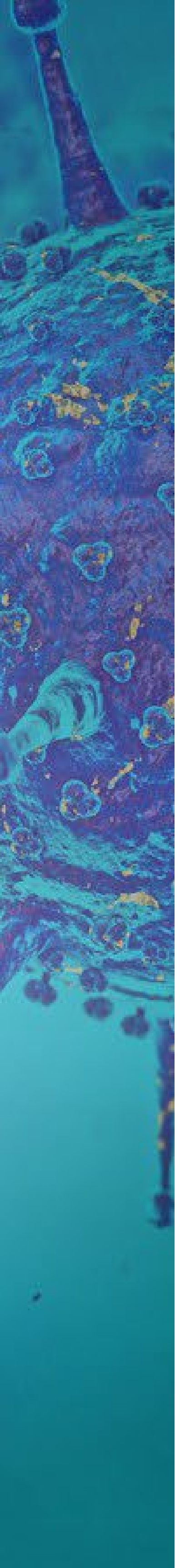


Pacific Northwest
NATIONAL LABORATORY

Integrated Capture and Conversion of CO_2 into Materials (IC^3M): Pathways for Producing CO_2-Negative Building Composites

David J. Heldebrant

Laboratory Fellow

Fellow of the American Chemical Society

U.S. DEPARTMENT OF ENERGY BATTELLE

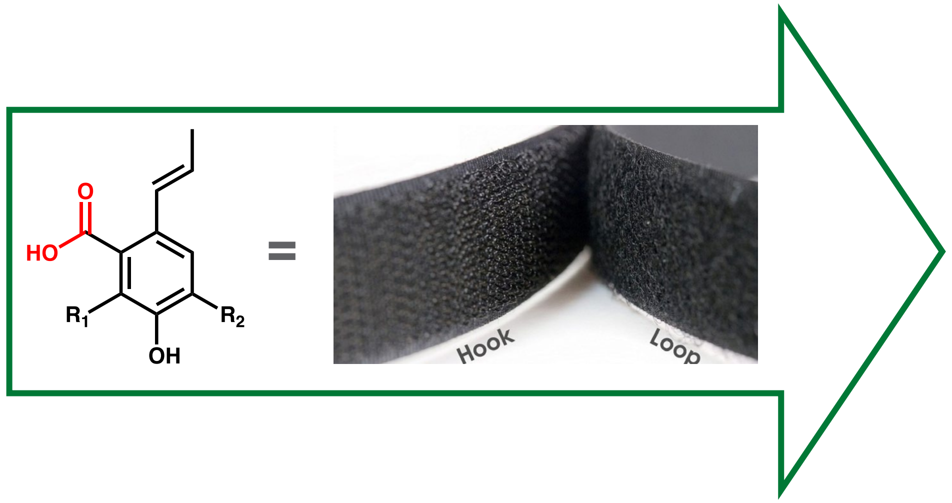
PNNL is operated by Battelle for the U.S. Department of Energy

Project Overview

Taking waste and making them economical large volume CO_2 sinks.

Recycled HDPE

Lignin or Lignite + CO_2



CO_2LIG

36-months

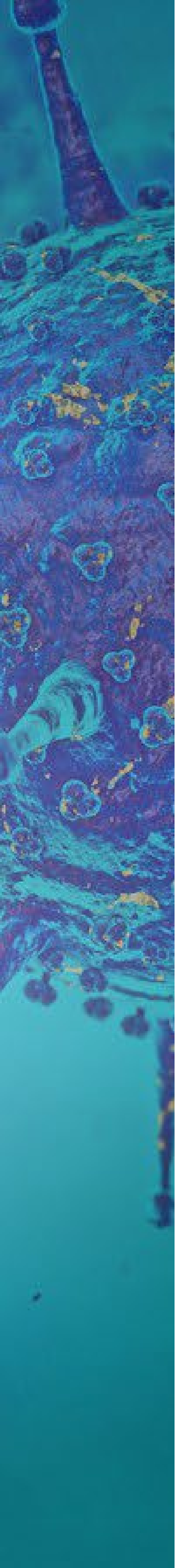
- **BP1 09/01/2021-09/30/2022**
- **BP2 10/1/2022 - 09/30/2023**
- **BP3 10/1/2023 - 09/30/2024**

- **DOE: $2.7M in Federal funds**
- **(FY1 $841K, FY2 $980K, FY3 $885K)**

Cost Share: $540K, SoCalGas

U.S. DEPARTMENT OF ENERGY
Fossil Energy and Carbon Management

SoCalGas



Project Structure

PNNL
PM/Co-PI:
Satish K. Nune

PM: Sai Gollakota

Flavio da Cruz

Ethan Simonoff

Siari Sosa

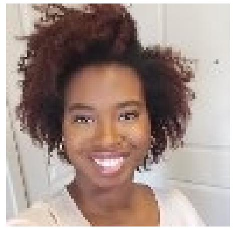
Materials

John Linehan

Nick Nelson

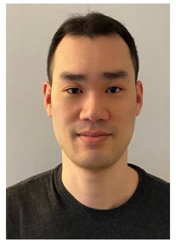
Raul Aranzazu

Operando Spectroscopy Catalysis & Kinetics



Jaelynne King

Katarzyna Grubel



Wontae Joo

Composites & Solvents

Md. Reza-E-Rabby

Keerti Kaapagantula

Jose Ramos

Aditya Nittala

Yelin Ni

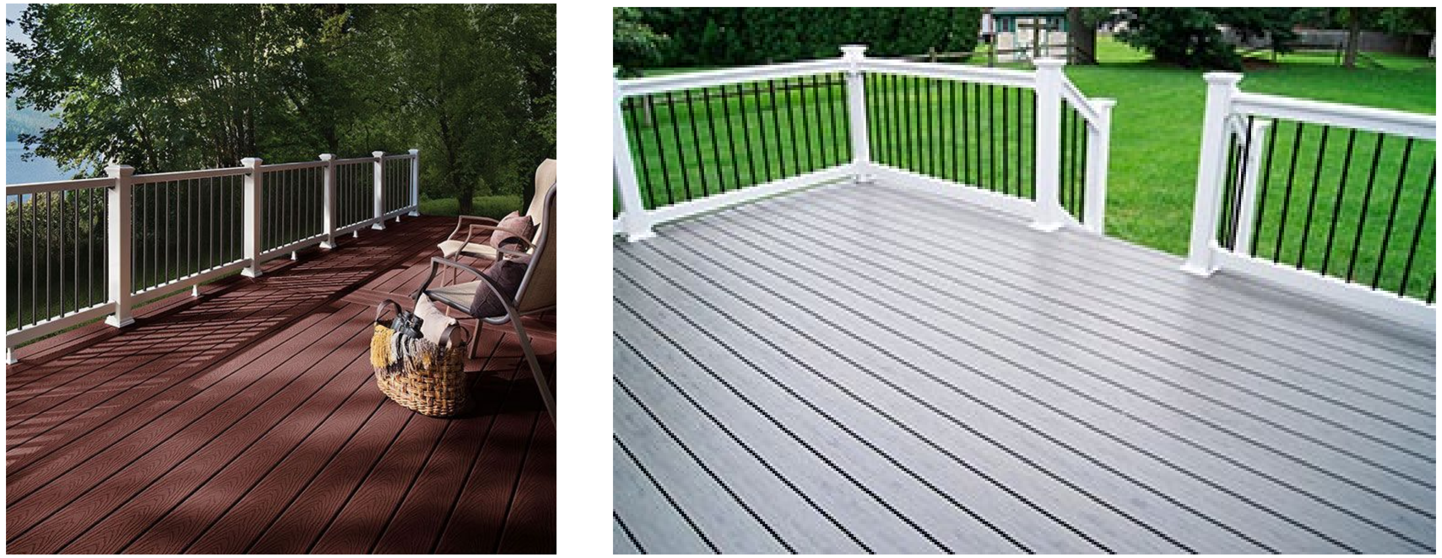
TEA/LCA

Yuan Jiang

Francesca Pierobon

The Vision: CO_2-Negative Building Composites

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.

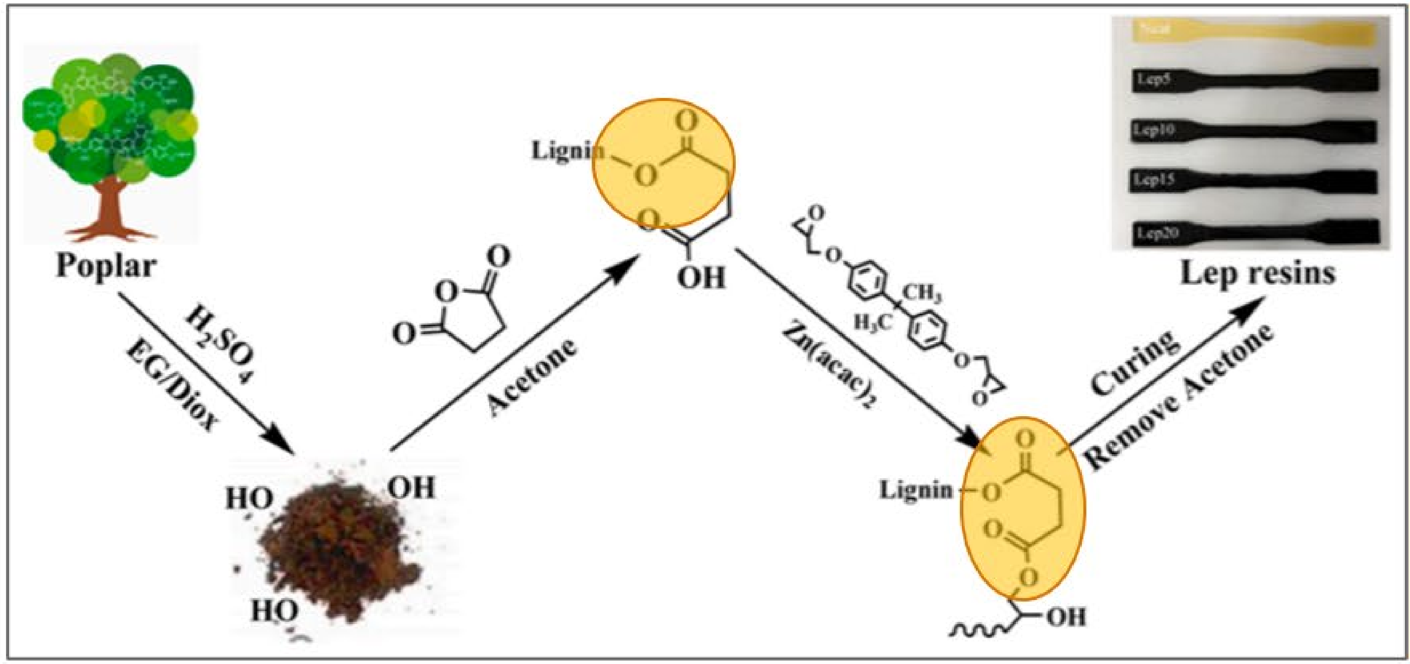
- Lignite: combustible sedimentary rock formed from naturally compressed peat.

