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Integrated Capture and Conversion of CO_2 into Materials (IC^3M):

Pathways for Producing CO_2-Negative Building Composites (FWP 78606)

&

Expanding IC^3M for C1 and C2 Production (FWP-80562)

David J. Heldebrant

U.S. DEPARTMENT OF ENERGY BATTELLE

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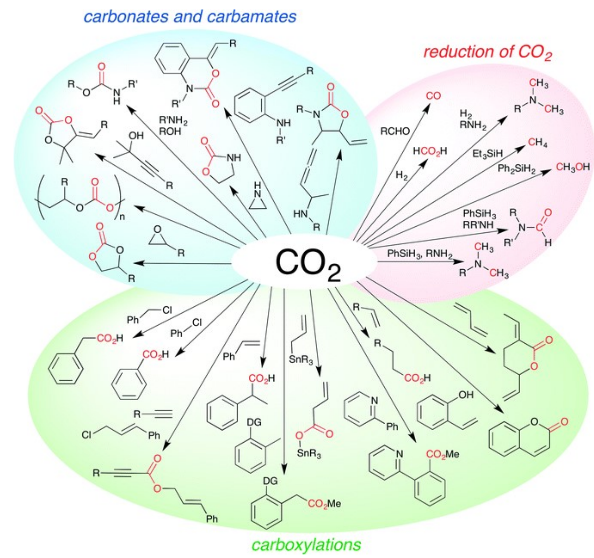
Brickett et al, Chem. Sci., 2022,13, 6445-6456

Integrated Capture and Conversion of CO_2 into Materials (IC^3M); A Multi-Product Platform for CCUS

Goal: *To design CO_2 capture units that concurrently produce materials from CO_2.*



FWP-80562

Near term targets
carbon-neutral fuels and chemicals:
CH_3OH, CH_4

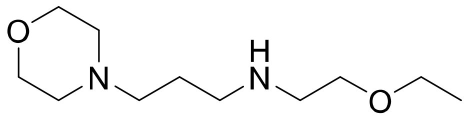
FWP 78606

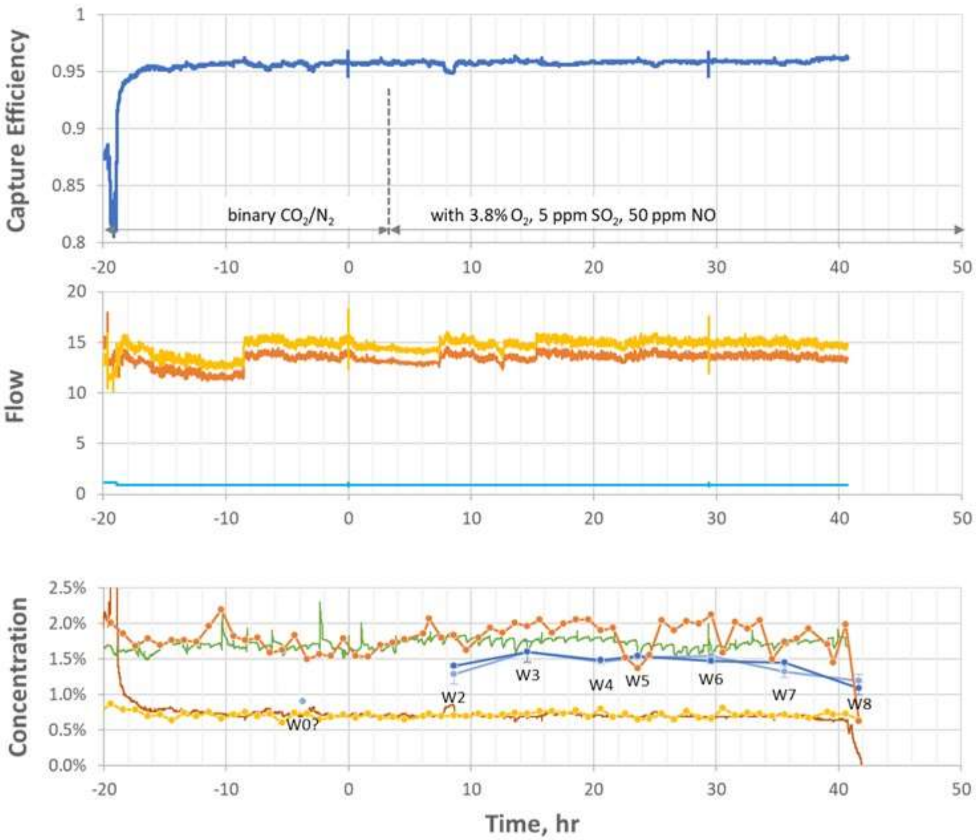
Intermediate term targets
carbon-negative building materials:
CO_2LIG

Long term targets
Mineralization materials:
$CaCO_3$ or $MgCO_3$

Bricket et al. Chem. Sci., **2022**,13, 6445-6456

EEMPA is a promising solvent (2.0 GJ/tonne CO_2)[1] with low costs of capture (\$39/tonne[2] CO_2).[2]

