AA nanotechnology:**



Phase-Change AA Nanotechnology

Li B, *et al.* Amino acids react with carbon dioxide (CO_2) and form nanofibers and nanoflowers. **US patent US10,583,388**. Date of patent granted: March 2020.

Before CO_2 bubbling



After CO_2 bubbling

Three-Switchable Pathways

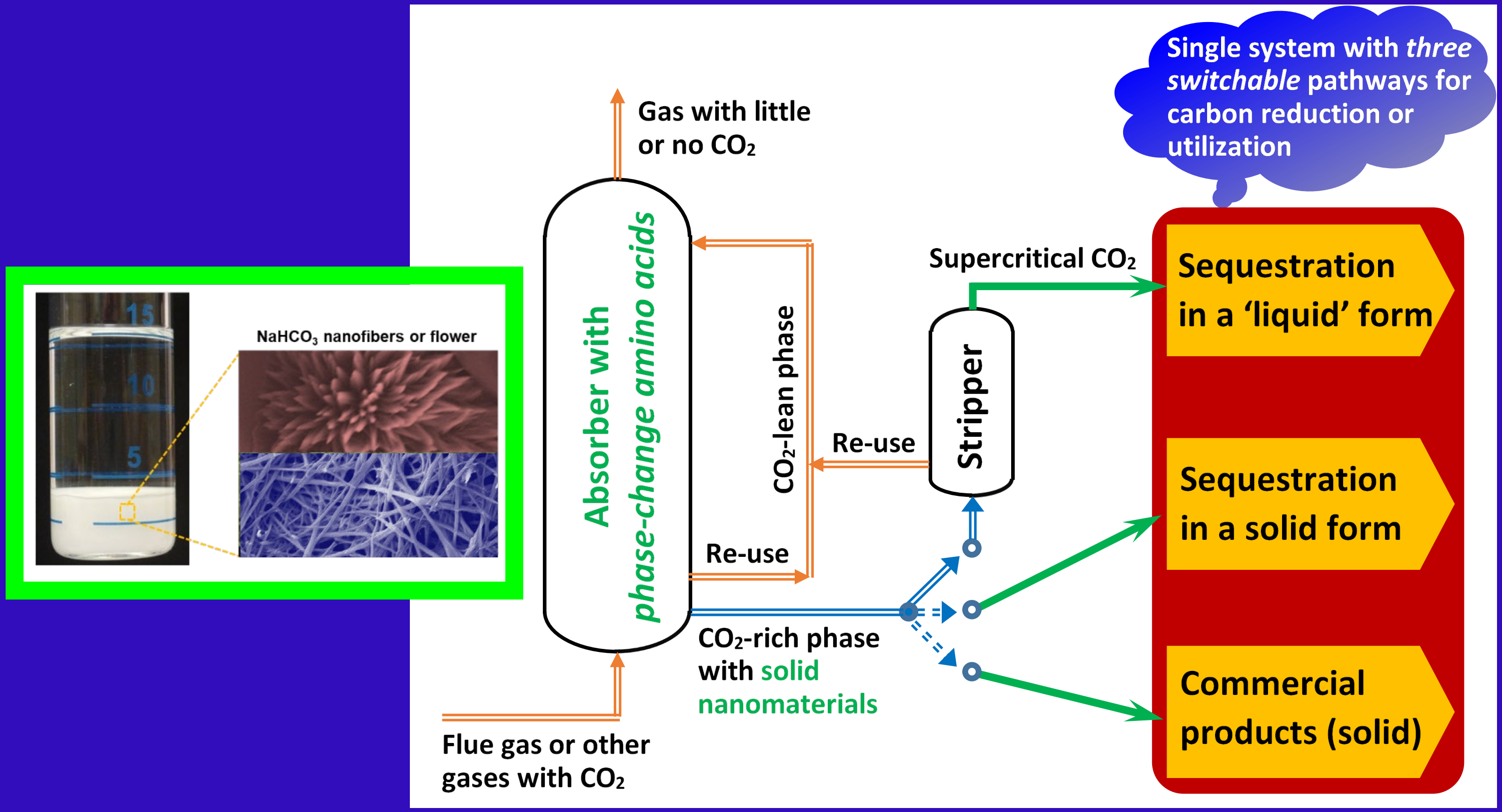


Fig. 4. Schematic diagram of the innovative phase-change nanotechnology process with *three flexible product pathways* for carbon reduction or utilization.

➢ Optimization and reproducibility:

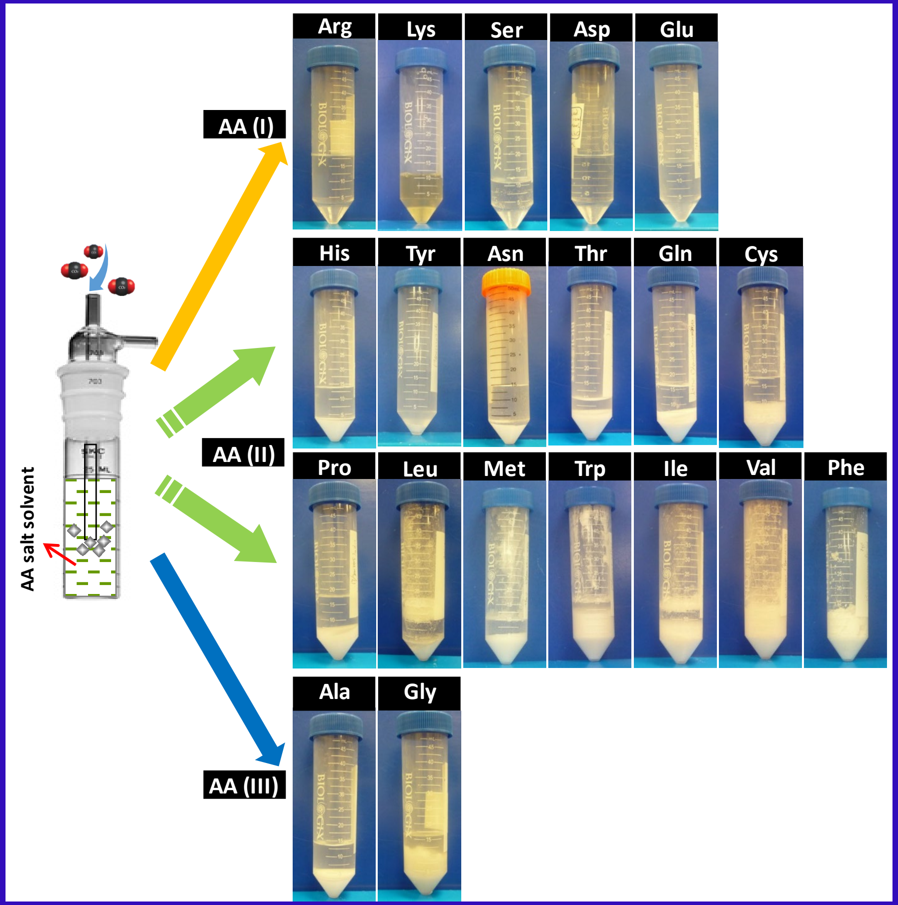


Fig. 5. 20 AA salt solvents after reacting with pure CO_2.