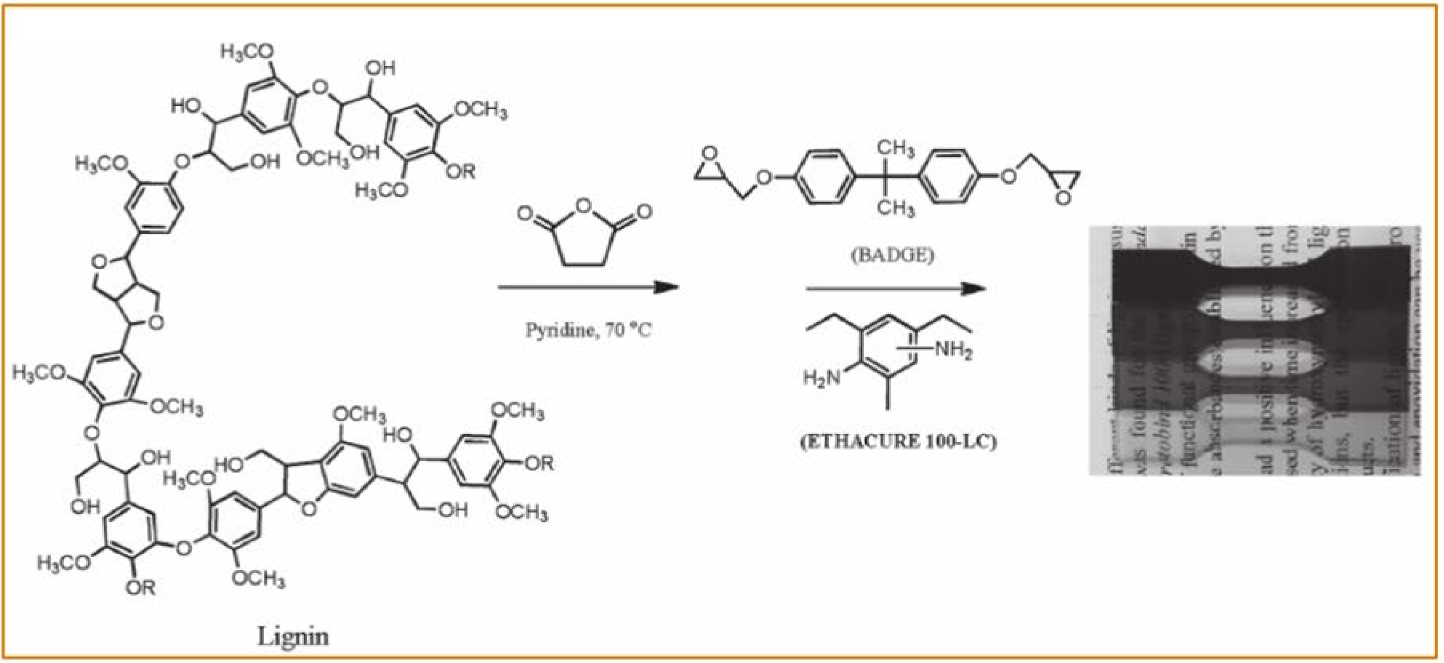
Lignin

Lignite

Producing Lignin and Lignite Composites

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





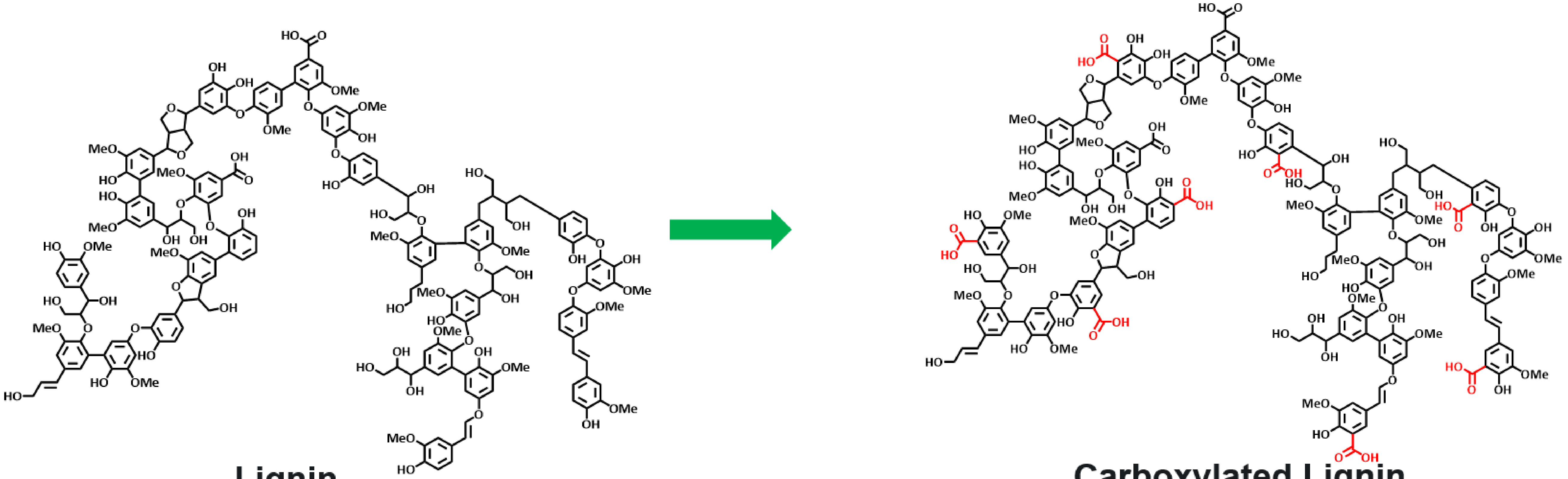
- Maleic Anhydride Polyethylene (MAPE) is chemically grafted on phenolic hydroxyls
- Functionalization is susceptible to hydrolysis of C-O-C linkage

Macromol. Mater. Eng. 2017, 302, 1700341

European Polymer Journal 150 (2021) 110389

Producing Lignin and Lignite Composites

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

***We add CO_2 to the surface of these particles to act like MAPE while being a CO_2 sink.**

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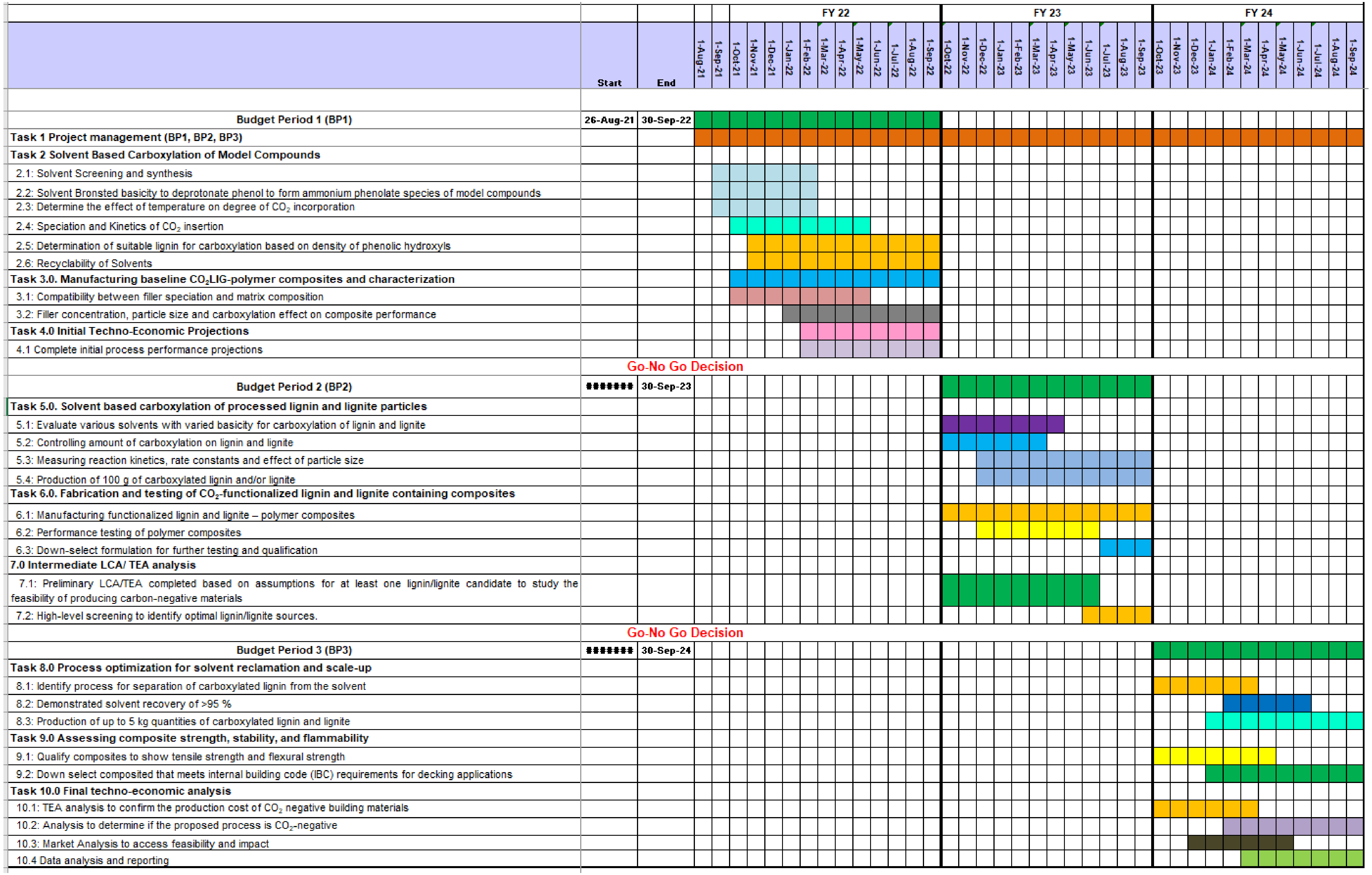
European Polymer Journal 150 (2021) 110389

Project Schedule: in BP3 10/01/2023 – 09/30/2024.



					FY 22												FY 23												FY 24											
	Start	End	1-Aug-21	1-Sep-21	1-Oct-21	1-Nov-21	1-Dec-21	1-Jan-22	1-Feb-22	1-Mar-22	1-Apr-22	1-May-22	1-Jun-22	1-Jul-22	1-Aug-22	1-Sep-22	1-Oct-22	1-Nov-22	1-Dec-22	1-Jan-23	1-Feb-23	1-Mar-23	1-Apr-23	1-May-23	1-Jun-23	1-Jul-23	1-Aug-23	1-Sep-23	1-Oct-23	1-Nov-23	1-Dec-23	1-Jan-24	1-Feb-24	1-Mar-24	1-Apr-24	1-May-24	1-Jun-24	1-Jul-24	1-Aug-24	1-Sep-24
Budget Period 1 (BP1)	26-Aug-21	30-Sep-22	■	■	■	■	■	■	■	■	■	■	■	■	■	■																								
Task 1 Project management (BP1, BP2, BP3)			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Task 2 Solvent Based Carboxylation of Model Compounds																																								
2.1: Solvent Screening and synthesis				■	■	■	■	■	■																															
2.2: Solvent Bronsted basicity to deprotonate phenol to form ammonium phenolate species of model compounds				■	■	■	■	■	■																															
2.3: Determine the effect of temperature on degree of CO_2 incorporation				■	■	■	■	■	■																															
2.4: Speciation and Kinetics of CO_2 insertion					■	■	■	■	■	■	■	■																												
2.5: Determination of suitable lignin for carboxylation based on density of phenolic hydroxyls						■	■	■	■	■	■	■	■	■	■	■																								
2.6: Recyclability of Solvents						■	■	■	■	■	■	■	■	■	■	■																								
Task 3.0. Manufacturing baseline CO_2LIG-polymer composites and characterization					■	■	■	■	■	■	■	■	■	■	■	■																								
3.1: Compatibility between filler speciation and matrix composition					■	■	■	■	■	■	■	■																												
3.2: Filler concentration, particle size and carboxylation effect on composite performance								■	■	■	■	■	■	■	■	■																								
Task 4.0 Initial Techno-Economic Projections									■	■	■	■	■	■	■	■																								
4.1 Complete initial process performance projections									■	■	■	■	■	■	■	■																								
	Go-No Go Decision																																							
Budget Period 2 (BP2)	#######	30-Sep-23															■	■	■	■	■	■	■	■	■	■	■	■												
Task 5.0. Solvent based carboxylation of processed lignin and lignite particles																																								
5.1: Evaluate various solvents with varied basicity for carboxylation of lignin and lignite																	■	■	■	■	■	■	■																	
5.2: Controlling amount of carboxylation on lignin and lignite																	■	■	■	■	■	■																		
5.3: Measuring reaction kinetics, rate constants and effect of particle size																			■	■	■	■	■	■	■	■	■	■												
5.4: Production of 100 g of carboxylated lignin and/or lignite																			■	■	■	■	■	■	■	■	■	■												
Task 6.0. Fabrication and testing of CO_2-functionalized lignin and lignite containing composites																																								
6.1: Manufacturing functionalized lignin and lignite – polymer composites																	■	■	■	■	■	■	■	■	■	■	■	■												
6.2: Performance testing of polymer composites																			■	■	■	■	■	■	■															
6.3: Down-select formulation for further testing and qualification																										■	■	■												
7.0 Intermediate LCA/ TEA analysis																																								
7.1: Preliminary LCA/TEA completed based on assumptions for at least one lignin/lignite candidate to study the feasibility of producing carbon-negative materials																	■	■	■	■	■	■	■	■	■															
7.2: High-level screening to identify optimal lignin/lignite sources.																									■	■	■	■												
	Go-No Go Decision																																							
Budget Period 3 (BP3)	#######	30-Sep-24																											■	■	■	■	■	■	■	■	■	■	■	■
Task 8.0 Process optimization for solvent reclamation and scale-up																																								
8.1: Identify process for separation of carboxylated lignin from the solvent																													■	■	■	■	■	■						
8.2: Demonstrated solvent recovery of >95 %																																	■	■	■	■	■			
8.3: Production of up to 5 kg quantities of carboxylated lignin and lignite																																■	■	■	■	■	■	■	■	■
Task 9.0 Assessing composite strength, stability, and flammability																																								
9.1: Qualify composites to show tensile strength and flexural strength																													■	■	■	■	■	■	■					
9.2: Down select composited that meets internal building code (IBC) requirements for decking applications																																■	■	■	■	■	■	■	■	■
Task 10.0 Final techno-economic analysis																																								
10.1: TEA analysis to confirm the production cost of CO_2 negative building materials																													■	■	■	■	■	■						
10.2: Analysis to determine if the proposed process is CO_2-negative																																	■	■	■	■	■	■	■	■
10.3: Market Analysis to access feasibility and impact																															■	■	■	■	■	■				
10.4 Data analysis and reporting																																		■	■	■	■	■	■	■