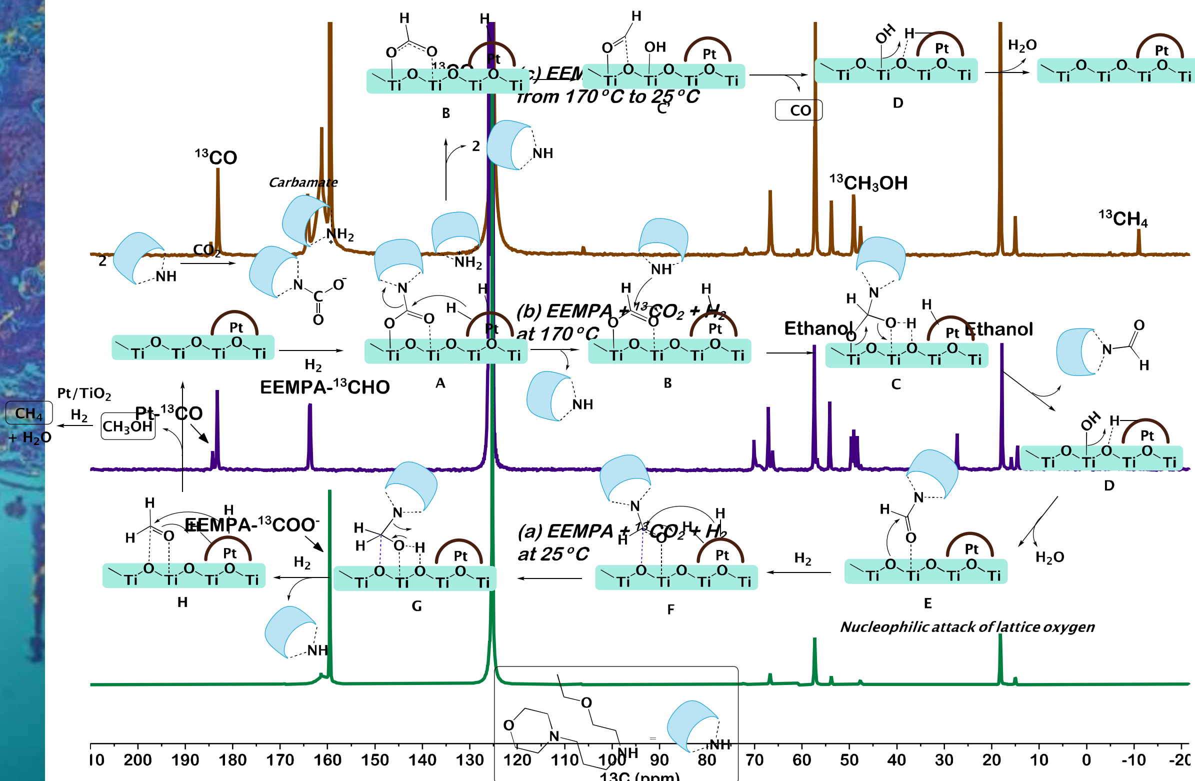




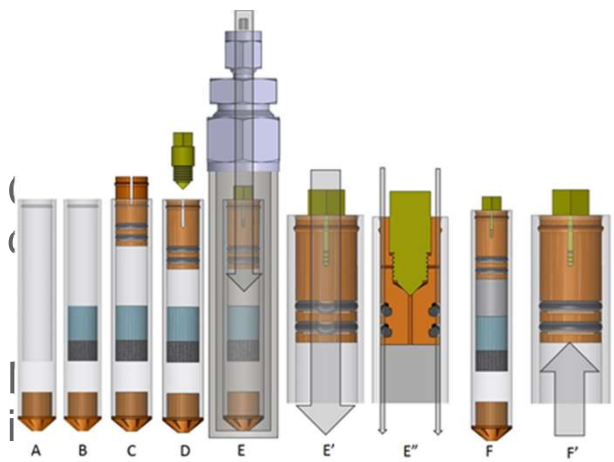
- Single component, water-lean solvent
- 19% cheaper and efficient than Shell's CANSOLV
- 90% lower corrosion and degradation than 5M MEA
- 0.5 MW coal fired plant demonstration, June, 2024

1. *Energy Environ. Sci.*, **2020**, *13*, 4106-4113, 2. J. *Clean. Prod.* **2023**, *388, 135696*

In-Situ ^{13}C MAS NMR Enables an Unprecedented View of Speciation and Kinetics of Catalytic Reactions



In situ ^{13}C MAS-NMR during the hydrogenation of $^{13}CO_2$ in the presence of 2-EEMPA and a 5 wt % Pt/TiO$_2$ catalyst at 170 °C under 60 bar H_2 (initial pressure) in an ethanol co-solvent, 2-EEMPA: EtOH=1:10 (molar ratio).



High-Temperature/Pressure WHiMS MAS Rotors

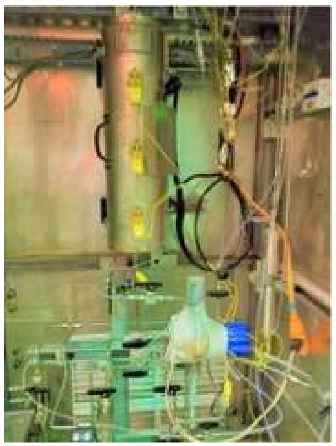
400 bar @ 20 °C; 300 bar @ 250 °C – limit of most HP rotors

- 1st ever selective C-N cleavage of an N-formamide with a heterogeneous catalyst

Advanced Energy Materials, (2022), *12*, 46, 2202369

Methanol formation is sensitive to temperature and space velocity in a Post-Combustion Solvent

Hydrogenation of captured CO_2 using a packed-bed flow reactor.



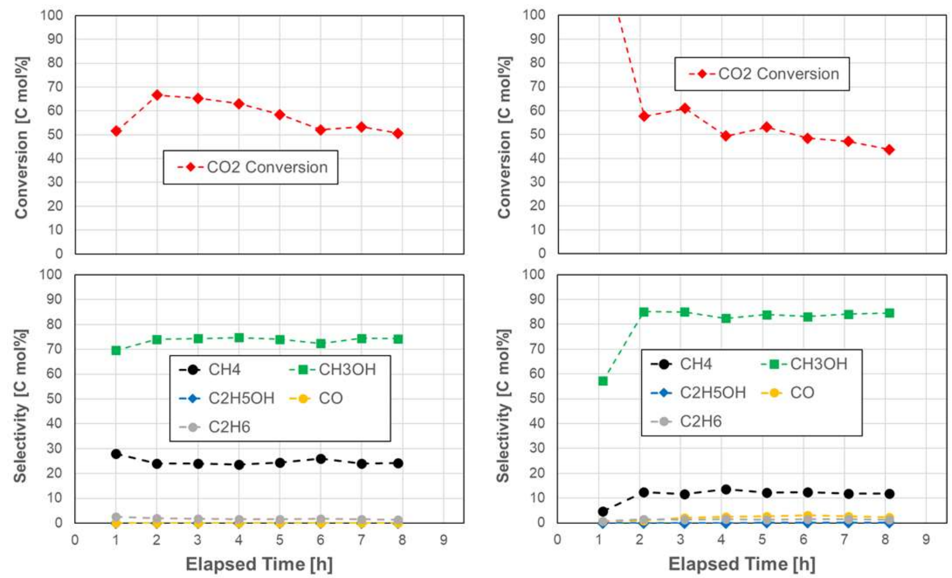
Entry	Reaction T (°C)	CO_2 Conv (%)	WHSV $g_{CO2}/g_{cat}/h$	TOS (h)	Selectivity (mol C%)					
					MeOH	EtOH	PrOH	BuOH	CH_4	C_2H_6
1	140	2.2	0.15	-	92.7	0.0	7.3	0.0	0.0	0.0
2	170	7.7	0.15	-	66.5	4.3	2.5	0.7	26.0	0.0
3	170	29.1	0.015	-	57.0	4.5	0.8	1.4	26.7	8.7
4	190	11.8	0.15	-	78.0	4.3	0.0	2.5	15.1	0.0
5	190	26.9	0.075	-	63.6	4.6	0.2	1.9	26.4	3.3
6	190	85.7	0.015	40	51.5	9.7	0.6	1.9	27.1	9.3
7	190	75.9	0.015	60	50.2	8.6	0.7	2.0	29.2	9.3
8	190	65.2	0.015	80	46.0	8.0	1.1	4.7	29.8	10.5