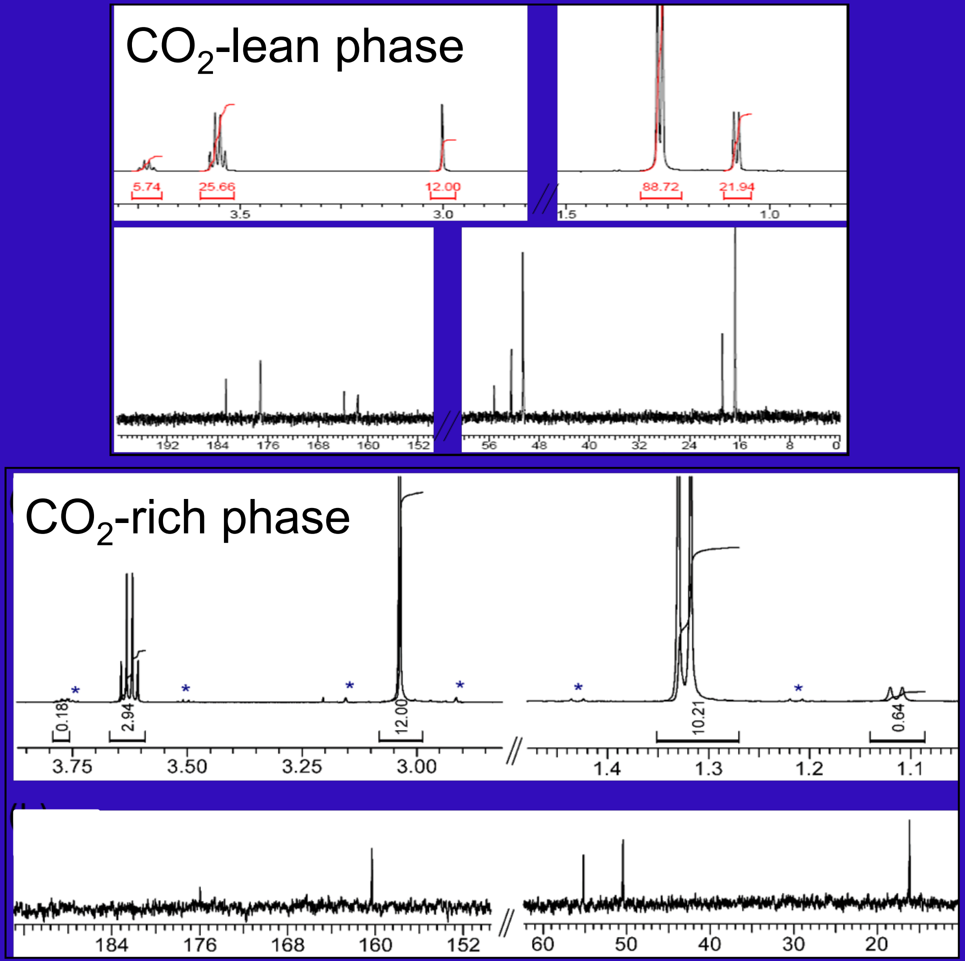


Fig. 6. Over 90% CO_2 absorbed was in the “milky” phase and ~95% as $NaHCO_3$.

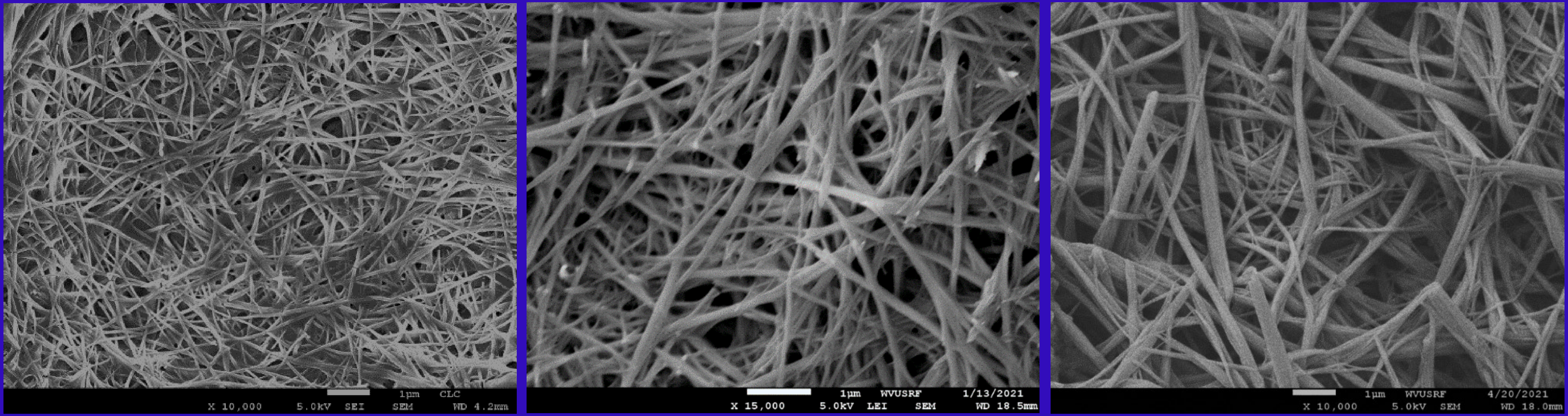


Fig. 8. Nanofibers developed by multiple individuals and at different times.

Task 5: Process optimization to produce high-purity nanomaterials

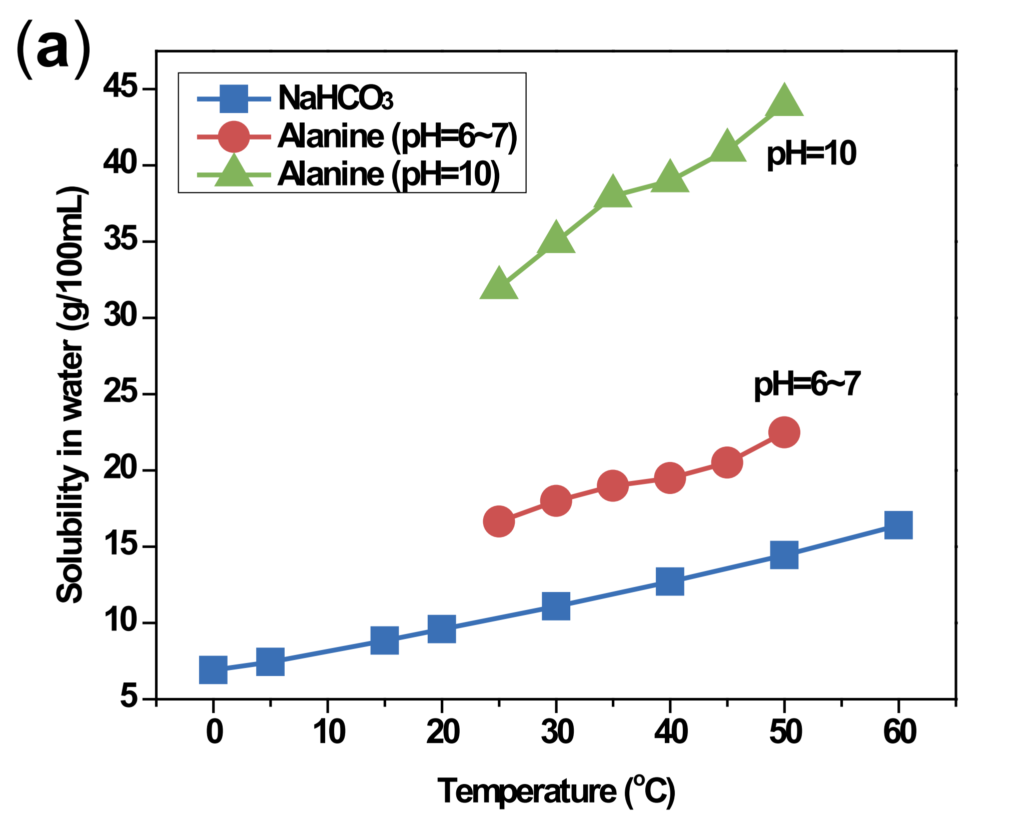
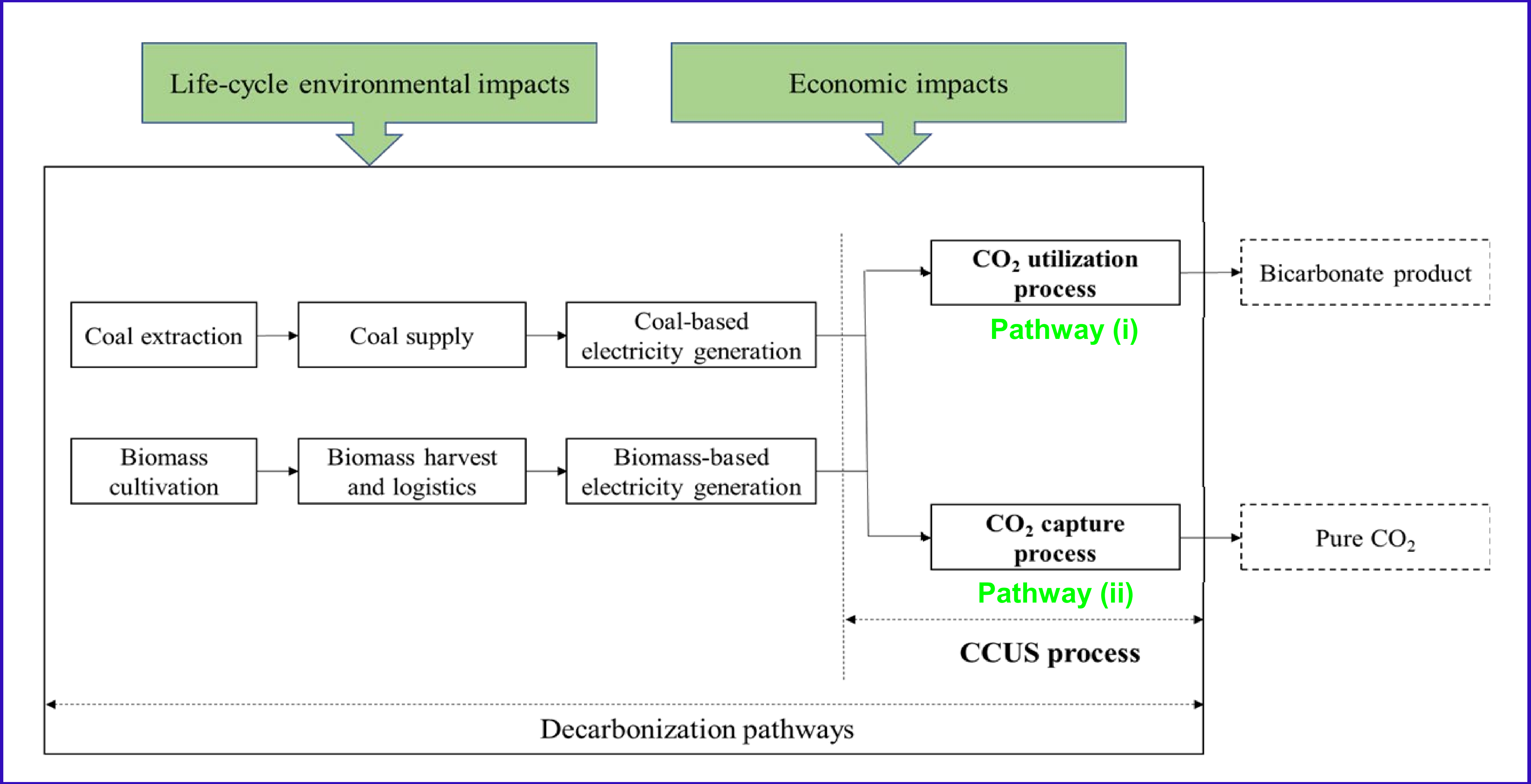