Project Major Tasks: BP3

Task 1.0 Project management

Task 8: Process optimization ~~for solvent reclamation~~* and scale-up

✓ Task 8.1 Identify process for separation of carboxylated lignin from the solvent

✓ Task 8.2: Demonstrated solvent recovery of >95 %*

✓ Task 8.3: Production of up to 5 kg quantities of carboxylated lignin and lignite

Task 9: Assessing composite strength, stability, and flammability

✓ Task 9.1: Qualify composites to show tensile strength and flexural strength

✓ Task 9.2: Down select composite that meets internal building code (IBC) requirements for decking applications

Task 10: Final techno-economic analysis

✓ Task 10.1: TEA analysis to confirm the production cost of CO_2 negative building materials

✓ Task 10.2: Analysis to determine if the proposed process is CO_2-negative

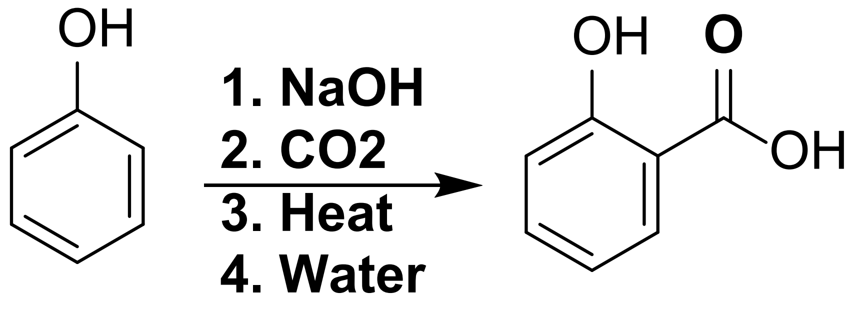
Task 10.3: Market Analysis to access feasibility and impact

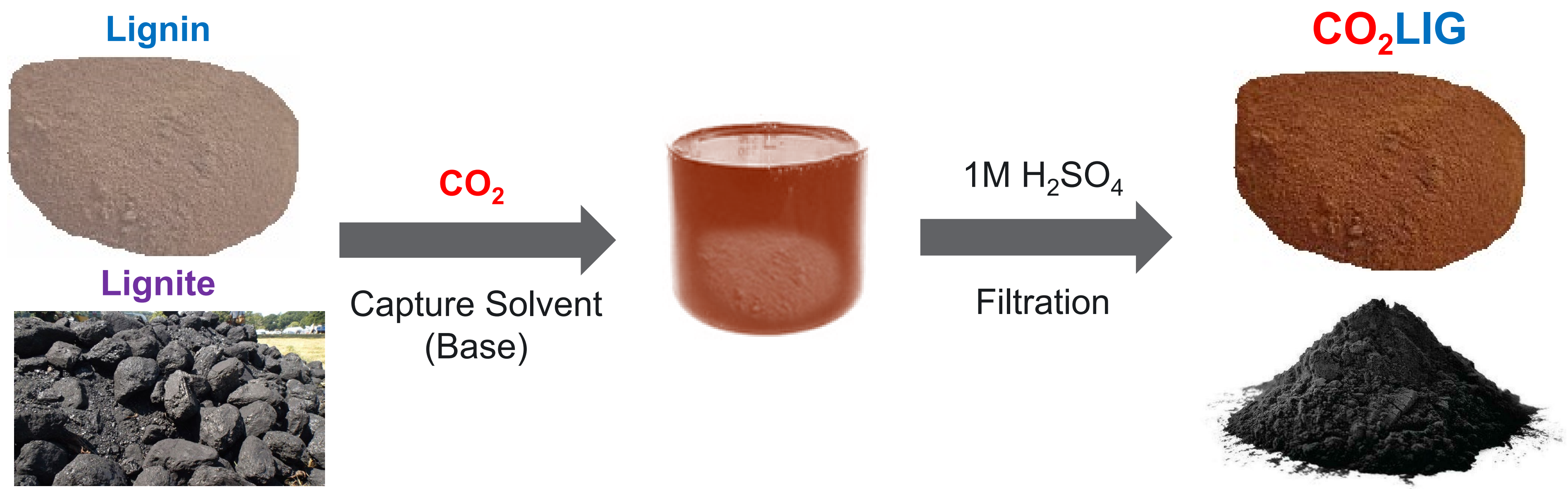
* CO_2BOLs did not have adequate basicity for carboxylation, therefore we used NaOH for carboxylation. We will optimize conditions for separating carboxylated lignin from reaction mixture at scale.

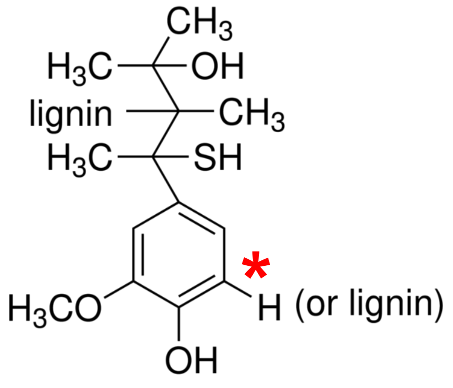
Step 1: Carboxylation of Fillers > 80 ˚C