Liquid feed: captured CO_2 in EEMPA solvent (5 wt.% CO_2) Reaction conditions: 1.0 g catalyst D1, 870 psig; Gas feed: 38 sccm H_2, 5 sccm N_2. Change in WHSV is achieved by changing the liquid feed flow (0.05, 0.025, 0.005 mL/min).

- Pt/TiO_2 is highly selective towards **methanol** with **93% selectivity** at **140 °C.**
- At 190 °C, the **CO_2 conversion** increased from **12%** to **86%** when space velocity was decreased by a factor of 10.
- Conversion decreased from 86% to 65% over a span of approximately 80 hours.

Advanced Energy Materials, (2022), *12*, 46, 2202369

Demonstration of Semi-Batch CO_2 Capture and Catalytic Conversion to Methanol



CO_2 Capture - LCFS			
Feed	CO_2/N_2 [dry basis]	15 / 85	[mol%]
	Dew Point	15.6	[°C]
Absorber	Avg. Temperature	32.3	[°C]
	Avg. Pressure	0.08	[psig]
Stripper	Avg. Temperature	95.1	[°C]
	Avg. Pressure	14.39	[psig]
Reboiler	Temperature	114.9	[°C]
Flow	Liquid	15.3	[kg/h]
	Gas	0.61	[kg/h]
	L/G	25.2	[-]
CO_2 Capture Efficiency		88.9	[%]

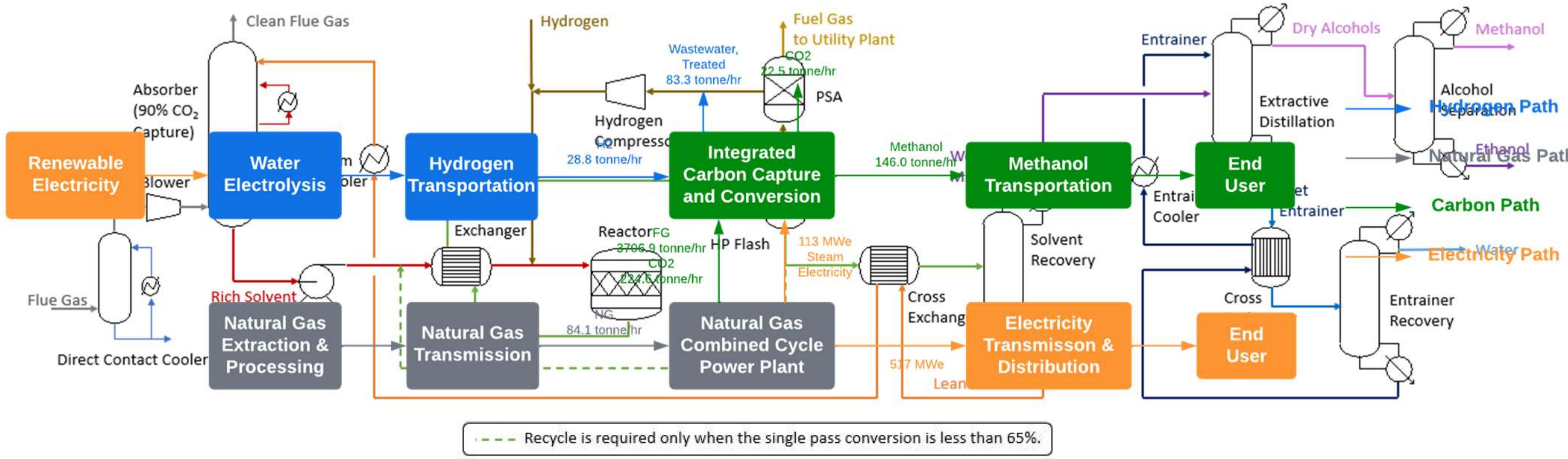
CO_2 Conversion - TCCS			
Gas Feed	H_2/N_2	93 / 7	[mol%]
	Flowrate	6.7 E-3	[kg/h]
Liquid Feed	2-EEMPA/CO_2/H_2O	78 / 5 / 17	[mol%]
	Flowrate	5.9 E-4	[kg/h]
Reactor	Temperature	170	[°C]
	Pressure	865	[psig]
	Catalyst: 5wt% Pt on TiO_2	2.5	[g]
CO_2 Conversion		55 → 0.8	[%]
Methanol Yield		94 → 0	[%]

- Single-pass operation: 8-hours on simulated coal-derived flue gas (CO_2, N_2, H_2O).
- 190°C, 865 psig, 0.053 g_{CO2}/g_{cat}/hr
- Conversion > 50%, CH_3OH selectivity ~ 80%, 8 hr TOS

Barpaga et al. *Green Chem, In Revision*; U.S. patent application filed.

Key Performance Measures for PNNL's IC^{3}M Technology (From Previous TEA Study*)