Fig. 9. Strategies to achieve high-purity bicarbonate: (a) Solubility differences, and (b) Freeze dryer.

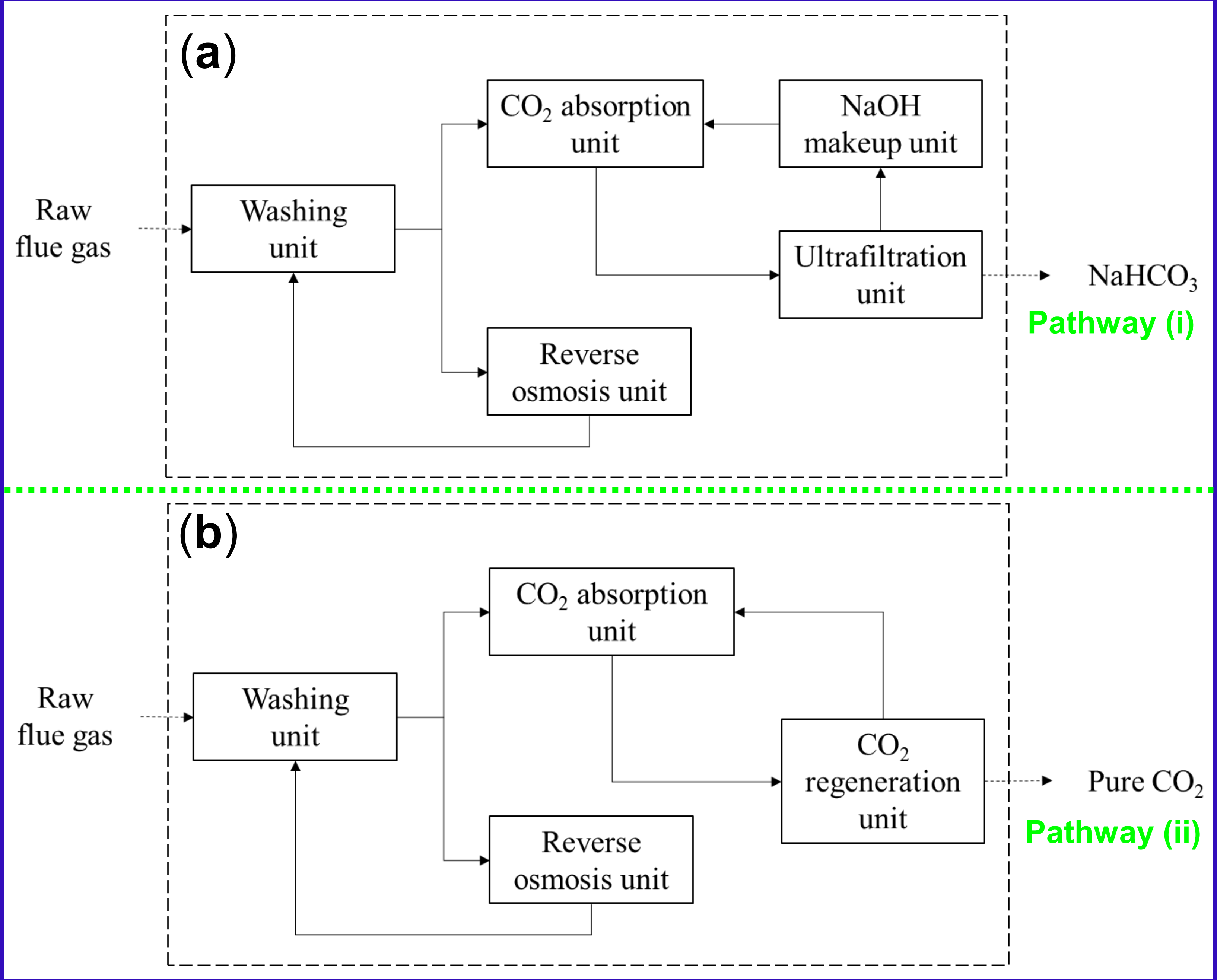
Task 6: Life cycle assessment (LCA)

- **Objective:**
  - Develop a cradle-to-gate LCA model to quantitatively evaluate the environmental impacts, especially the global warming potential (GWP) impact, of the AA-based phase-change processes for both CO_2 capture and CO_2 utilization.

- **Method:**
  - Integrated consequential and attributional cradle-to-gate LCA with TRACI 2.1 to quantify the life-cycle environmental impacts.
  - Carrying out TEA of the CO_2 capture process using Gly to produce bicarbonate nanomaterials using Aspen Plus v.10.



Scheme 1. Analysis modeling framework of LCA.



Scheme 2. (a) CO_2 utilization process to produce nanomaterials and (b) CO_2 capture process to obtain CO_2 for sequestration.