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

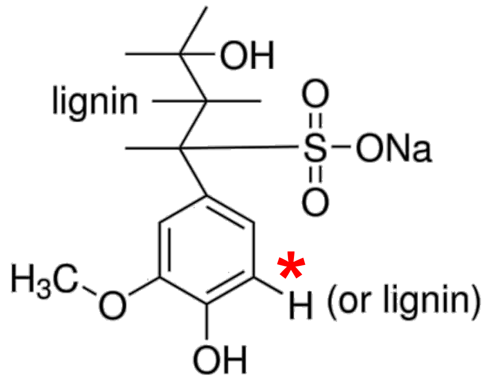
Kolbe-Schmidt Reaction



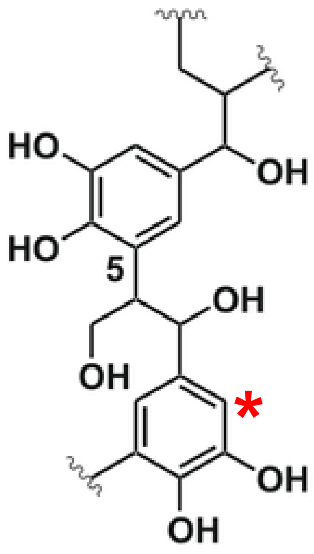




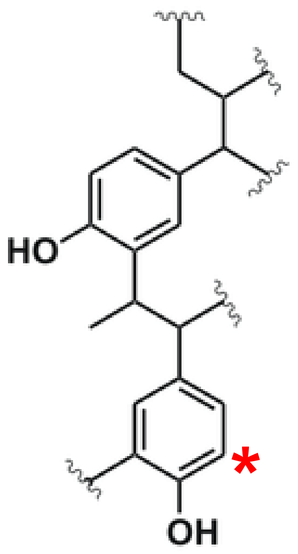
Lignin alkali



Sodium lignin sulfonate



Lignite

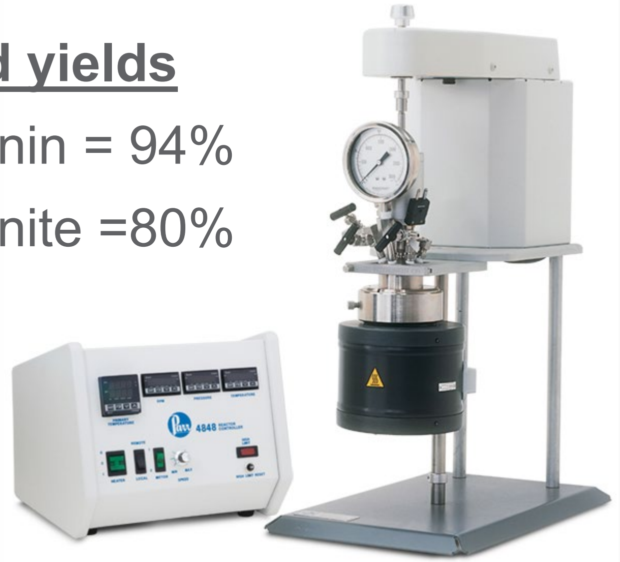


Sub-bituminous

__Isolated yields__

Lignin = 94%

Lignite =80%



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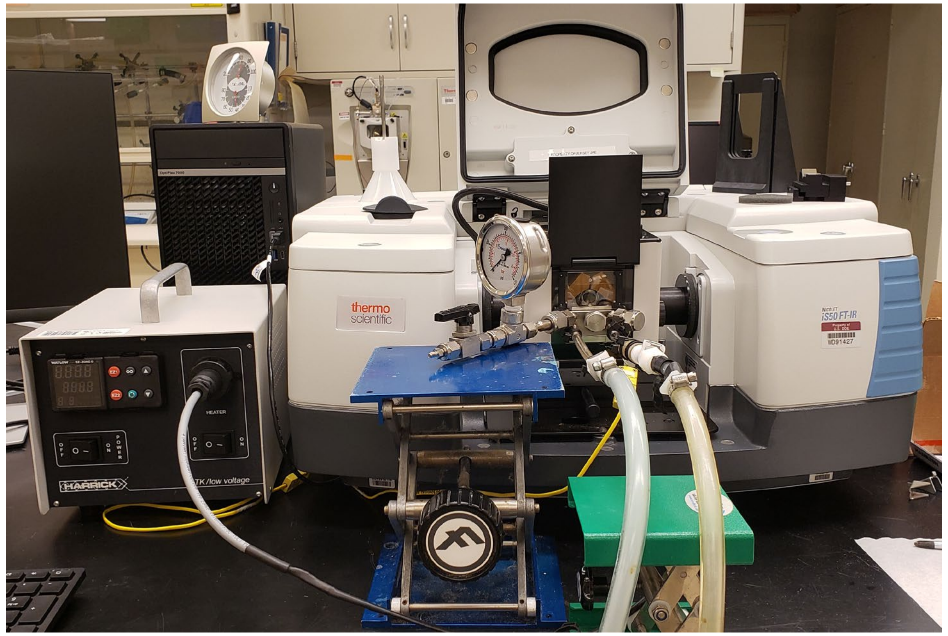
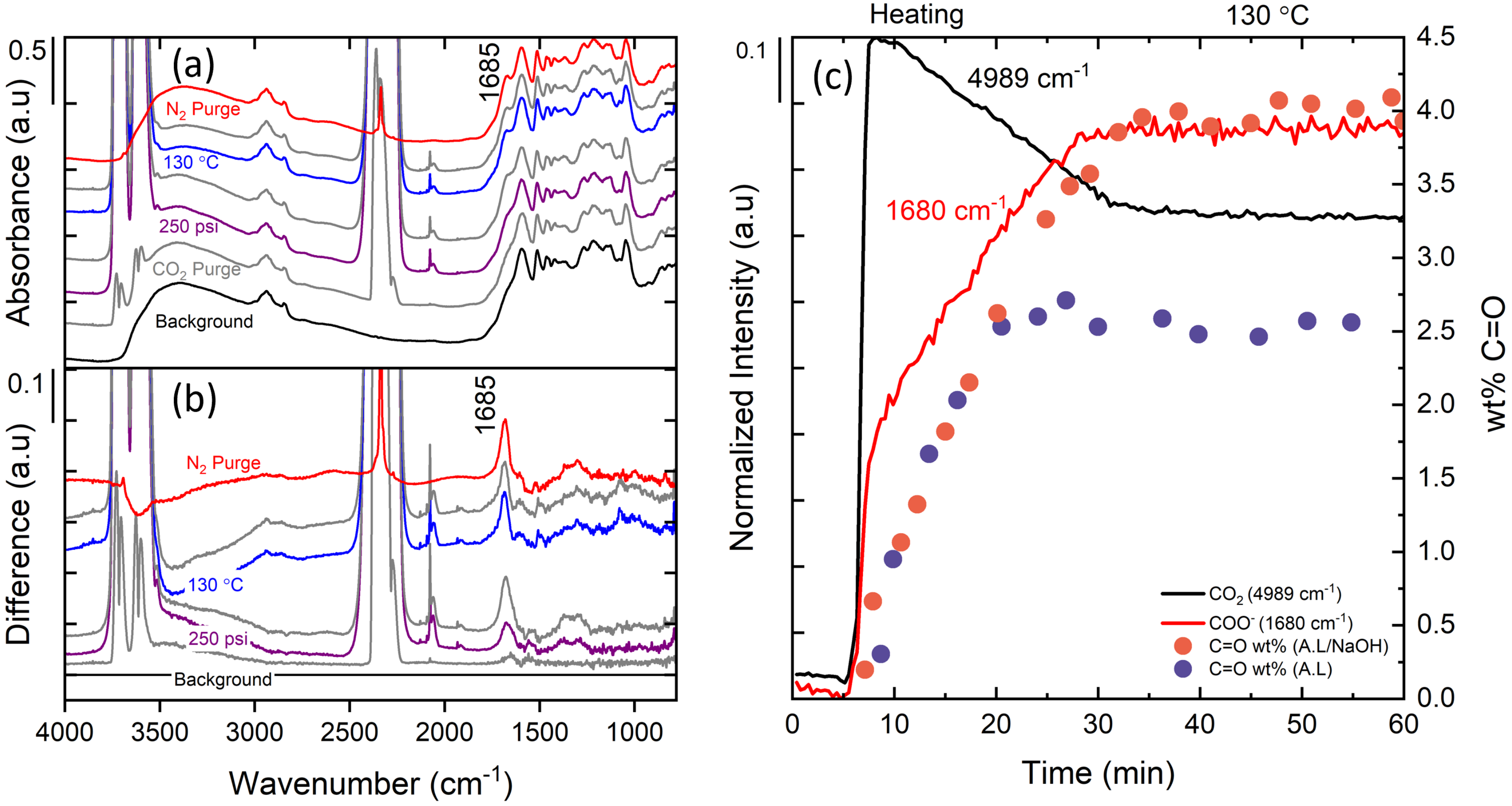
Step 2: Quantification of CO_2 loading and kinetics

In-situ FT-IR to determine CO_2 loading, optimal reaction conditions and reaction rate.

- Praying Mantis DRIFTS Cell:
  - Temp ~ 130 °C (vacuum)
  - Pressure ~ 1.5 Mpa (~250 PSI)
- Monitor carboxylate peak growth
- Built calibration standards
- CO_2 content ranges 2- 4.2 wt.%
- *Operando* kinetic measurements





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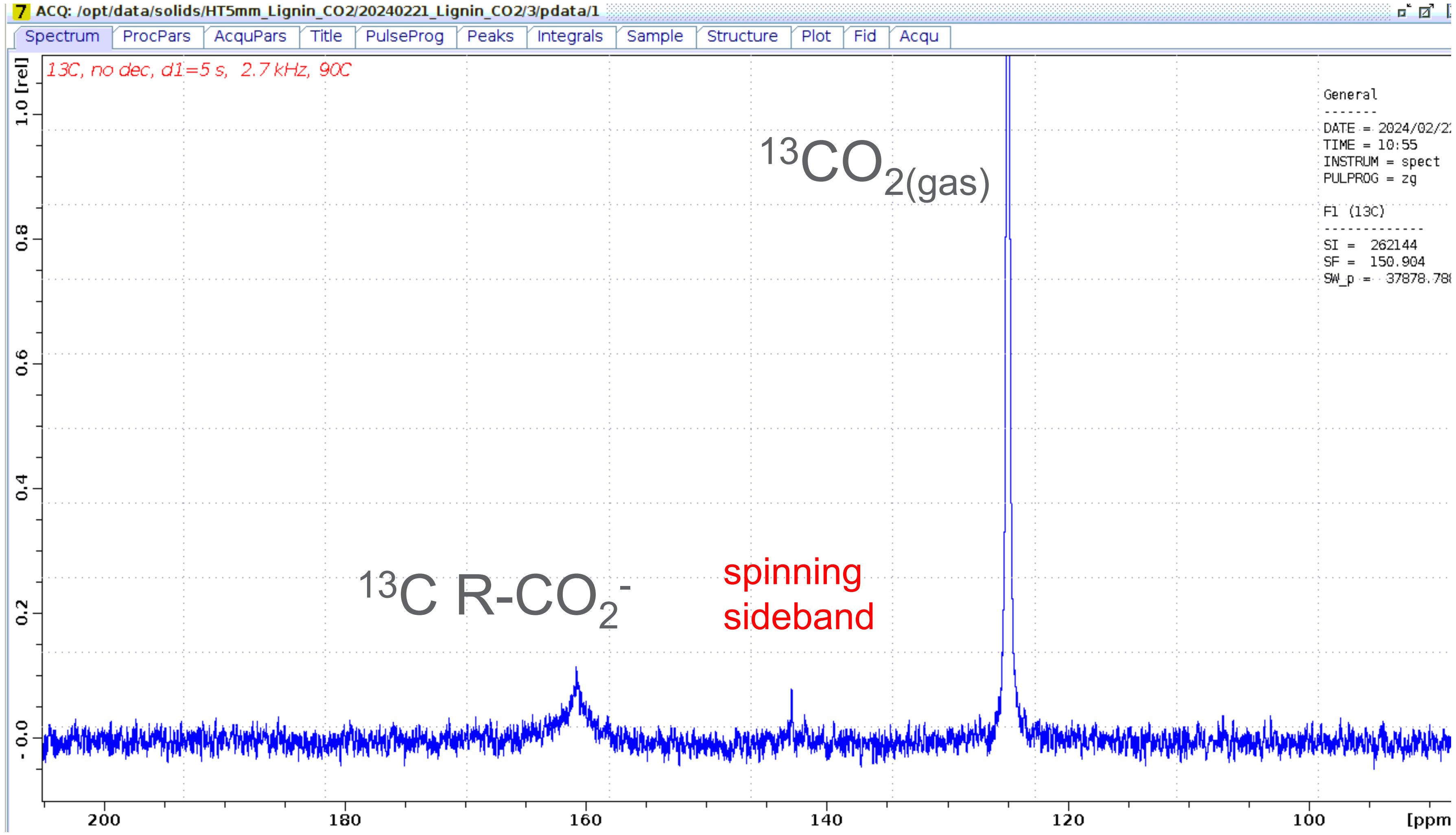
Step 2: Quantification of CO_2 loading and kinetics

NMR confirms production of the desired carboxylic acid.

$^{13}CO_2$ 300 psi, alkaline lignin, 90 ˚C

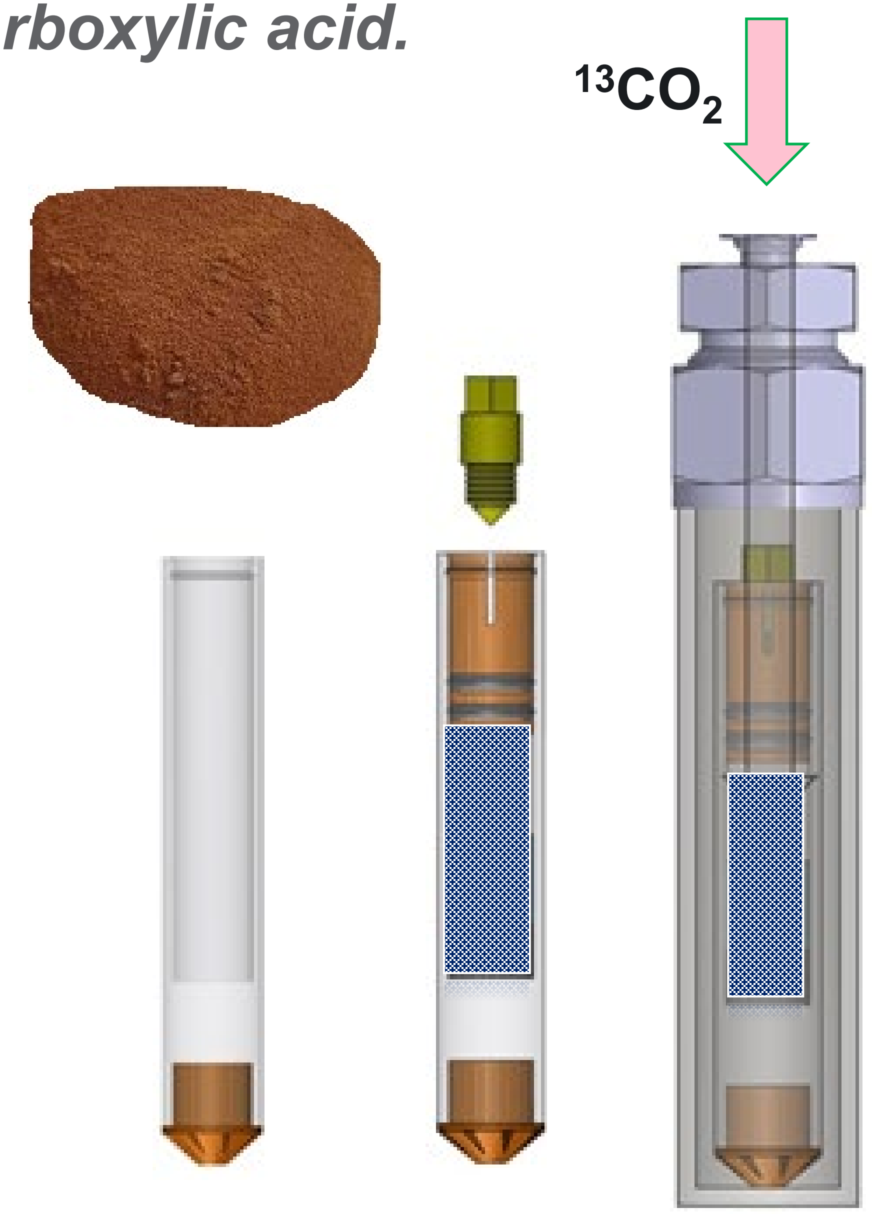


```
ACQ: /opt/data/solids/HT5mm_Lignin_CO2/20240221_Lignin_CO2/3/pdata/1
```

13C, no dec, d1=5 s, 2.7 kHz, 90C

```
General
-------
DATE = 2024/02/2
TIME = 10:55
INSTRUM = spect
PULPROG = zg

F1 (13C)
--------------
SI =  262144
SF =  150.904
SW_p =  37878.78
```