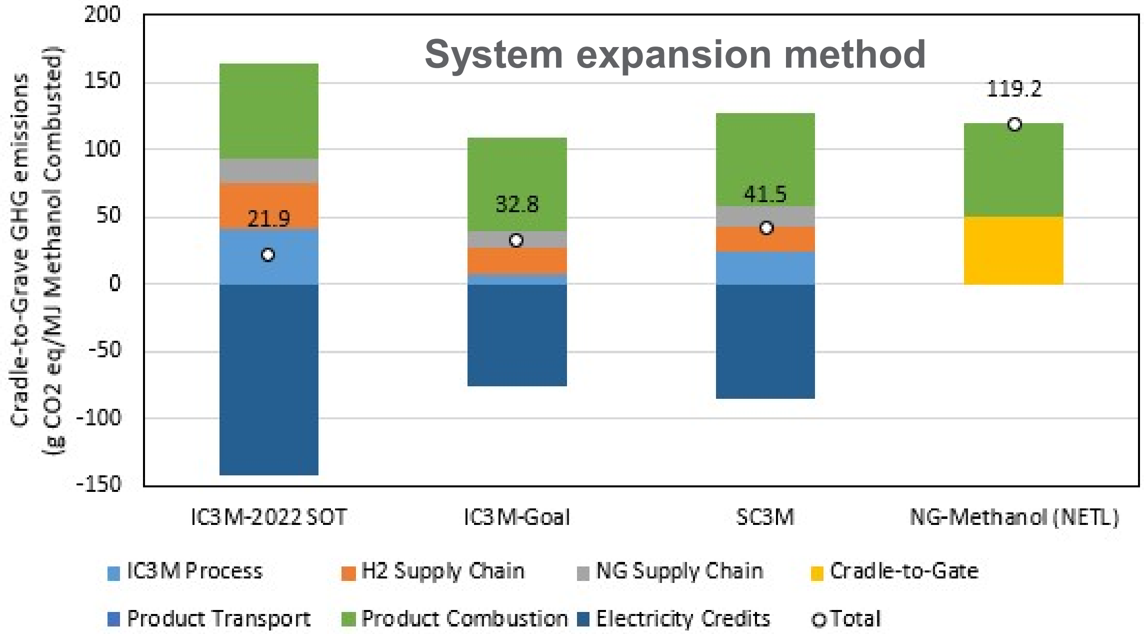
	SOT	Goal Case
WHSV ($gCO_2/gCat/hr$)	0.075	0.15
Single-pass CO_2 conversion (%)	26.9	85.7
Methanol selectivity (C %)	63.6	100
Methane selectivity (C %)	26.4	0
Source	Experiment	R&D Target



Advanced Energy Materials, (2022), *12*, 46, 2202369

Jiang et al. In Preparation

IC^{3}M could achieve significant GHG emission reductions compared to conventional processes.



- Life Cycle GHG Emission Impact Assessment for byproducts
- Un-optimized 2022 SOT and Goal > 72% reduction in GHG emissions vs fossil-derived methanol
- IC^{3}M results in 21% lower GHG emissions than separate capture and conversion (SC3M)
- Further GHG reductions via improvement in the catalyst performance

Jiang et al. In Preparation

Composite materials may be economical large volume CO_2 sinks.

- Wood flour (~50 wt.% filler) and HDPE plastic
- US Market: 3.55 billion linear board feet, $2.8 billion USD per year
- Storing 5 wt. % CO_2 in decking could sequester 250,000 tonnes per year (emissions of 54,000 cars)
- *Susceptible to rot and UV damage, 20-year lifespan

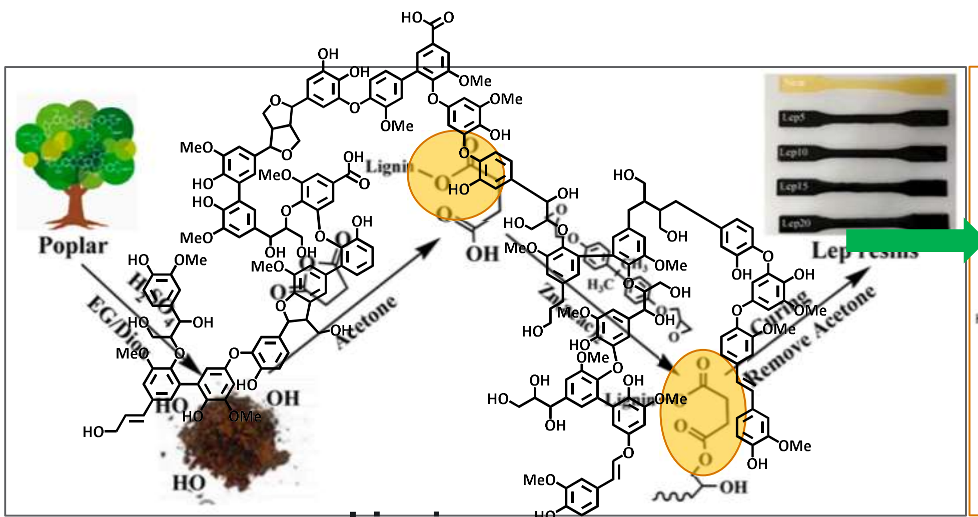
Goal: Replacing wood fluor with abundant, cheap and highly chemically/UV durable biopolymers. Their use in composites also provides CO_2 emission avoidance.

- Lignin: complex organic polymer that forms structural materials in the support of plants.
- Lignite: combustible sedimentary rock formed from naturally compressed peat.

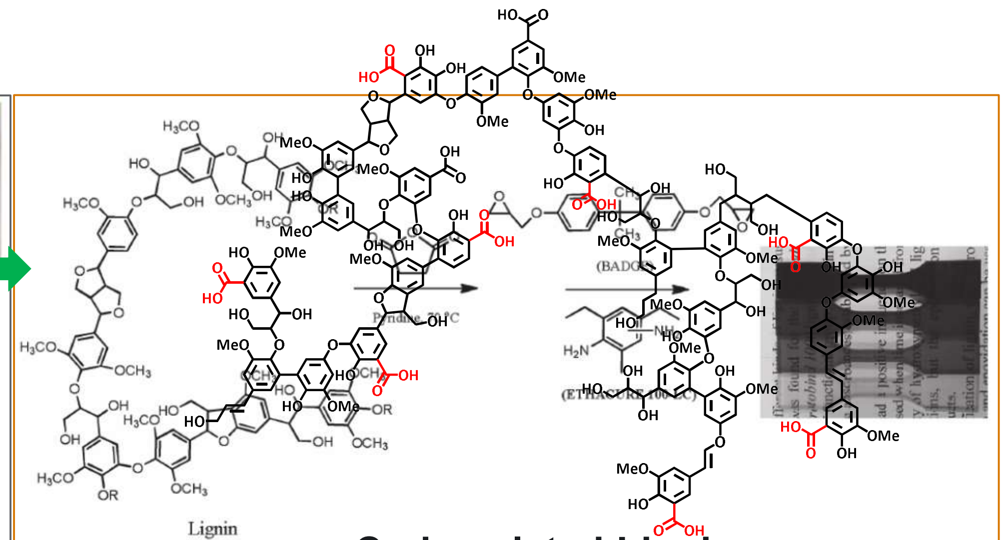
Lignin

Lignite

Lignin and lignite are strong, cheap, and chemically durable but they cannot bind well in polymer matrixes without chemical modification.