➢ Environmental impact:

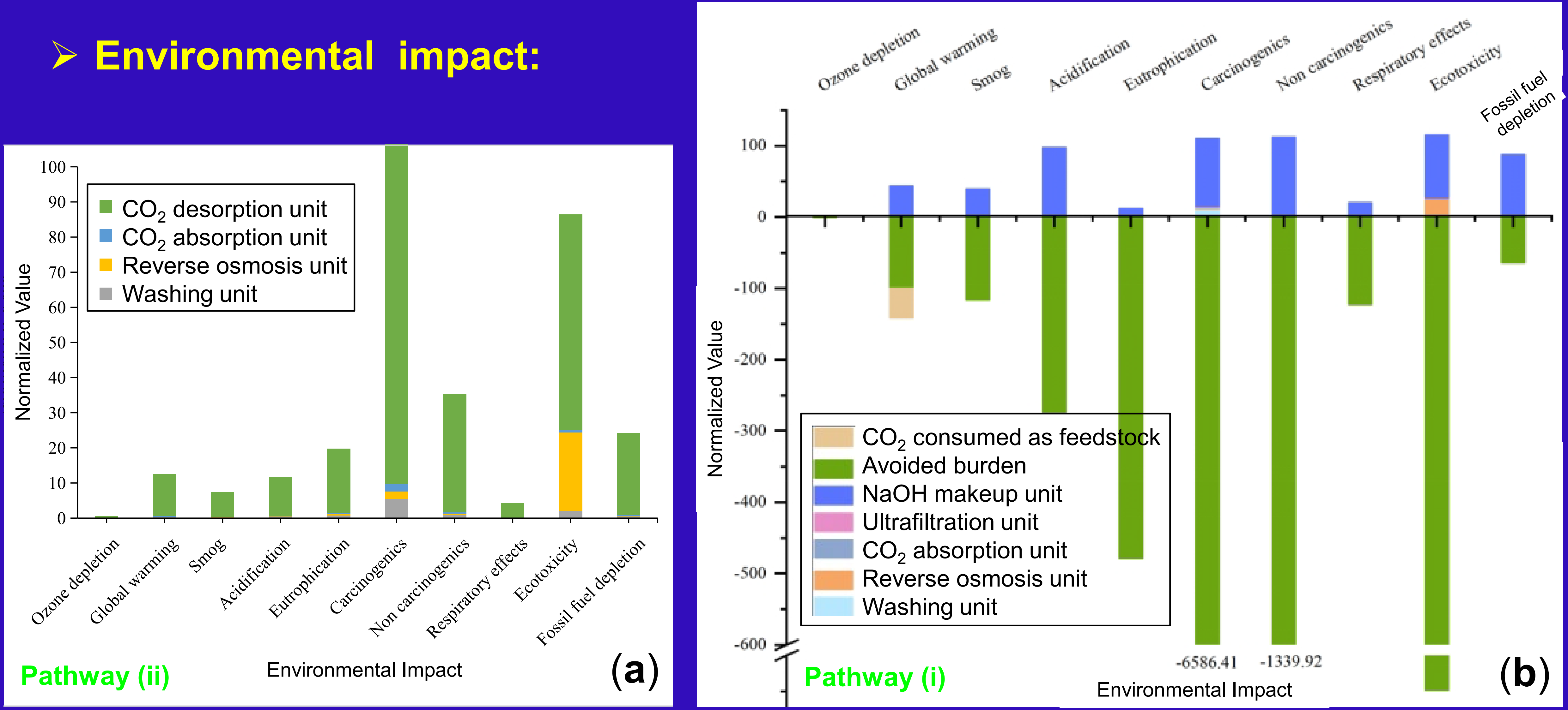


Fig. 10. Normalized life-cycle environmental impact of (a) CO_2 capture process and (b) CO_2 utilization process for coal-fired flue gas by impact and unit process.

➢ Environmental impact – GWP:

- CO_2 utilization process (pathway i): the overall GWP impact is (-2367.61) ton CO_2 eq./1,000 ton CO_2 utilization.
- CO_2 capture process (pathway ii): the overall GWP impact is 303.47 metric ton CO_2 equivalent (eq.)/1,000 metric ton CO_2 captured.

➢ Economic impact:

- CO_2 utilization process (pathway i): The operation of 1,000 ton CO_2 utilization can provide 2.44-3.25 employment, $196,591-261,591 labor income, $150,663-476,659 value-added, and $1,045,944-1,528,849 industry output.
- CO_2 capture process (pathway ii): The operation of 1,000 ton CO_2 capture can provide 0.29-0.35 employment, $21,231-25,199 labor income, $50,246-52,300 value-added, and $102,777-107,570 industry output to the national economy.

Task 7: Process and techno-economic analysis (TEA)

- Process development

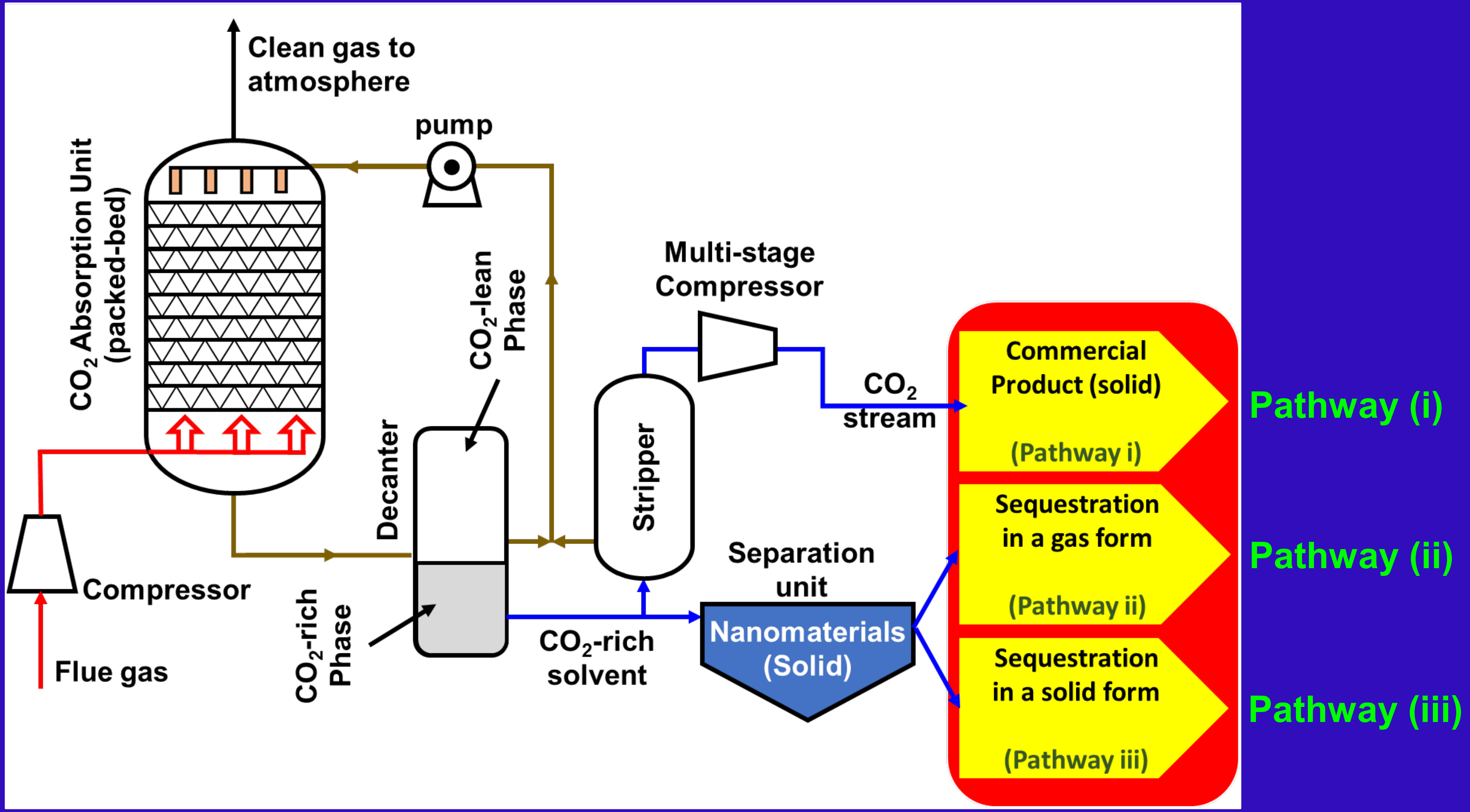


Fig. 11. Schematic diagram of our innovative phase-change nanotechnology approach with three potential product pathways for carbon management.