Fill Rotor with solid and/or liquid

Cap Rotor

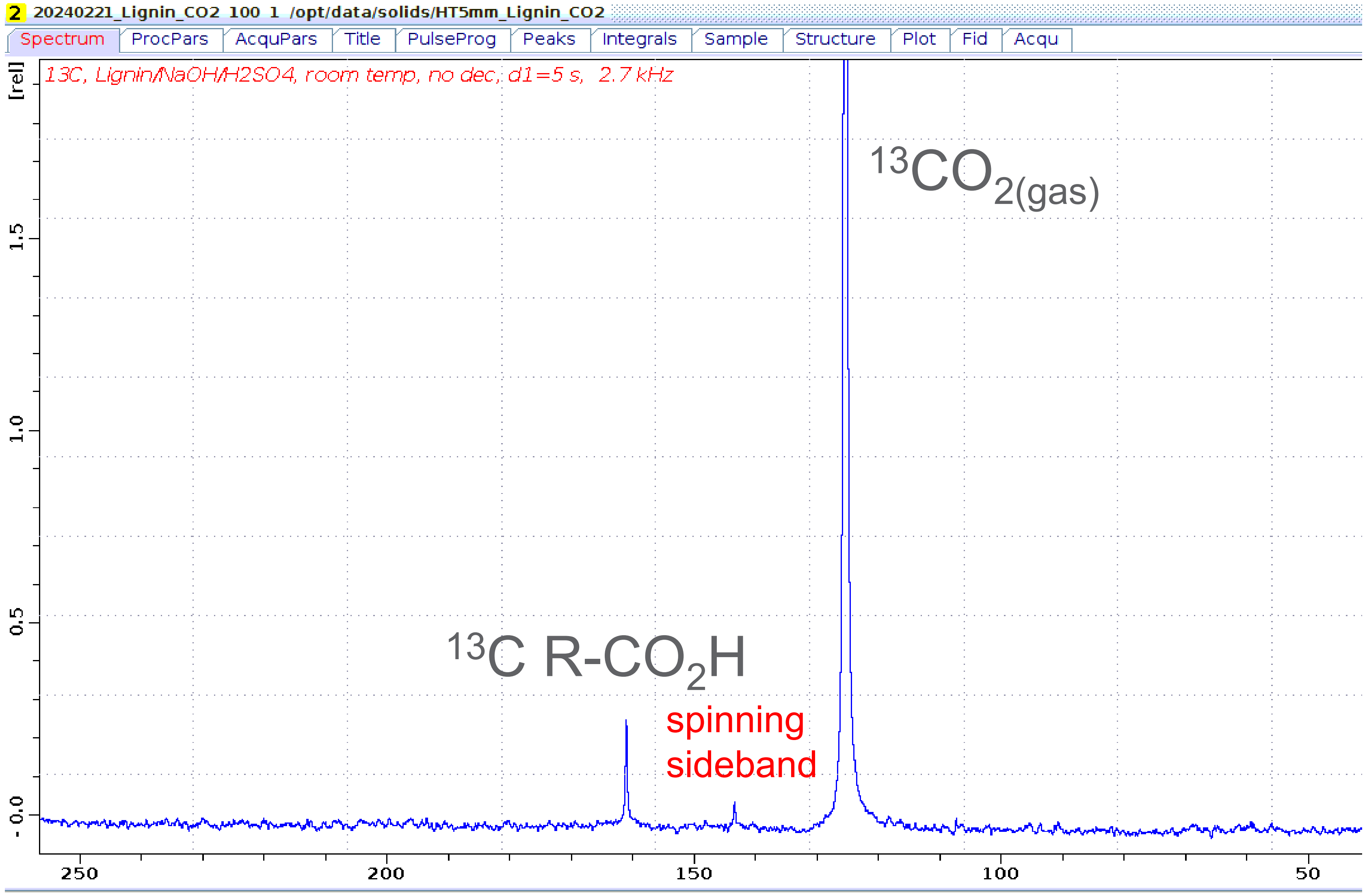
Add CO_2

**Lignin appears below the baseline since it is natural abundance and 1/10,000th scale*

Step 2: Quantification of CO_2 loading and kinetics

NMR confirms production of the desired carboxylic acid.

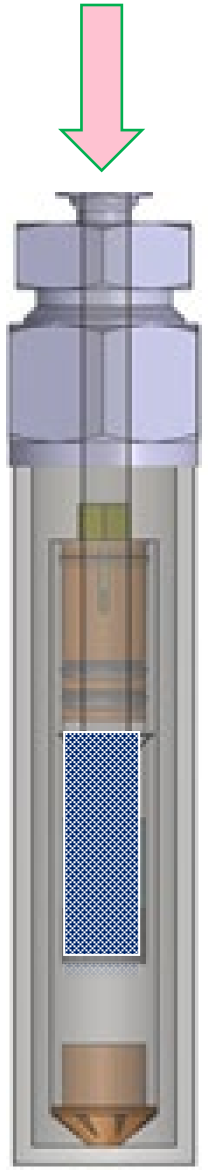
^{13}C-enriched CO_2 at 300 psi, alkaline lignin, 90 ˚C, *in-situ* acidification.



2 20240221_Lignin_CO2 100 1 /opt/data/solids/HT5mm_Lignin_CO2

13C, Lignin/NaOH/H2SO4, room temp, no dec, d1=5 s, 2.7 kHz

1M H_2SO_4

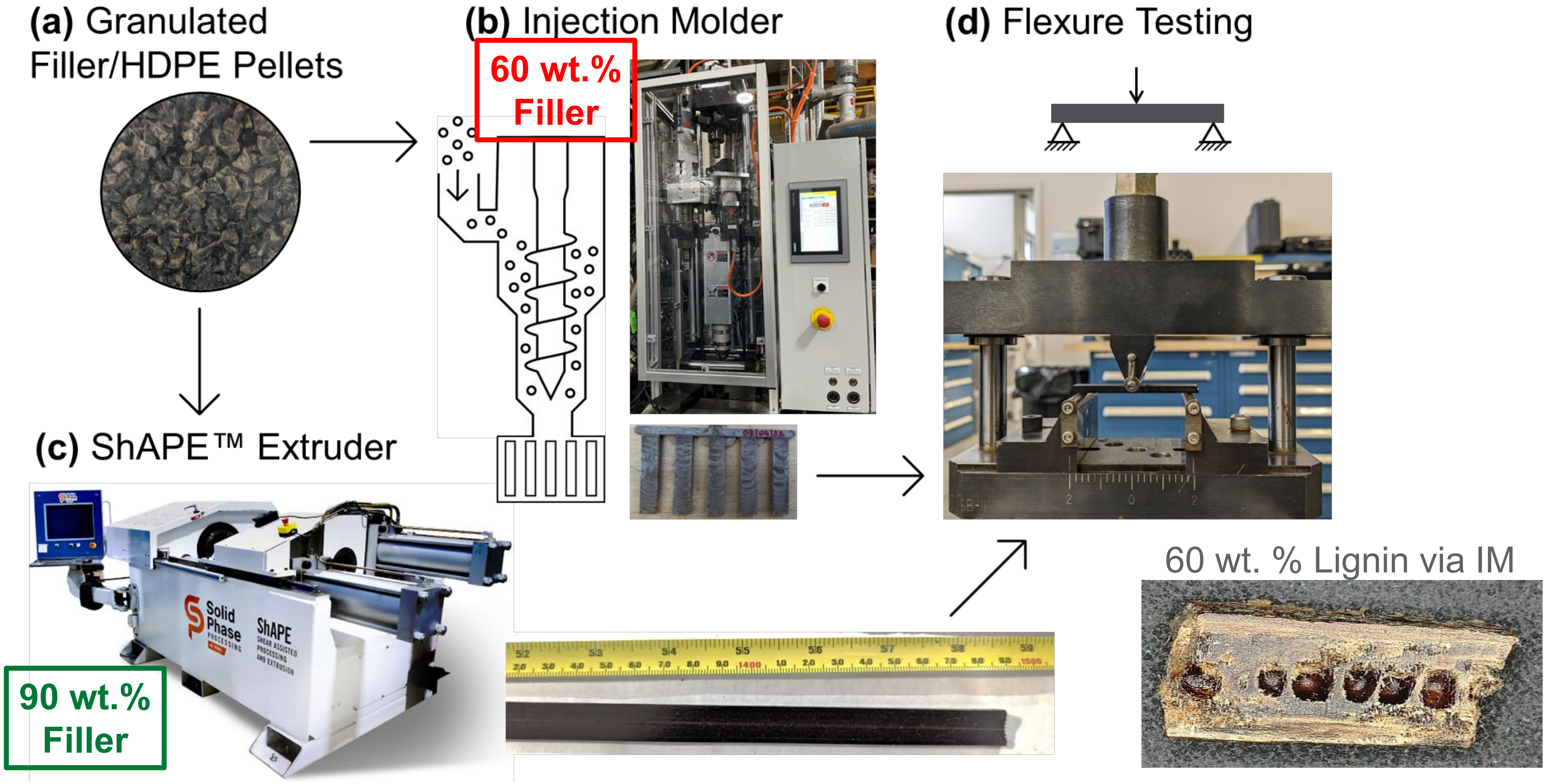


Addition of H_2SO_4 under pressure

**Peak retention confirms carboxylic acid and not bicarbonate or carbonate.*

Step 3: Composite Manufacturing and testing

Injection molding or friction extrusion produces composites with up to 60 and 90 wt.% filler respectively.



(a) Granulated Filler/HDPE Pellets

(b) Injection Molder

60 wt.% Filler

(c) ShAPE™ Extruder

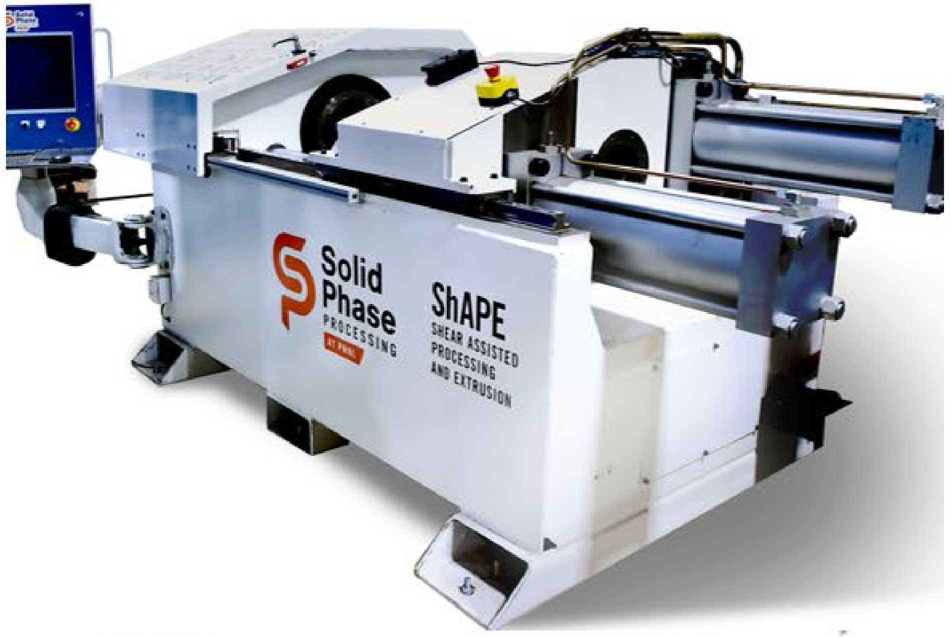
90 wt.% Filler

(d) Flexure Testing

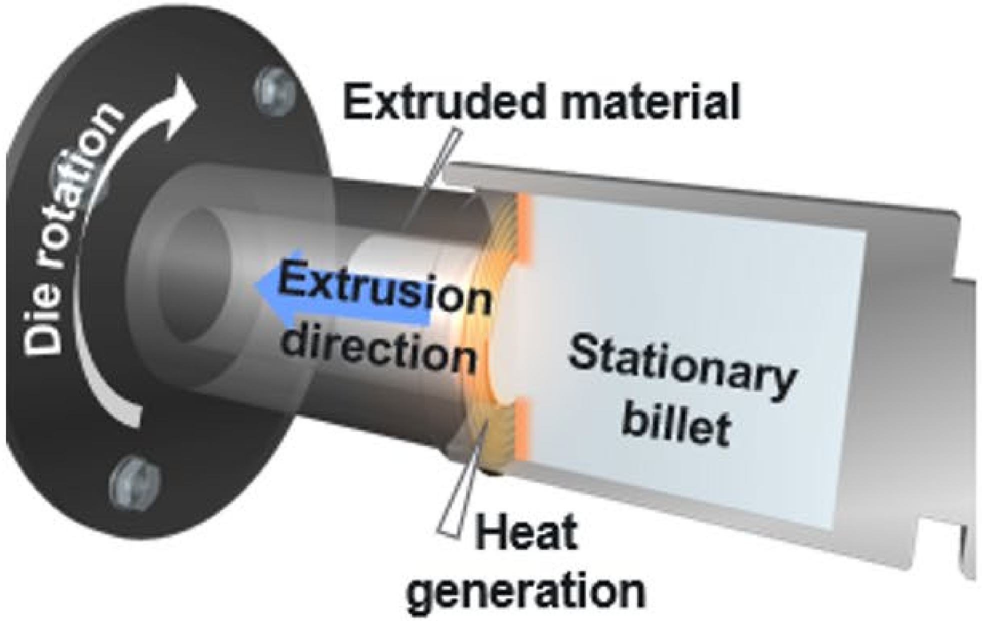
60 wt. % Lignin via IM

Step 3: ShAPE Friction Extrusion Manufacturing

Solid-Phase Processing enables production of composites with 80-90 wt.% filler.