Lignin



Carboxylated Lignin

- Maleic Anhydride Polyethylene (MAPE) is chemically grafted on phenolic hydroxyls
- Functionalization is susceptible to hydrolysis of C-O-C linkage

***How can we add CO_2 to the surface of these particles to act like MAPE while being a CO_2 sink ?**

Macromol. Mater. Eng. 2017, 302, 1700341

European Polymer Journal 150 (2021) 110389

Turning CO_2 Into the “Velcro” to Improve Binding with Polymer Matrixes via Reactive Carbon Capture

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Capture Solvent

HDPE

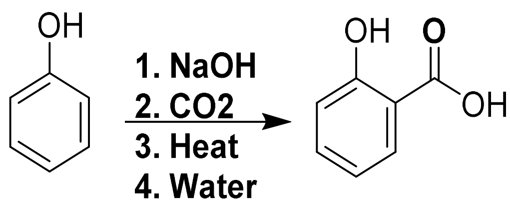
Lignin or Lignite + CO_2

Workup & solvent recovery

(CO_2LIG) Composite

How can we add CO_2 to polyphenolic polymers…?

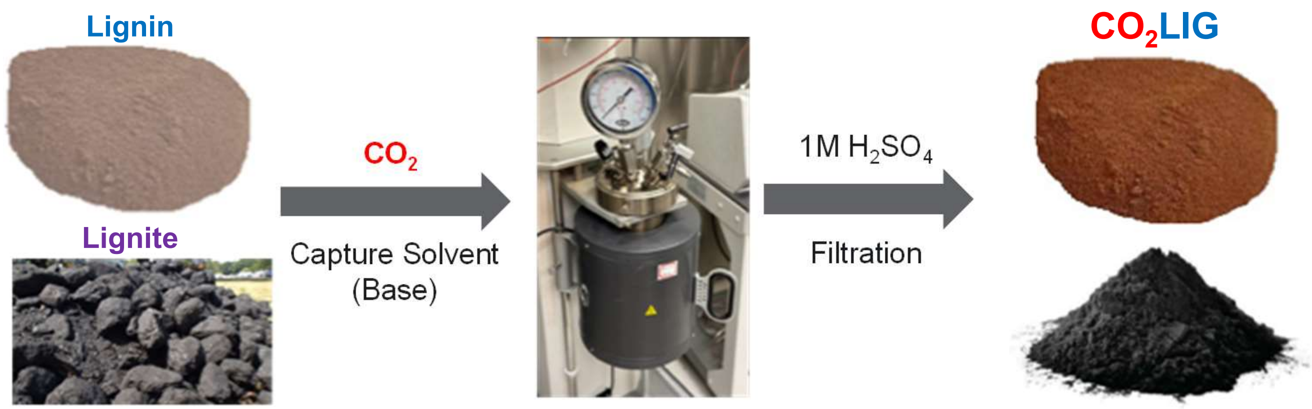
Kolbe-Schmidt Reaction

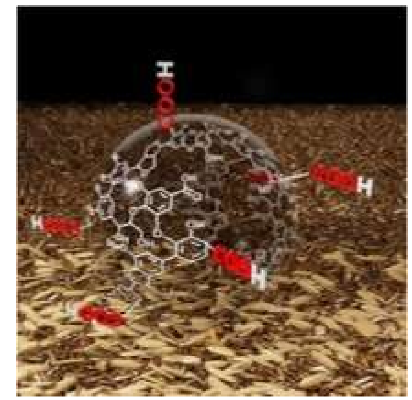


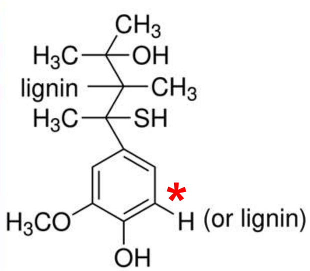
Production of Salicylic Acid for Aspirin

- Chemically durable (C-C bonded) composite fillers utilizing CO_2 in its entirety
- Can use any inorganic or strong organic base (capture solvent)

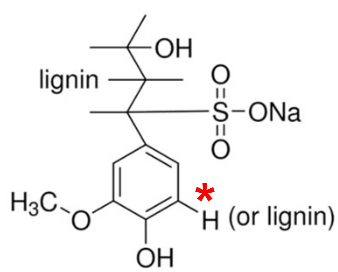
Carboxylating 200g batches of alkaline lignin, sodium lignosulfate,DEC25, Buelah Zap Lignite, and DEC26, Wyodak Sub-bituminous coal.



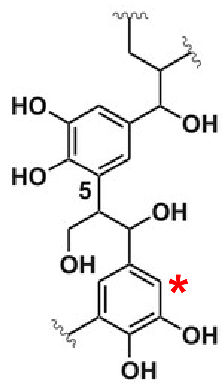




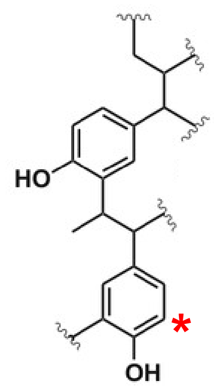
Lignin alkali



Sodium lignin sulfonate



Lignite



Sub-bituminous

Isolated yields

Lignin = 64-98%

Lignite = 39-65%

Manuscript in preparation.

In-situ FT-IR (Fourier Transform Infrared) to determine CO_2 loading, optimal reaction conditions and reaction rate.