➢ Objective:

To use Aspen Plus v.10 to perform TEA of the post-combustion CO_2 capture process using actual plant flue gas and Gly in two pathways:

- **Pathway (i)** to capture CO_2 to produce innovative sodium bicarbonate ($NaHCO_3$) nanomaterials.
- **Pathway (ii)** to capture CO_2 for Enhanced Oil Recovery (EOR) or sequestration purposes.

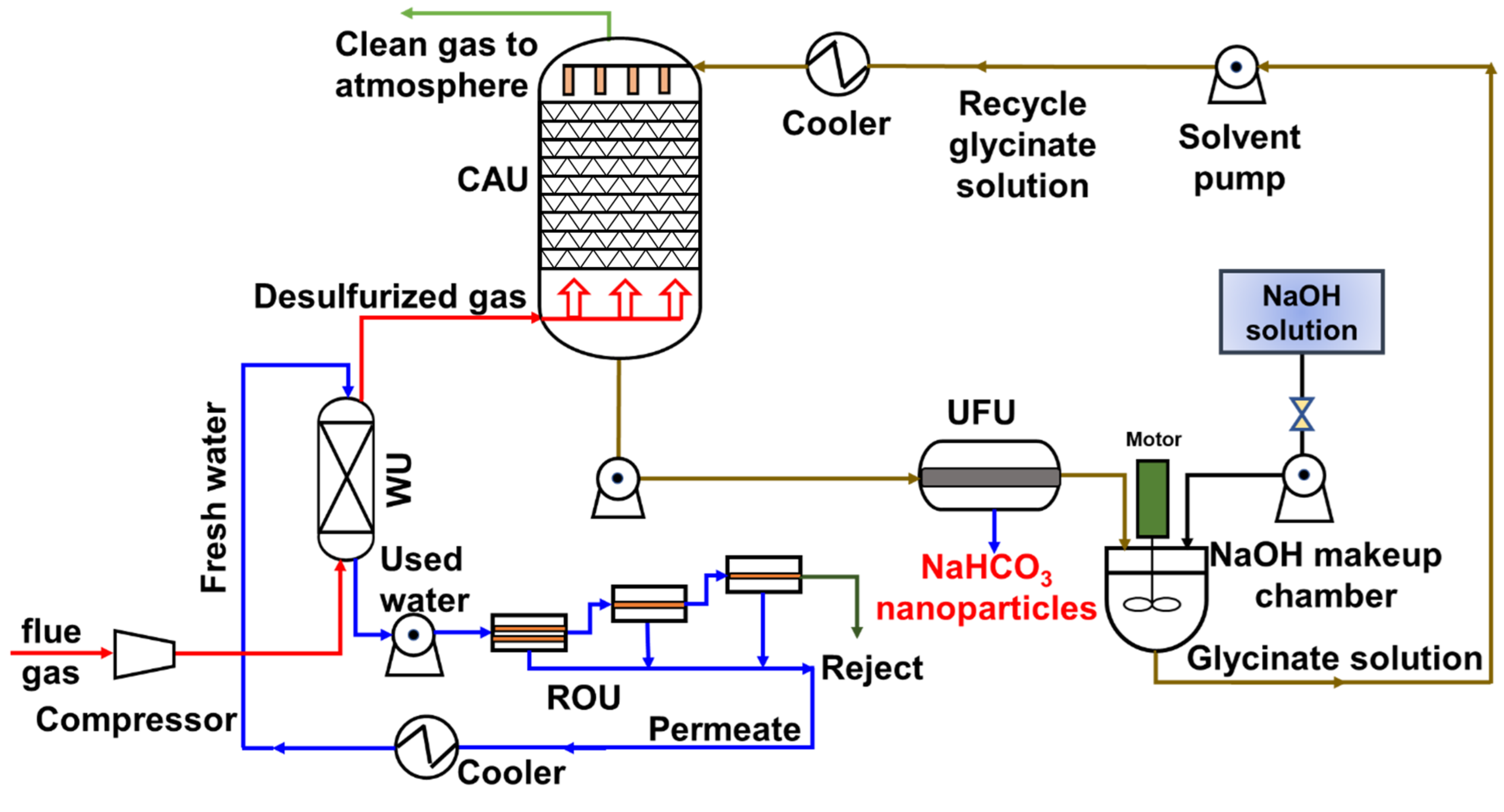
➢ Case study — Case 1: Flue gas from Wolverine Coal Power Plant (600 MWe)[1] representing 10 MWe

Pressure	1	atm
Temperature	353.15	K
Flow rate	12.43 12.38	kg/s m^3/s
Components	**mol %**	**wt %**
CO_2	13.33	20.18
H_2O	12.31	7.63
N_2	70.36	67.79
O_2	4.00	4.400
SO_2	2.35×10^{-3}	5.20×10^{-3}

Table 1. Flue gas pressure, temperature, and composition.

[1] Hoffman, H., Wu, S., Pardini, R., Tripp, E., & Barnes, D. (2010). *Expansion of Michigan EOR Operations Using Advanced Amine Technology at a 600 MW Project Wolverine Carbon Capture and Storage Project*. Wolverine Power Supply Cooperative.

Pathway i: Process for CO_2 capture to produce $NaHCO_3$ nanomaterials



Process main units and constraints

Main units

- Washing unit (WU)
- CO_2 capture unit (CAU)
- Reserve Osmosis Unit (ROU)
- NaOH makeup chamber
- Ultrafiltration and $NaHCO_3$ production Unit (UFU)

Constraints

- 99.9% SO_2 removal
- ≥ 90 mol% CO_2 absorption in CAU
- No flooding in WU and CAU
- Packing height to diameter ratio ≥ 6
- The water content in CO_2 stream for sequestration ≤ 600 ppm

TEA calculations

$$\mathrm{CAPEX} = \; Cost\ of\ all\ process\ units\ and\ rotating\ equipment$$

$$\mathrm{OPEX}_{2020} = (37\sum \mathrm{W}) + \mathrm{C}_{\mathrm{NaOH}}\dot{m}_{NaOH} - \mathrm{C}_{\mathrm{NaHCO3}}\dot{m}_{NaHCO3} + 0.04(\mathrm{CAPEX}_{2020})$$

$$\mathrm{LCOC} = (\frac{f_{CR}}{f_c})\sum(CAPEX_{2020})/\dot{m}_{CO2} + OPEX_{2020}/\dot{m}_{CO2}$$

$$f_{CR} = \frac{i(1+i)^N}{(1+i)^N - 1}$$

TEA of pathway (i)