- First-generation machine developed at PNNL
- Consolidated and extruded continuously without external heating
- Tool design and process conditions are key for manufacturing



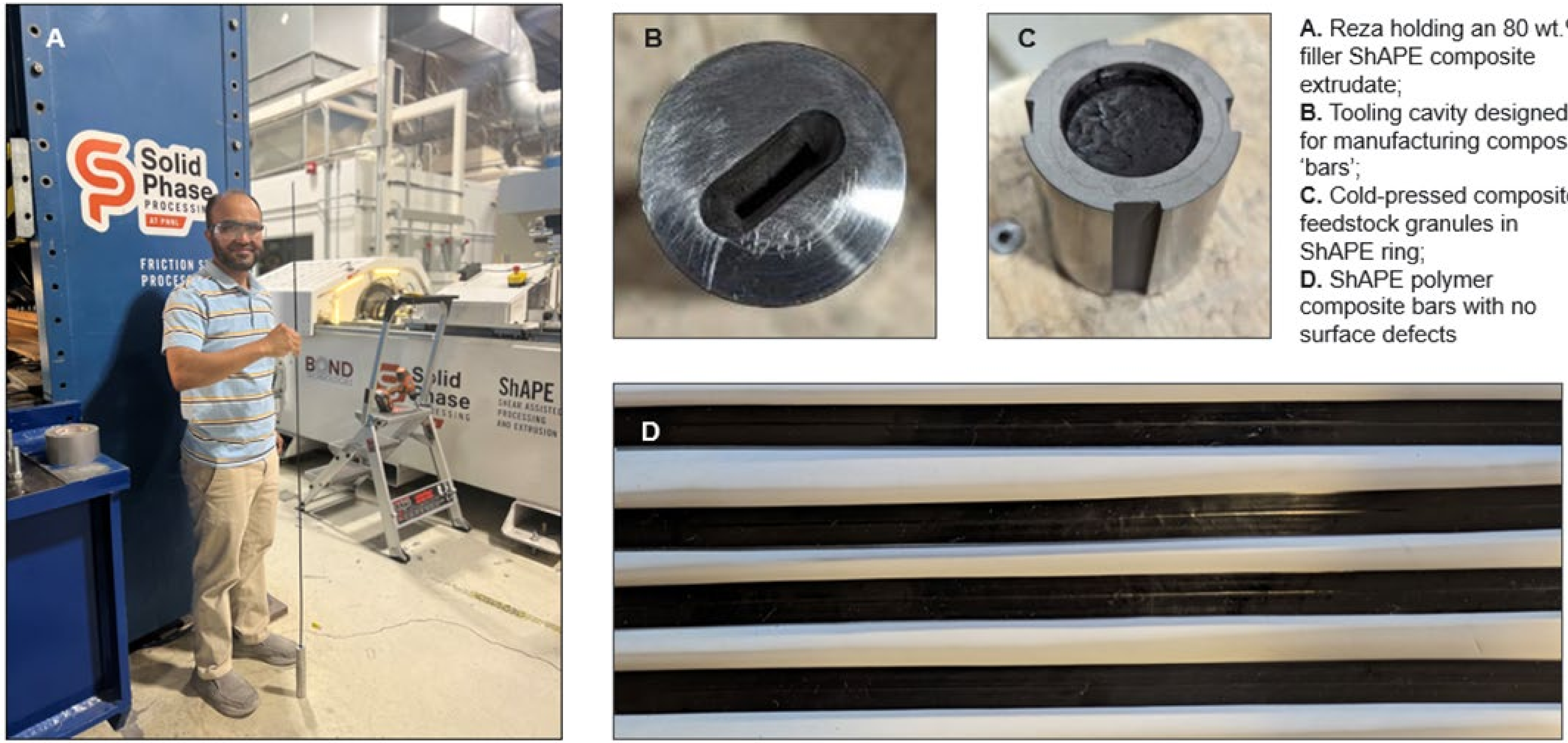
Step 3: ShAPE Friction Extrusion Manufacturing

Solid-Phase Processing enables production of composites with 80-90 wt.% filler.

- First-generation machine developed at PNNL
- Consolidated and extruded continuously without external heating
- Tool design and process conditions are key for manufacturing

Step 3: ShAPE Friction Extrusion Manufacturing

ShAPE extrude wires, bars, or ribbons for property testing.

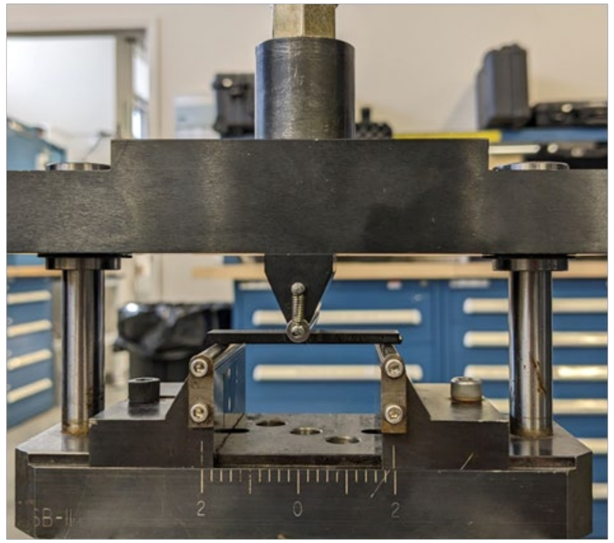


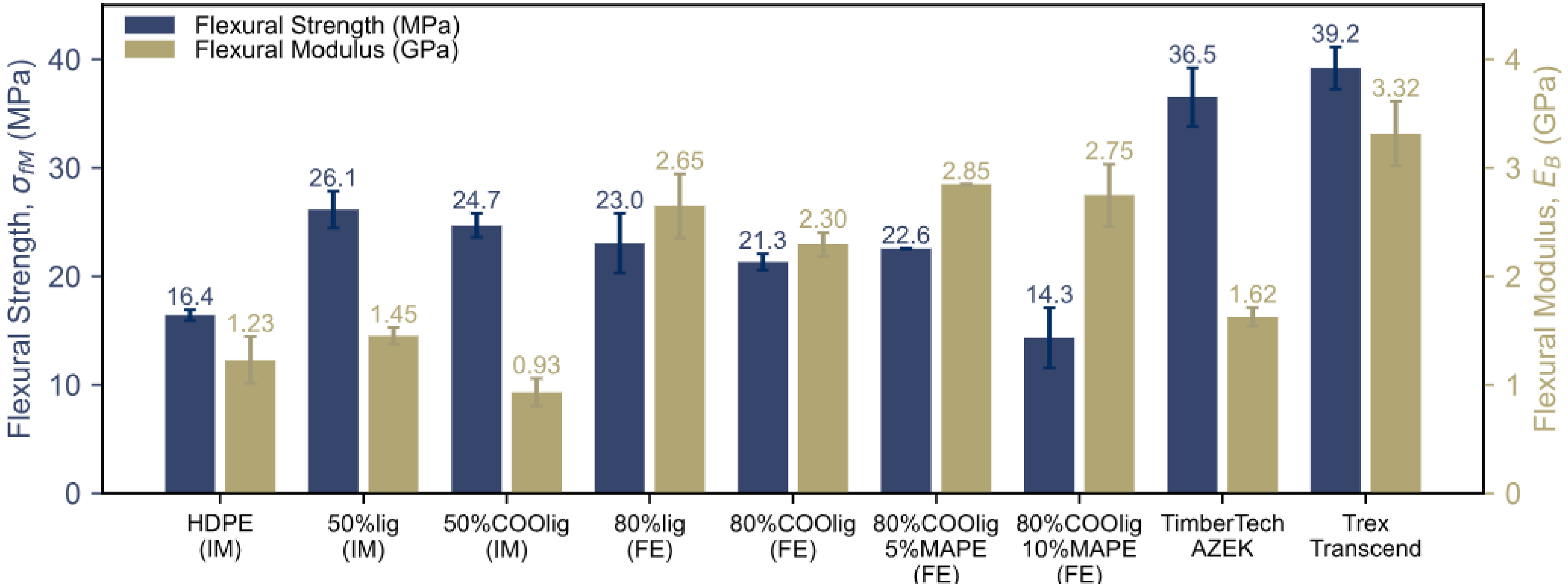
A. Reza holding an 80 wt.% filler ShAPE composite extrudate;
B. Tooling cavity designed for manufacturing composite 'bars';
C. Cold-pressed composite feedstock granules in ShAPE ring;
D. ShAPE polymer composite bars with no surface defects

Step 4: Testing the Composites

Composite flexural strength and modulus meet International Building Code requirements, establishing product viability.

- Flexural strength and modulus of injection molded (IM) and friction extruded (FE) lignin polymer composites
- 50 and 80 wt.% functionalized and unfunctionalized lignin fillers and the corresponding uniform live load
- **Composites with recycled HDPE are currently being tested**





Materials	Uniform live load (psf)
HDPE (IM)	92.38
50% Lig (IM)	109.17
50% CO2Lig (IM)	70.02
50% CO2Lig + 5% MAPE (IM)	107.59
80% Lig (FE)	199.35
80% CO2Lig (FE)	172.80
80% CO2Lig + 5% MAPE (FE)	214.36
TimberTech AZEK	122.20
Trex Transcend	249.68

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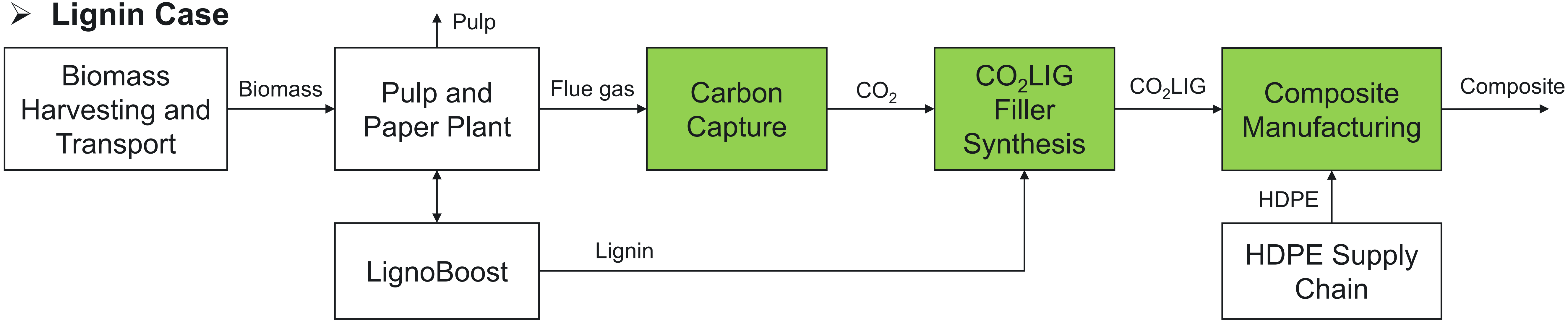
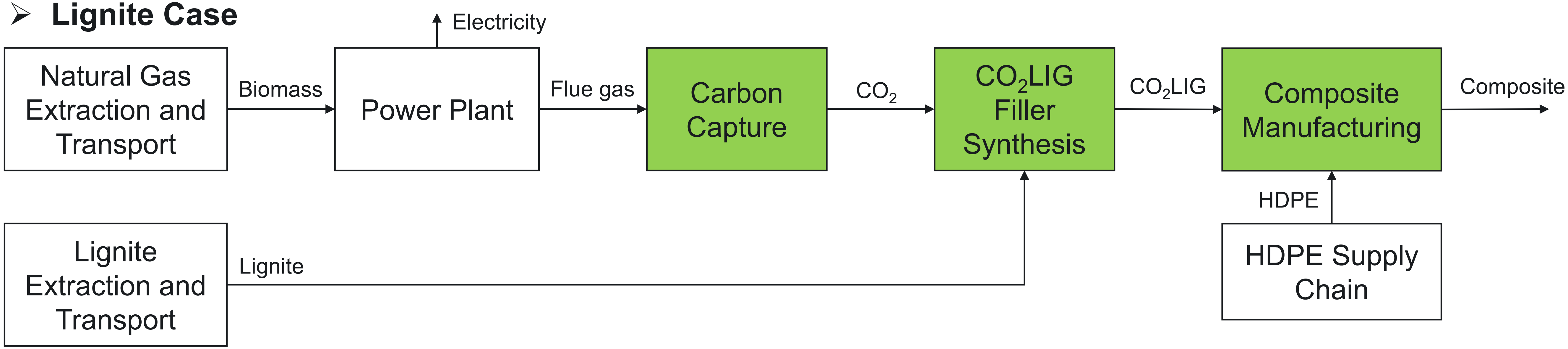
Step 5: Techno-Economic and Life-cycle Analyses

Model and experimental data-based TEA and cradle-to-gate LCA to quantify economic and environmental benefits.