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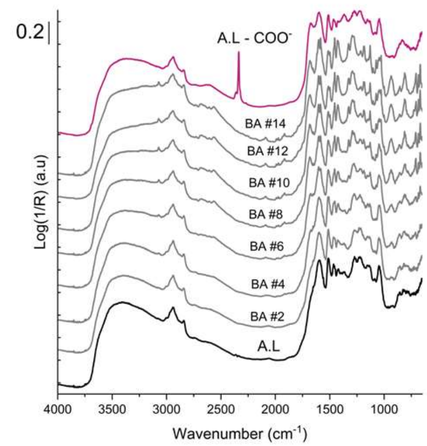
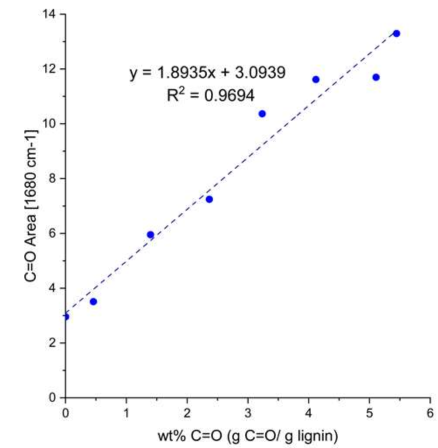
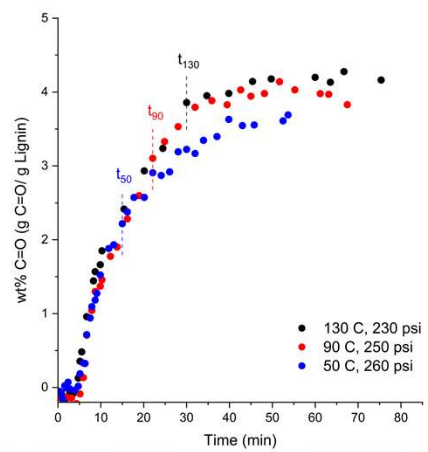
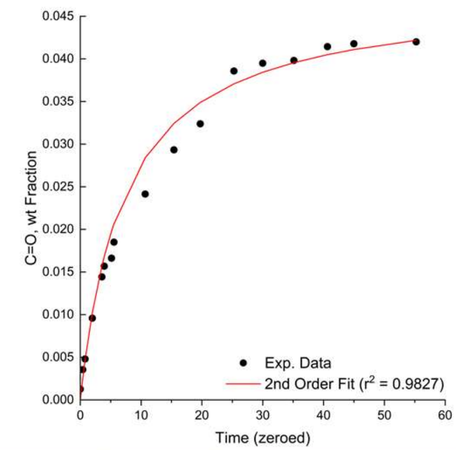
- Praying Mantis DRIFTS Cell:
  - Max temp ~ 910 °C (under vacuum)
  - Max Pressure ~ 1.5 Mpa (~215 PSI)
- Monitor carboxylic acid peak growth
- Built calibration standards
- CO_2 content in fillers ranges 2- 4.2 wt.%
- Operando kinetic measurements



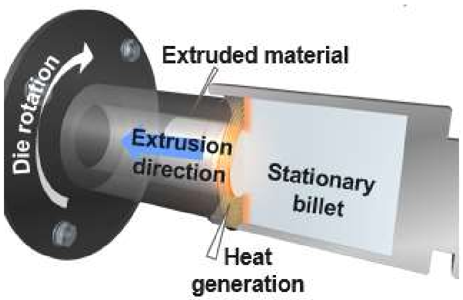


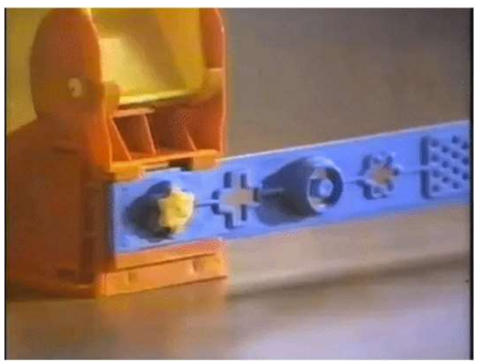




Manuscript in preparation.

Shear Assisted Processing and Extrusion (ShAPE) manufacturing of wires, bars, or ribbons for property testing.



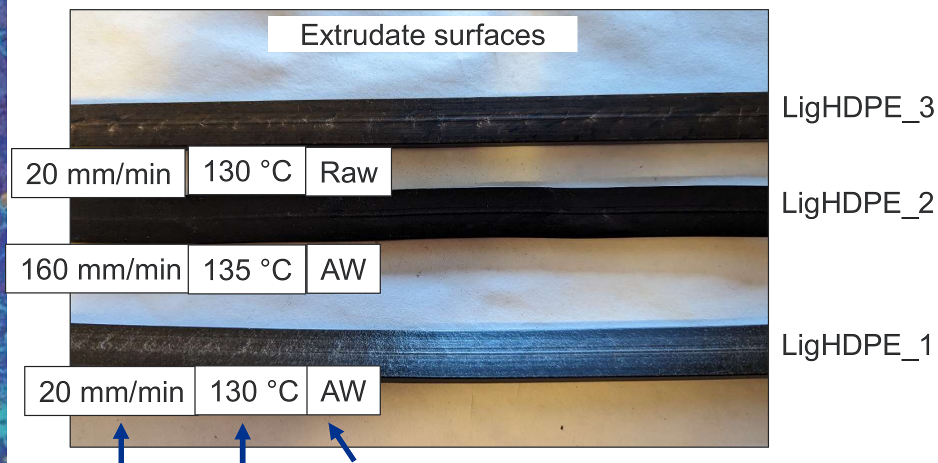


A. Reza holding an 80 wt.% filler ShAPE composite extrudate;
B. Tooling cavity designed for manufacturing composite 'bars';
C. Cold-pressed composite feedstock granules in ShAPE ring;
D. ShAPE polymer composite bars with no surface defects

- ShAPE enables 80 wt.% CO_2LIG filler content, vs 50% for conventional injection molding

Patent pending, Manuscript in preparation.

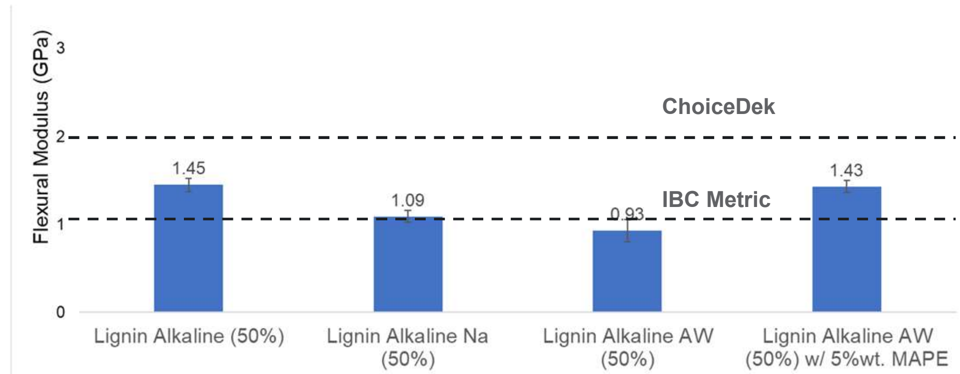
The Flexural Moduli of ShAPE Extruded Bars 80% Lignins / 20% wt.% HDPE are Above 2 GPa, Meeting International Building Code Requirements