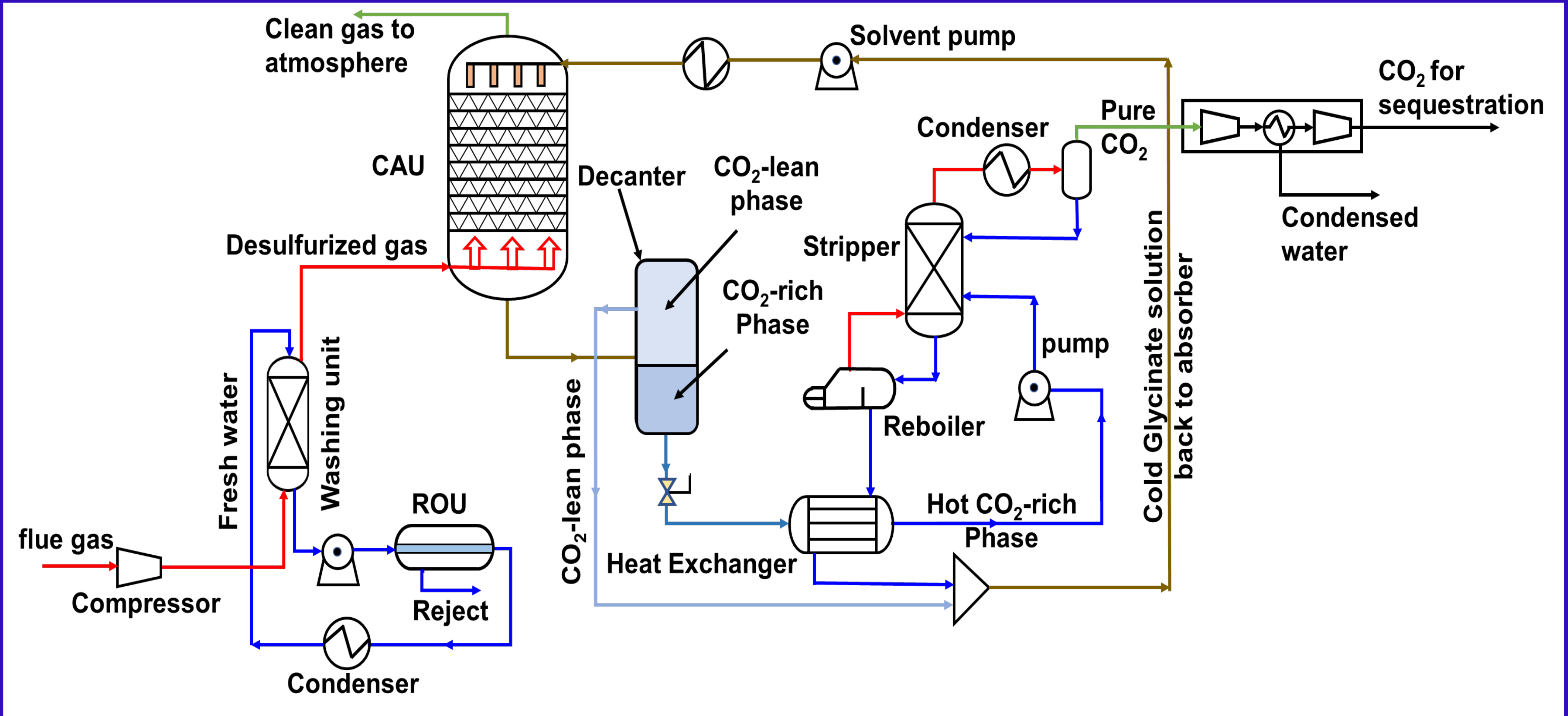
Cost category	Cost
Total CAPEX, 2020 $	4,450,552
NaOH makeup, $/h	3,460
$NaHCO_3$ production, $/h	-3,278
Total OPEX, $/h	233
$\dot{m}_{CO2}$**, ton/h**	8.47
$NaHCO_3$ produced, ton/h	16.15
Total LCOC, $/ton CO_2	**35.49**

*Gly sodium salt is used for the TEA.
CAPEX: Capitol cost
OPEX: Operating cost
LCOC: Levelized cost of CO_2 captured

f_{CR} = 0.106079 = Capital recovery factor, 1/yr
f_c = Capacity factor = 0.8
Electricity cost = 37 $/MWh[2]
W = total power requirements, MWe
C_{NaOH} = NaOH makeup cost[3]
$\dot{m}_{NaOH}$ = NaOH makeup, ton/h
C_{NaHCO3} = $NaHCO_3$ produced prices, $/ton[4]
$\dot{m}_{NaHCO3}$ = $NaHCO_3$ produced, ton/h
O & M cost = 4% of the total CAPEX in $/yr
$\dot{m}_{CO2}$ = CO_2 captured, ton/h
N = project lifetime, 30 yrs
i = discount rate = 10%/yr

[2] $NaHCO_3$: https://www.alibaba.com/product-detail/Nahco3-Nahco3-Bicarbonate-Sodium-99-Stain_1600164672445.html?spm=a2700.galleryofferlist.normal_offer.d_title.1df1215fLzYXIB&s=p
[3] NaOH: https://www.alibaba.com/product-detail/Naoh-Naoh-Sodium-Hydroxide-Price-Sodium_1600193949000.html?spm=a2700.galleryofferlist.topad_creative.d_title.79a5125bELCd9P
[4] NREL, Commercial electricity rate in Industry, https://www.electricitylocal.com/states/pennsylvania/industry/#ref.

Pathway (ii): CO_2 capture for EOR or sequestration purposes



TEA comparison between Gly and MEA

Cost category	Gly Pathway (i)	Gly Pathway (ii)	MEA Pathway (ii)
Total CAPEX, 2020 $	4,450,552	12,085,346	$14,596,990
NaOH makeup, $/h	3,460	--	--
$NaHCO_3$ production, $/h	-3,278	--	--
Total OPEX, 2020 $/h	233	250	420
$\dot{m}_{CO2}$, ton/h	8.47	8.21	8.27
$NaHCO_3$ produced, ton/h	16.15	-	-
Total LCOC, $/ton CO_2	35.49	52.68	77.52

*MEA: monoethanolamine.

➢ Case study — Case 2: Flue gas from Longview Power plant (780 MWe)[5] representing 10 MWe

Pressure, atm	1	
Temperature, K	324.82	
Flow rate	11.82 10.52	kg/s m^3/s
Components	**mol %**	**wt %**
CO_2	12.022	17.668
CO	3.144e-3	2.94e-3
O_2	4.79	5.12
N_2	79.198	74.086
H_2O	0.03	1.805
Ar	0.98	1.307
SO_2	3.319e-3	7.10e-3
NO_2	3.547e-3	5.45e-3

Table 2. Flue gas pressure, temperature, and composition.

[5] Ron Rosinski (Personal communication, April 29, 2021)

TEA comparison between Gly and MEA

Cost category	Gly Pathway (i)	Gly Pathway (ii)	MEA Pathway (ii)
Total CAPEX, 2020 $	4,171,205	10,749,326	$13,177,583
NaOH makeup, $/h	2,823	--	--
$NaHCO_3$ production, $/h	-2,674	--	--
Total OPEX, 2020 $/h	175	191	322
$\dot{m}_{CO2}$, ton/h	6.90	6.89	6.95
$NaHCO_3$ produced, ton/h	13.17	-	-
Total LCOC, $/ton CO_2	34.51	51.34	75.03