- **Lignin Case**



- **Lignite Case**



☐ Included in LCA system boundary 🟩 Core areas for process modeling and TEA

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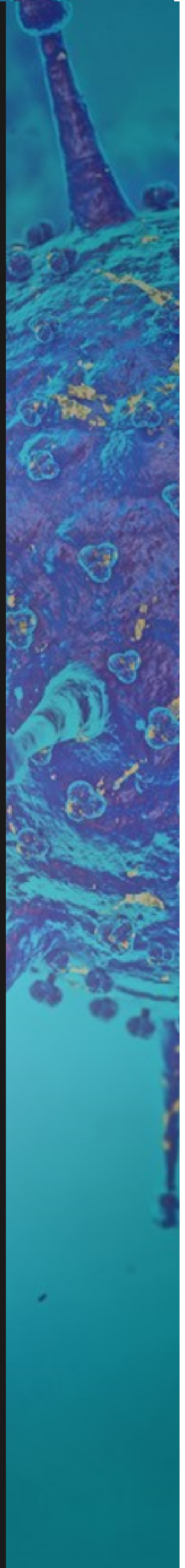

Step 5: Techno-Economic Projections

Modeling in Aspen Plus using the standard approach.

- **Approach:** Wooley and Putsche, Development of an Aspen Plus Physical Property Database for Biofuel components, NREL/TP-425-20685, 1996.

- **Properties of Kraft Lignin**

Wt%	Mun et al., 2021	NREL Model	Our Model
C	63.12	71.6	66.9
H	5.67	11.4	5.4
O	28.78	17.0	27.7
N	0.48		
S	1.96		

- **Properties Required by Aspen: Solids**

Property	Aspen	Value
Heat of Formation	DHSFRM	Riley, 1995
Heat Capacity*	CPSPO1	Domalski et al., 1987
Density	VSPOLY	1.5 g/cc

*1.2 kJ/kg/K @25 °C, similar to Pervan, 2014.

- **Aspen Plus Specification** * A formula corresponds to a single repeat unit.

Component	Formula *	CPSPO1 (K, J/kmol-K)		VSPOLY (K, m^3/kmol)	DHSFRM (kJ/mol)
		1	2	1	
Lignin	$C_{6.8}H_{6.6}O_{2.1}$	31431.7	394.427	0.0817	-1592.6
Lignin-ONa	$C_{6.8}H_{5.6}O_{2.1}Na$	37098.5	465.538	0.0964	-1797.6
Lignin-COONa	$C_{7.8}H_{5.6}O_{4.1}Na$	48442.9	607.909	0.1259	-2170.1
Lignin-COONa-ONa	$C_{7.8}H_{4.6}O_{4.1}Na_2$	54110.5	679.017	0.1406	-2348.5
Lignin-COOH	$C_{7.8}H_{6.6}O_{4.1}$	42779.8	536.83	0.1112	-1986.8

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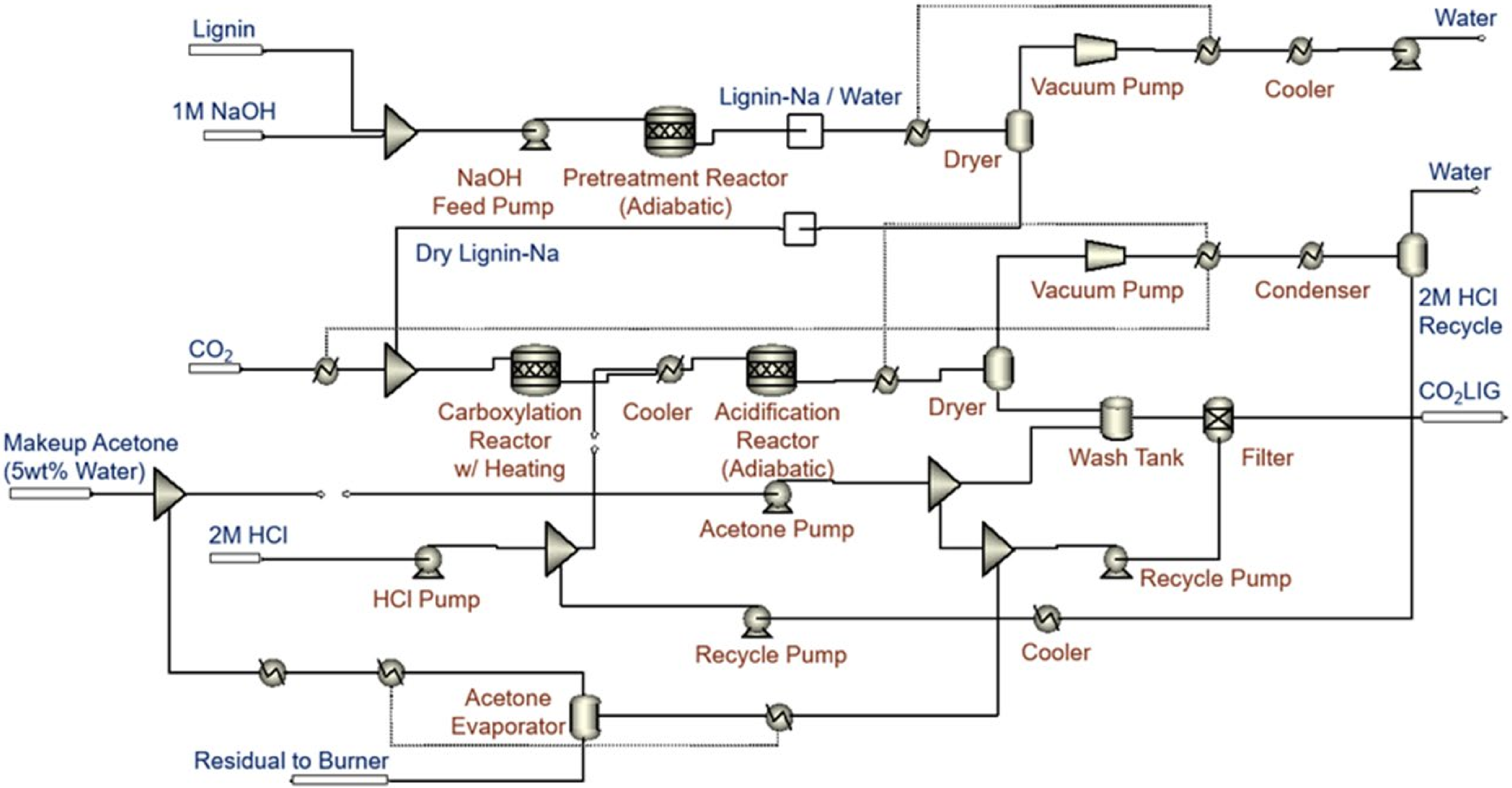
Step 5: Techno-Economic Projections

Modeling in Aspen Plus using the standard approach.



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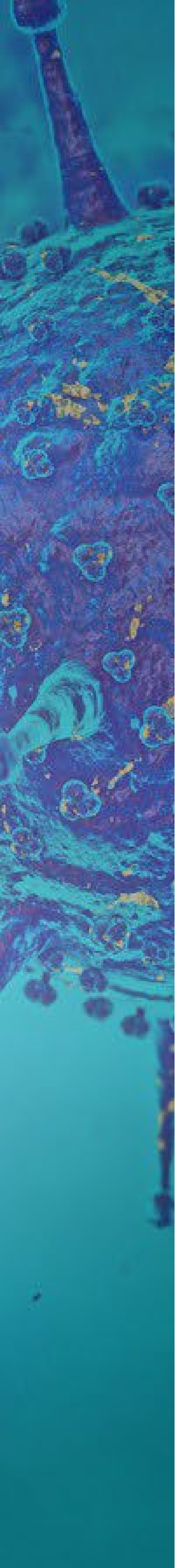

Step 5: Techno-Economic Projections

TEA and LCA studies run with comprehensive list of operating conditions and performance measures of the carboxylation unit.

	Lignin-HCl	Lignin-H_2SO_4	Lignite-H_2SO_4
NaOH treatment			
Solvent (per g lignin/lignite)	1 ml 1M NaOH	1.5 ml 0.67M NaOH	2 ml 1M NaOH
Temperature/pressure	Room	Room	Room
Residence time	3 h	3 h	1 h
Water removal	Vacuum dryer @ 130 °C	Filtration	Filtration
Carboxylation			
Temperature/pressure	130 °C, 15 bar	130 °C, 15 bar	130 °C, 28 bar
Residence time	3 h	3 h	1 h
Acidification			
Acid (per g lignin/lignite)	1 ml 2M HCl	3 ml 0.67M H_2SO_4	2 ml 1M H_2SO_4
Temperature/pressure	Room	Room	Room
Residence time	5 min	5 min	5 min
CO_2LIG Recovery			
Wash (per g lignin)	200 ml acetone (5% H_2O)	100 ml ice water	100 ml 25°C water
Separation	Vacuum dryer @ 130 °C	Filtration	Filtration
CO_2LIG recovery rate	80%	65%	88%
Waste Stream Treatment	Acetone recycled; Lignin sent to burner	Quick lime to adjust PH; then send to wastewater treatment	Quick lime to adjust PH; then send to wastewater treatment