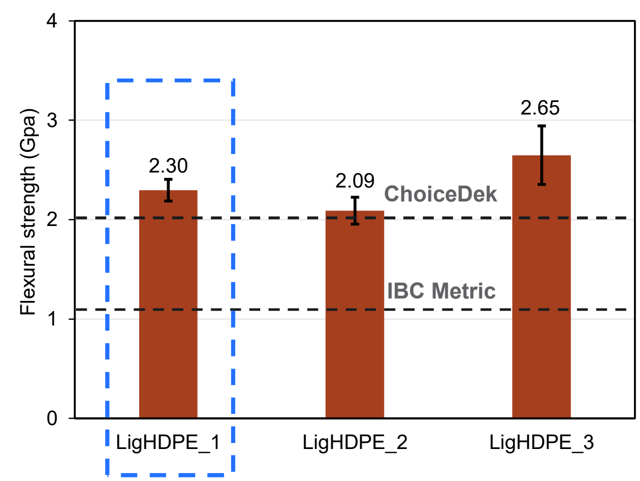


Feed rate
Temp

- AW: functionalized, acid washed
- Raw: non-functionalized (as received)

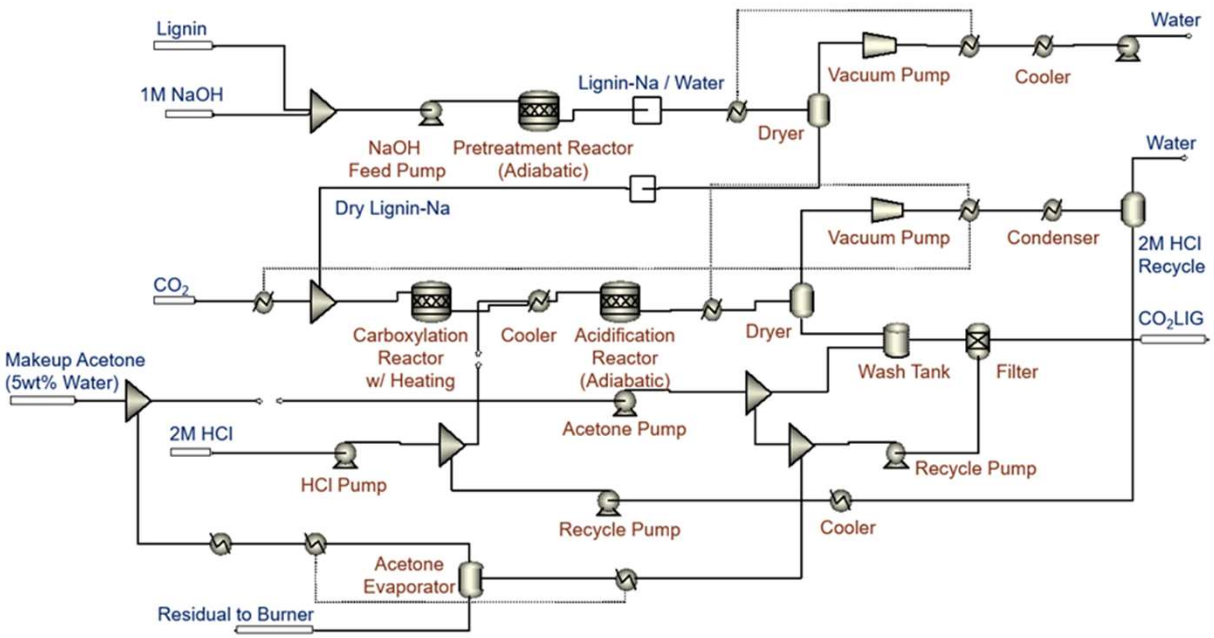
- Higher modulus was obtained for non-functionalized fillers (LigHDPE_1 vs. LigHDPE_3), and for low-speed extrusion (LigHDPE_1 vs. LigHDPE_2)





Patent pending, Manuscript in preparation.

TEA results based on real experimental data suggests that CO_2LIG can be produced at a cost lower than the HDPE ($1/kg)



Minimum selling price	($/kg)
Lignin	0.375
Chemicals	0.085
Utilities	0.028
By-product credits	-0.043
Capital depreciation	0.071
O&M	0.088
Return on Investment	0.106
Others (tax, etc.)	0.112
Total	**0.820**

- Projected selling price of CO_2LIG lignin fillers are $0.82/kg (linear board foot)

Manuscript in preparation.

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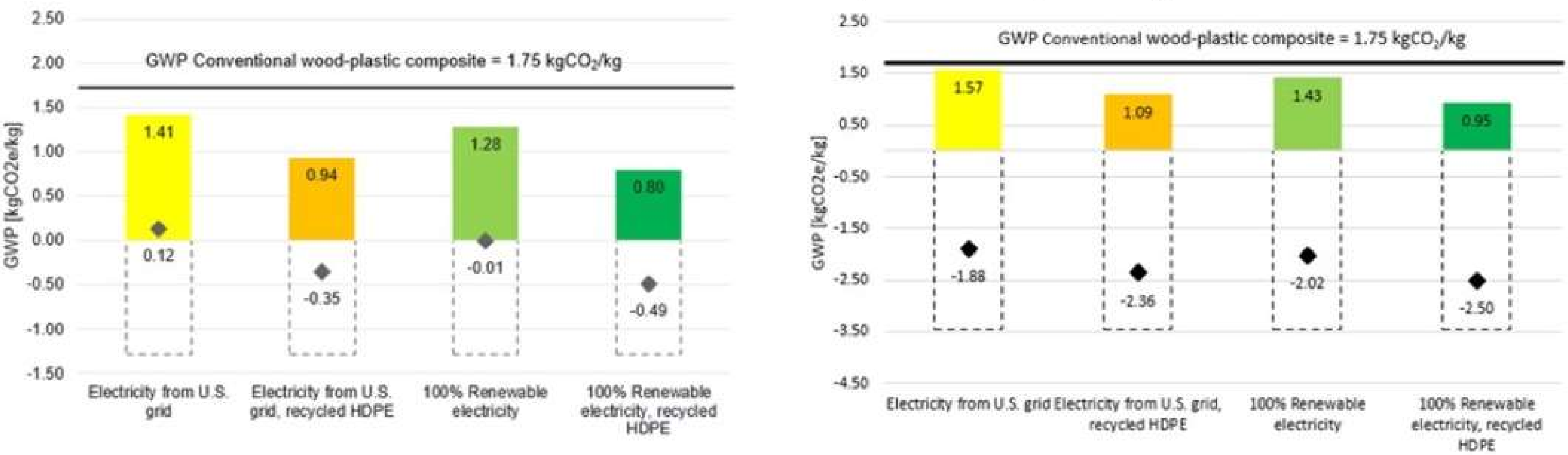
LCA for lignin composites suggests the global warming potential of CO_2LIG is much lower than that of conventional wood-plastic composites.