Production of Inorganic Materials – Solid Carbon Products

Technology Performance Data

	Units	Measured/Current Performance	Projected/Target Performance
***Reaction Thermodynamics*[1,2]**			
Reaction[3]		Thermochemical reaction	
Chemical Equation		(1) ${}^{-}OOCCH_2NH_3^{+} + OH^{-} = {}^{-}OOCCH_2NH_2 + H_2O$ (2) $CO_2(g) + 2\,{}^{-}OOCCH_2NH_2 = {}^{-}OOCCH_2NHCOO^{-} + {}^{-}OOCCH_2NH_3^{+}$ (3) ${}^{-}OOCCH_2NHCOO^{-} + H_2O = {}^{-}OOCCH_2NH_2 + HCO_3^{-}$	
ΔH°_{rxn}	kJ/mol	(1) -88.66 (2) -139.24 (3) 34.94	
ΔG°_{rxn}	kJ/mol	(1) -93.20 (2) -97.14 (3) 28.56	
Reaction Conditions			
CO_2 Source[4]	-	Coal-fired flue gas (Longview power plant)	Coal-fired flue gas (Longview power plant)
Catalyst[5]	-	None	None
Pressure	bar	1.0	1.0
CO_2 Partial Pressure	bar	0.124	0.124
Temperature	°C	51.67	51.67
Nominal Residence Time[6]	sec	34.6	34.6
***Once-Through Performance*[7]**			
CO_2 Conversion[8]	%	90.4	92.0
Selectivity to Desired Product[9]	%	99.88	99.88
Yield of Desired Product[10]	%	90.31	91.89
Product Composition			
Desired Product[11]	-	$NaHCO_3$ nanomaterials	$NaHCO_3$ nanomaterials
Main Product Impurities[12]	-	0.05% carbamates	0.05% carbamates
Purity of Finished Product[13]	%	99.95	99.95
Product Production[14]	kg/hr	92,566	470,918
Co-Products[15]	-	--	--
Co-Product Production[16]	kg/hr	--	--
***Product Properties*[17]**			
Density	kg/m³	TBD	2,159
Particle Size	(microns)	0.045 × 15	0.045 × 15
Surface Area	m²/g	TBD	41.23
***Commercial Product Properties*[18]**		**Current**	
Density	kg/m³	2,200	
Particle Size	microns	44	
Surface Area	m²/g	0.062	
U.S. Market Size	Tonnes/yr	1.1 million (2021)	
Global Market Size	Tonnes/yr	5.7 million (2021)	
Market Price	$/kg	0.26 – 0.30 (2021)	

TBD: to be determined.

Summary

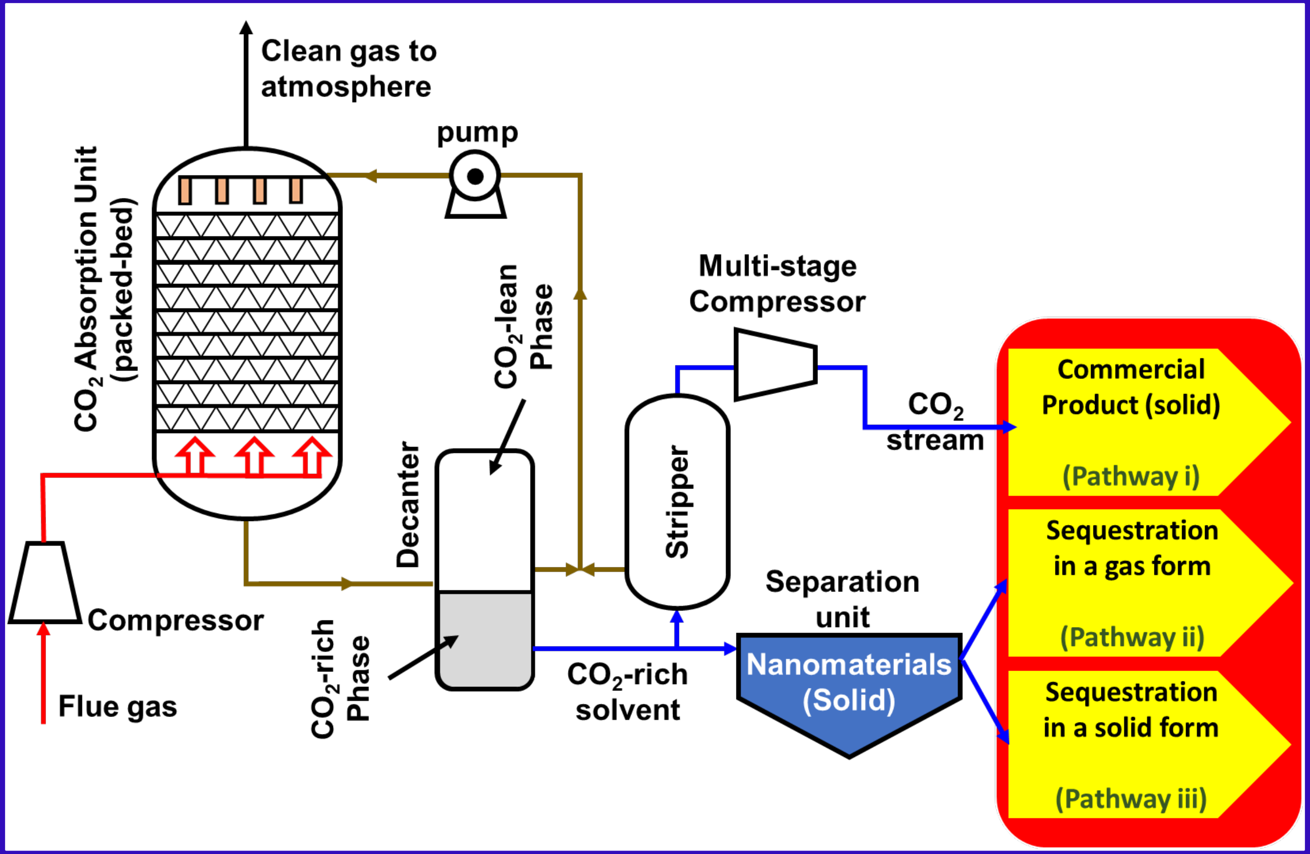
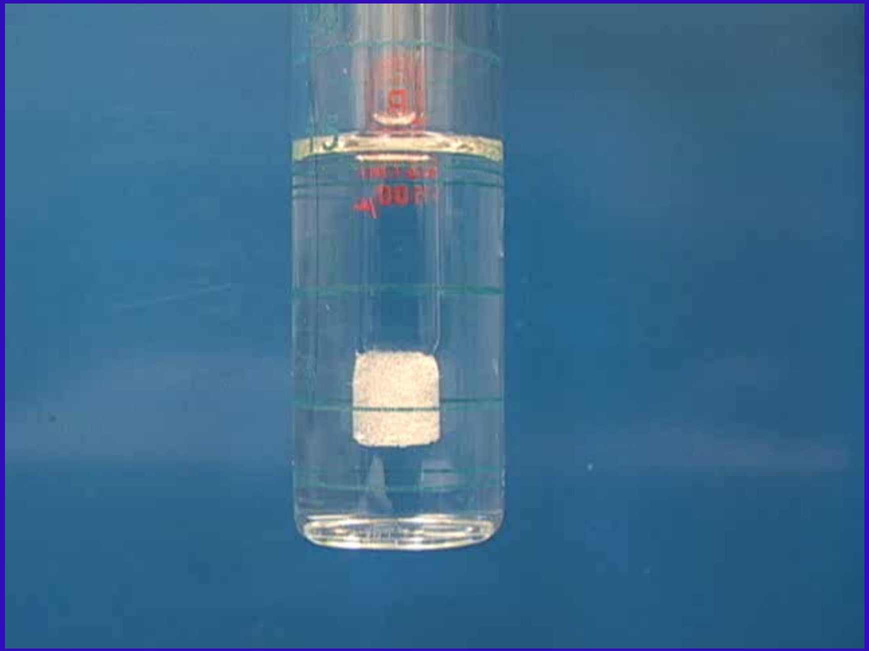


Fig. 12. Development of an innovative phase-change nanotechnology with *three flexible product pathways* for carbon reduction or utilization.