(a) Results include the CO_2 stored into CO_2LIG only

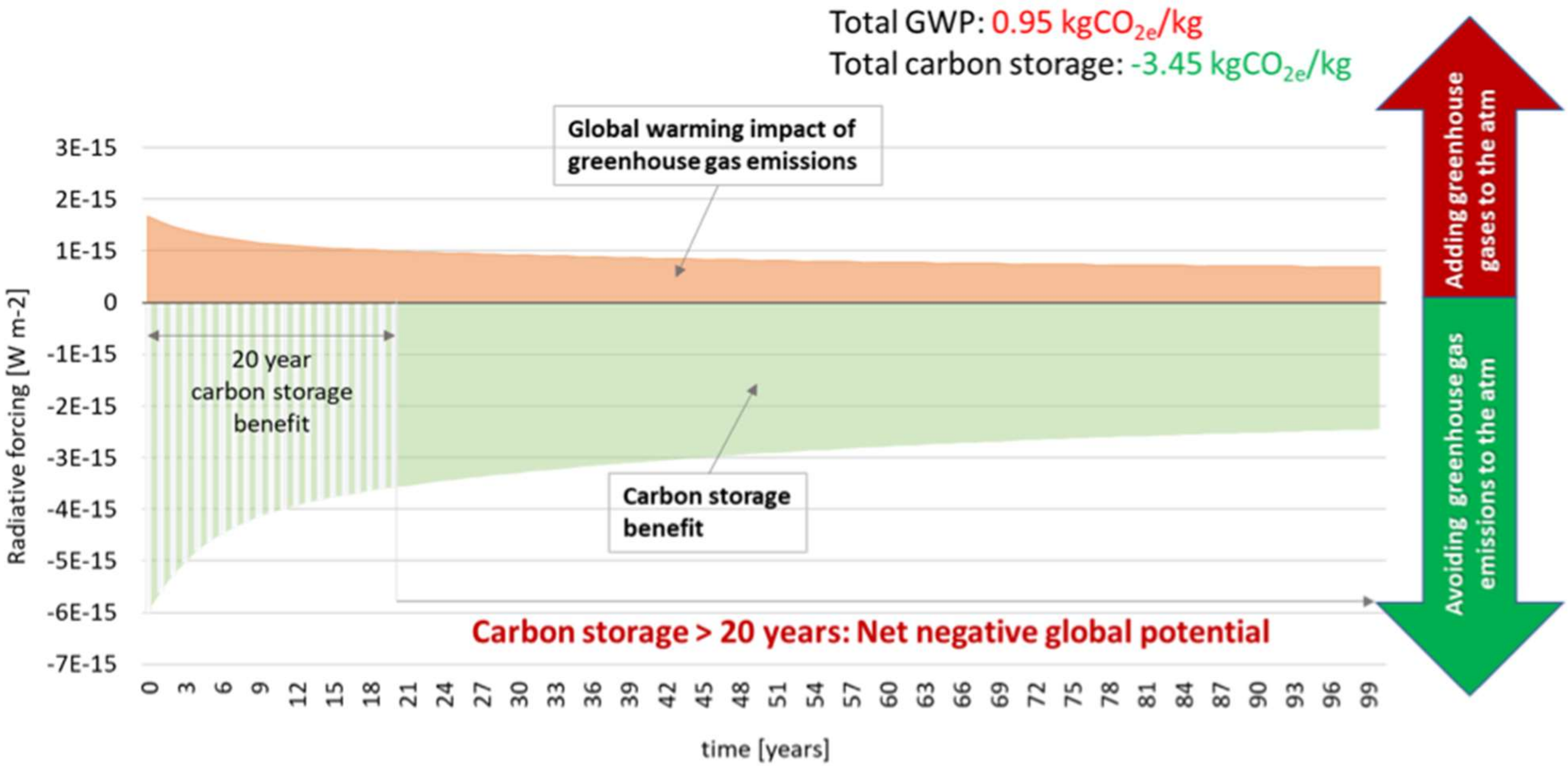
(b) Results include the CO_2 stored into CO_2LIG and the additional CO_2 sequestered and stored in the ground



- GWPs of the CO_2LIG-plastic composite panel are lower in all the scenarios, with an overall reduction between 18 and 54% (carbon storage benefits excluded).

Manuscript in preparation.

*Temporal radiative forcing analysis CO_2 on CO_2LIG-plastic composite (lifetime of the product) needed to achieve carbon neutrality.



*100% renewable electricity, recycled HDPE with benefits from subsurface CO_2 storage

Manuscript in preparation.

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Reactive CDR can reduce costs and energy demand for CO_2-derived fuels, chemicals and CO_2-negative composites.

IC^{3}M thermocatalytic reduction = Cheaper, more efficient fuels and chemicals

- Solvent drives condensed-phase catalytic hydrogenations
- Different mechanisms, free energy landscapes and chemical equilibria to exploit
- Minimizes enthalpy of sorbent regeneration and CO_2 compression energy
- 72% reduction in GHG emissions vs fossil-derived methanol
- 21% lower GHG emissions than separate capture and conversion (SC^{3}M)

IC^{3}M CO_2LIG = Economically profitable CO_2-negative building materials

- Solvent's Bronsted basicity captures and promotes Kolbe-Schmidt reactions
- 2-5 wt. % CO_2 fixation on lignin and lignite ~ 80 ^oC Up to 94% and 65% isolated yields respectively
- Lignin (50-70 wt.% filler) and Lignite composites (80 wt.% filler) using shear assisted processing and extrusion
- Manufactured composites meet IBC metrics for flooring or decking
- Carbon neutrality is achieved after 20 years of storage, and > 20 years results in a net negative GWP

Acknowledgements

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PNNL-FWP-80562

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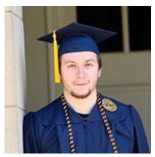


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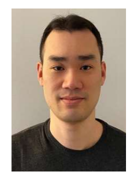
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Md. Reza-E-Rabby


Keerti Kaapagantula


Deepika Malhotra


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Aditya Nittala


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