Converting CO_2 into Nanomaterials

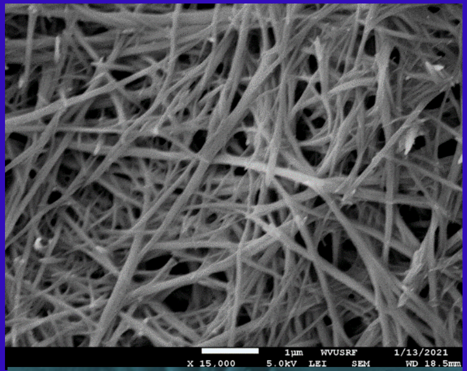
Longview
(our collaborator)

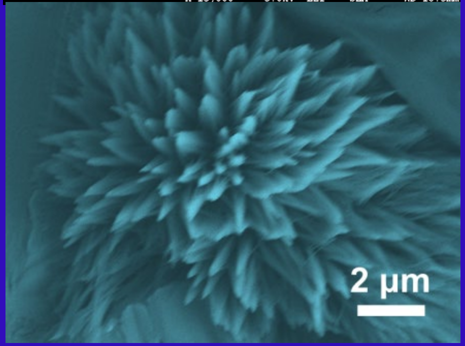
Before CO_2 bubbling



Innovative process
(Patent US10,583,388)

After CO_2 bubbling





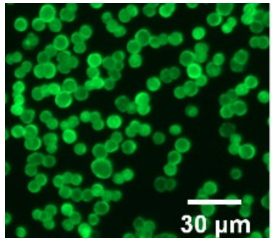
Final products

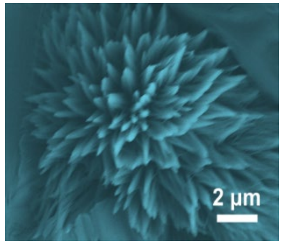
Product Market Potential

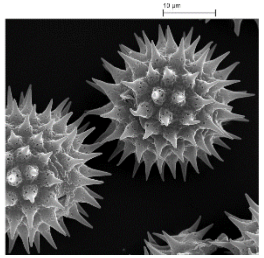
- **Sodium Bicarbonate Market**
  - 5.7M tpy: 3M tpy CO_2 to meet current market (33.4B tpy CO_2 produced globally)
  - $9B by 2024 (Global Market Insights-GMI)
  - 5.3% annual compound growth (GMI)
  - 24% animal feed 20% food (IHS Markit)
  - Flue gas sulfur removal, pharmaceuticals, detergents, cosmetics, explosives, pigments, fire extinguishers, etc.

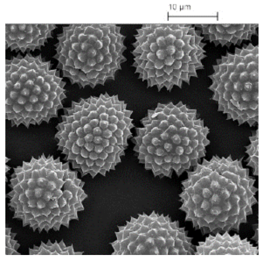
- **WVU's Unusual Shapes → New Applications - Drug Encapsulation**
  - $9.1B 2020 (Transparency Market Research)
  - Templates to make hollow micro- and nano-structured materials

Lipids

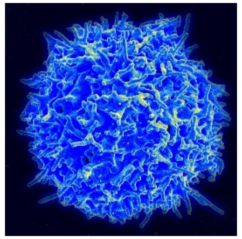








Microcapsules from sunflower pollens.



Human T cell

- AA candidates for phase-change CO_2 conversion have been identified and optimized for an innovative phase-change CO_2 management process with three potential pathways.
- The environmental and economic impacts of our technology have been assessed using life cycle assessment and an economic input-output model. The results have indicated that the CO_2 utilization process could be carbon negative. The operation of 1,000 ton CO_2 utilization can annually provide 2.44-3.25 employments, \$196,595-261,591 labor income, \$150,663-476,659 value-added, and \$1,045,944-1,528,849 industry output to the US economy.
- Using the actual flue gases from two power plants in the US, our TEA has shown that the unique phase-change nanotechnology is cost-effective and achieves much lower LCOCs compared to MEA, as shown below

Cost category	Wolverine Coal Power Plant			Longview Power Plant		
	Gly Pathway (i)	Gly Pathway (ii)	MEA Pathway (ii)	Gly Pathway (i)	Gly Pathway (ii)	MEA Pathway (ii)
Total CAPEX, 2020 \$	4,450,552	12,085,346	\$14,596,990	4,171,205	10,749,326	\$13,177,583
Total OPEX, 2020 \$/h	233	250	420	175	191	322
Total LCOC, \$/ton CO_2	**35.49**	**52.68**	**77.52**	**34.51**	**51.34**	**75.03**

- **Workforce training, publication, and proposal submissions**

DOE/NETL Award
DEFE0031707
DoE: $800,000
Cost-share: $218,205
(3 yrs)

Workforce

- Research group: 3
- Institution: 3 (WVU, Pitt, Longview)
- Student: 11
- Postdoc: 2

Publication

- Patent: 1 (US10,583,388)
- Manuscript: 6
- Abstract: 12

➢ Publications (6):

- Wang R, Ashkanani HE, <u>Li B</u>, and Morsi B. (**2022**) Development of an innovative process for post-combustion CO_2 capture to produce high-value $NaHCO_3$ nanoparticles. **Int J Greenhouse Gas Control** 120:103761.
- Bao Z, Li Q, Akhmedov NG, Li BA, Xing M, Wang J, Morsie BI, <u>Li B*</u>. (**2022**). Innovative cycling reaction mechanisms of CO_2 absorption in amino acid salt solvents. **Chem Eng J Adv** 10:100250.
- Li Q, Bao Z, Akhmedov N, Li BA, Duan Y, Xing M, Wang J, Morsi BI, <u>Li B*</u>. (**2022**). Unravelling the role of glycine in K_2CO_3 solvent for CO_2 removal. **Ind Eng Chem Res** DOI: https://doi.org/10.1021/acs.iecr.2c01637.
- Wickramasinghe S, Wang J, Morsi B, <u>Li B*</u>. (**2021**). Carbon dioxide conversion to nanomaterials: Methods, applications, and challenges. **Energy & Fuels** 35(15):11820-34.
- Wang X, Bao Z, Akhmedov NG, Hopkinson D, Hoffman J, Duan Y, Egbebi A, Resnik K, <u>Li B*</u>. (**2022**). Unique biological amino acids turn CO_2 emission into novel nanomaterials with three switchable product pathways. **ACS Nano** (submitted).
- Zhang X, Wang J, <u>Li B</u>, Morsi B, Wang R. (**2022**). Environmental and economic impacts of an innovative amino-acid-based CO_2 capture and utilization technology and its decarbonization pathways. Ready to be submitted.

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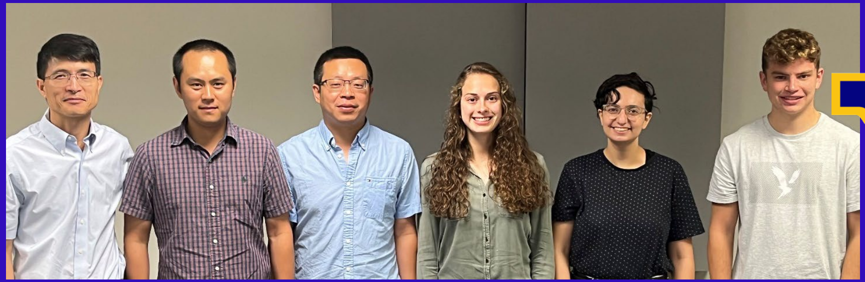
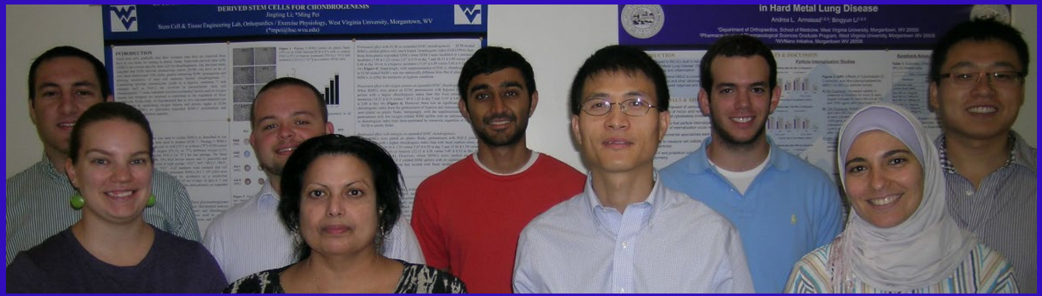
Trina Waffle, Ron Rosinski

NETL project manager: Naomi R. O'Neil (Andy Aurelio, Steven A. Mascaro)





Trainees Since 2005 (103):

- PhD students
- master's students
- undergraduate students
- MD students
- high school students
- postdoctoral fellows
- orthopaedic residents
- visiting scholars