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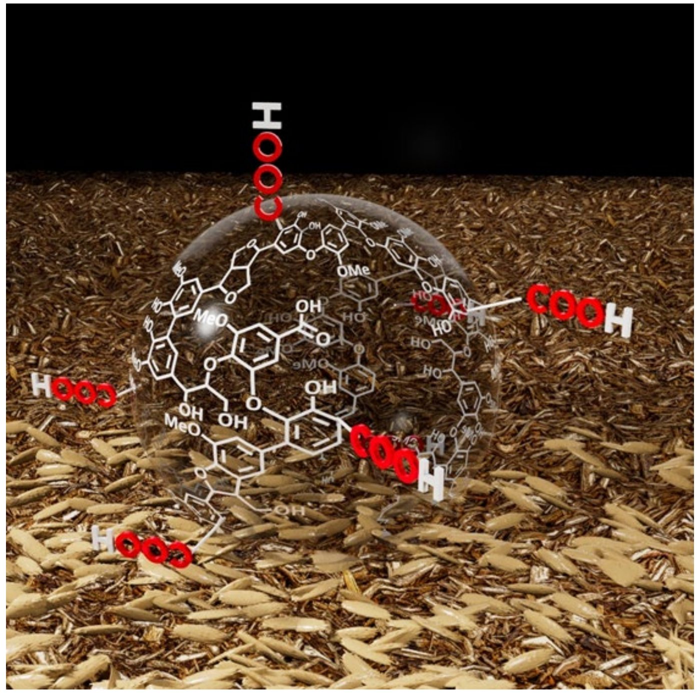
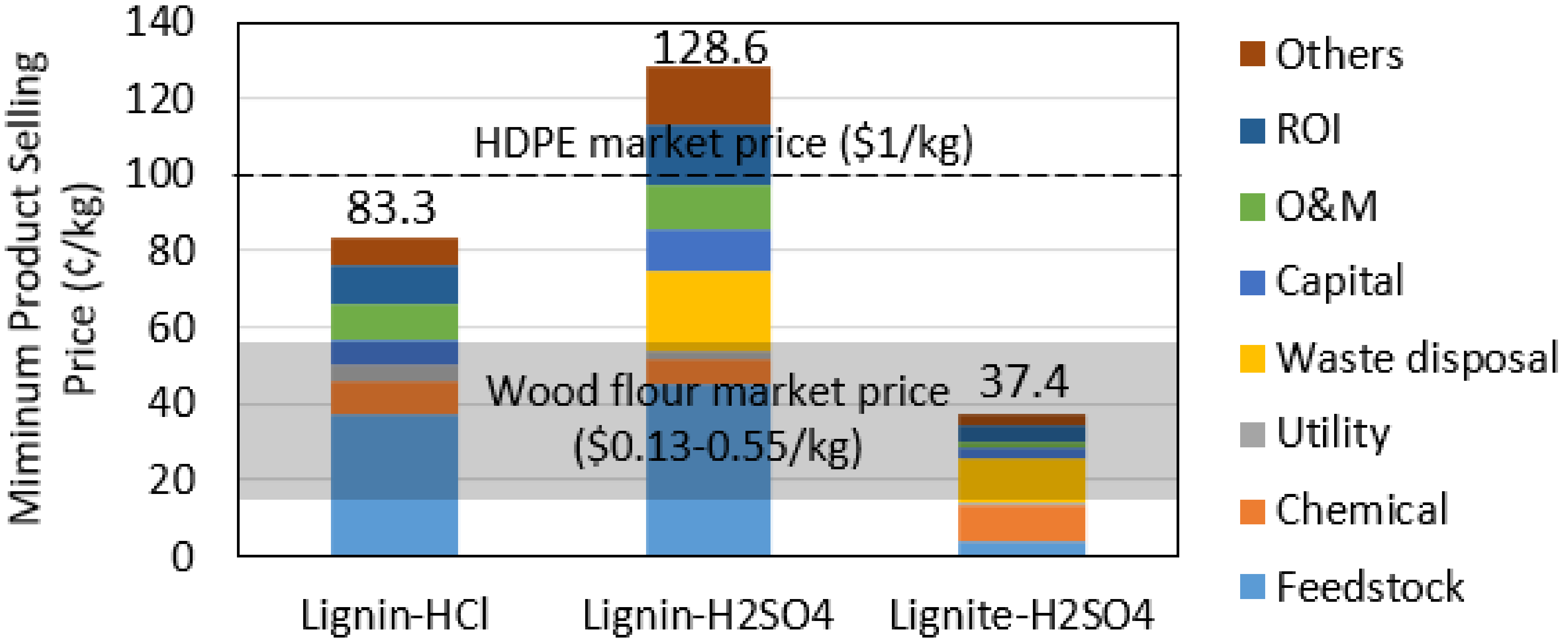
Step 5: Techno-economic Projections

CO_2LIG fillers can be made cheaper than HDPE ($1/kg) suggesting economic viability as filler.





- Lignite has comparable price to wood flour filler
- Lignin is more expensive primarily due to feedstock costs
- Price is sensitive to process conditions and reagents, e.g. HCl VS H_2SO_4 acid workup

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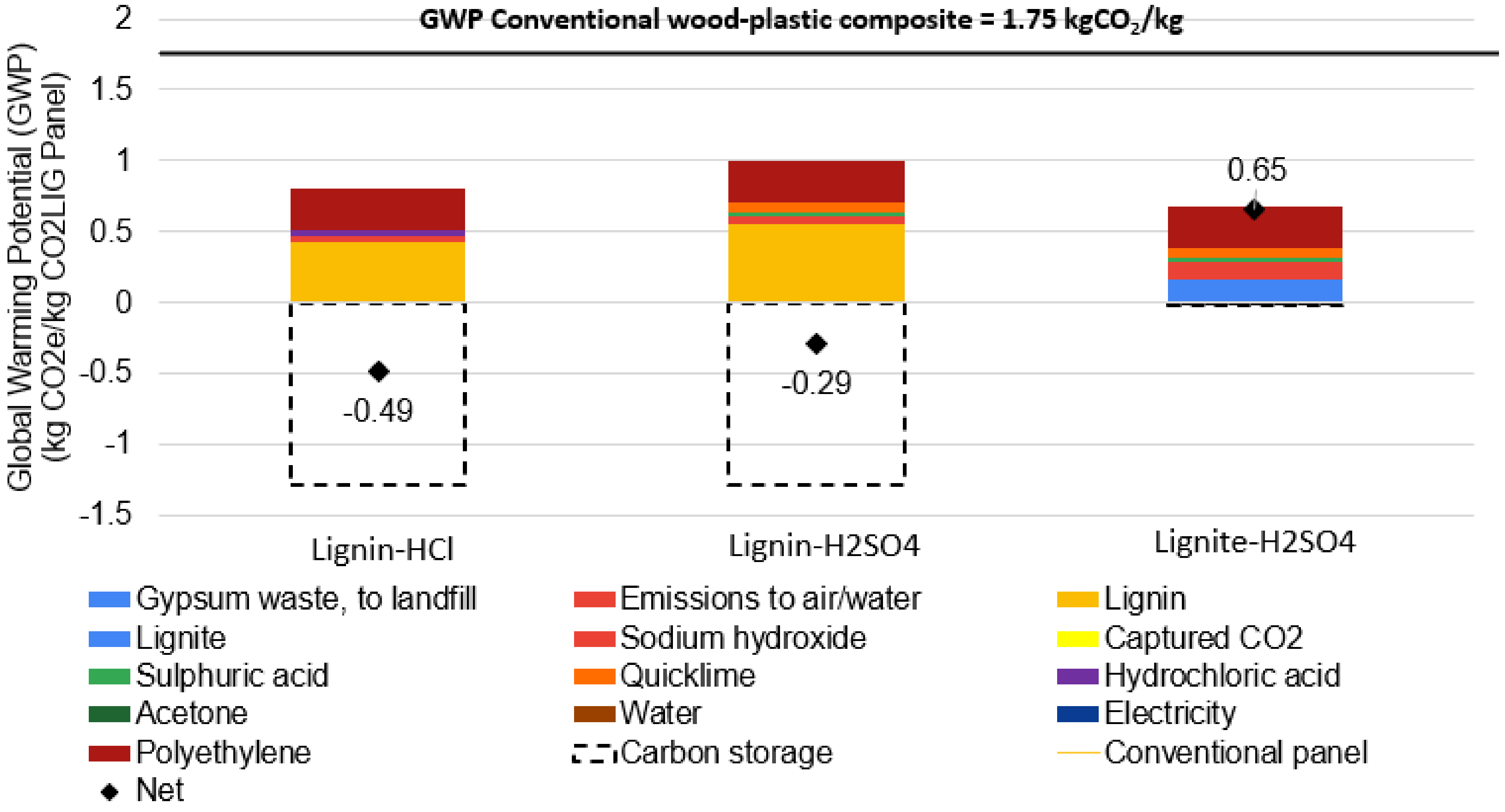
Step 5: Preliminary Life Cycle Analysis*

The global warming potential (GWP) of CO_2LIG composites using 100% renewables, recycled HDPE is lower than wood-plastic composites (WPC).



CO_2LIG GWP:

- Lignite: 63% lower than WPC
- Lignin: CO_2-negative

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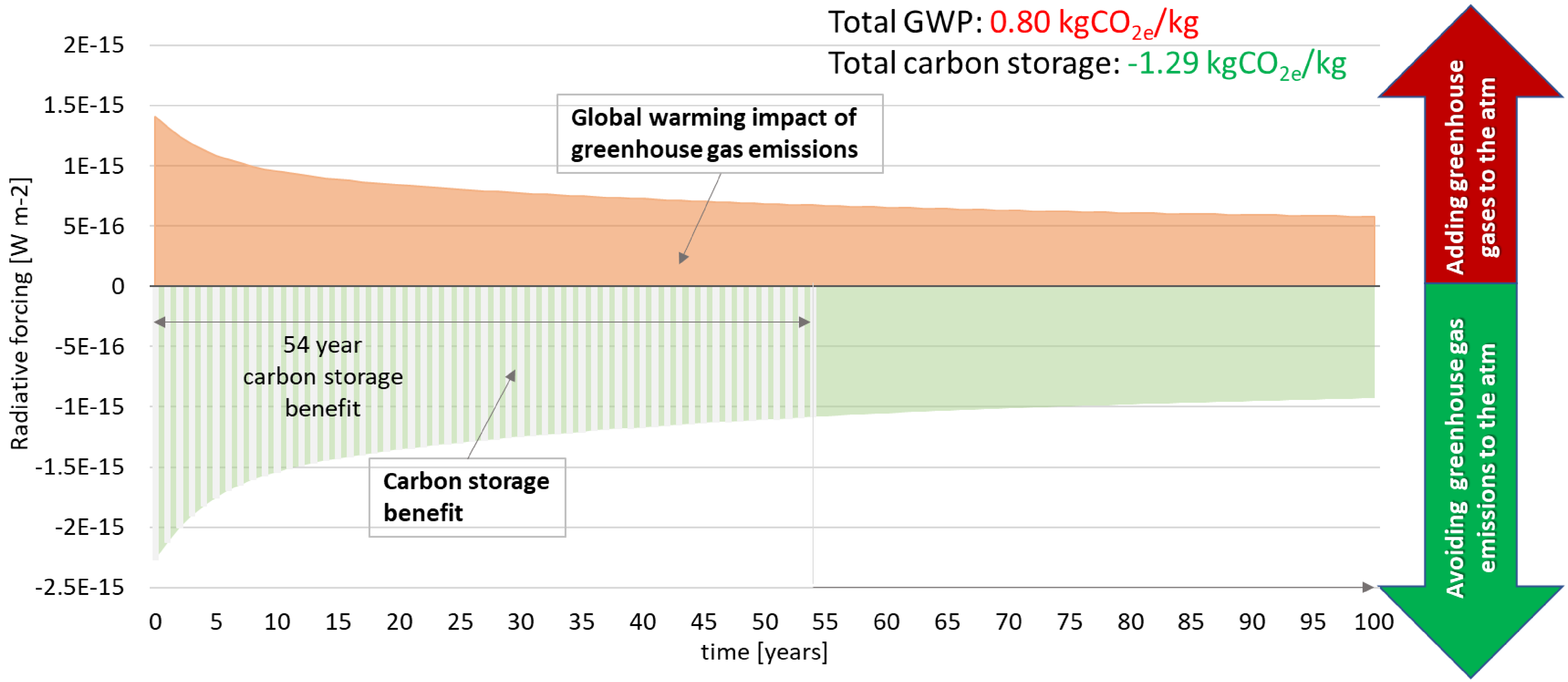
Step 5: Preliminary Life Cycle Analysis*

Conservative temporal radiative force analysis suggests carbon neutrality after 54 years and carbon negativity in subsequent years.

Total GWP: 0.80 $kgCO_{2e}/kg$

Total carbon storage: -1.29 $kgCO_{2e}/kg$



Carbon storage > 54 years: Net negative global potential

*** ShAPE^{TM} enables re-extrusion of old composites extending product lifetime.**

*100% renewable electricity, recycled HDPE

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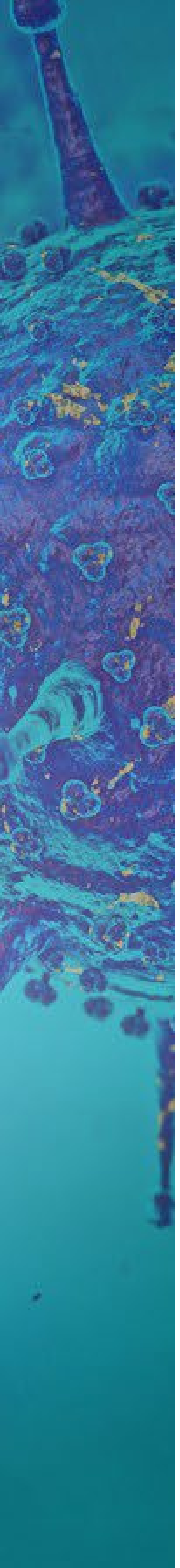
Milestones and Success Criteria

Project team has met all success criteria in BP2 and BP3.

No.	Milestone Description	Planned Completion	Actual or Estimated Completion
M8.1	Complete analysis and process optimization for separation of carboxylated lignin from the solvent	3/31/2024	5/31/2024
M8.2	Demonstrate solvent recovery (>95 %)	6/30/2024	-*
M8.3	Produce up to 5 kg of carboxylated lignin and lignite	8/31/2024	07/31/2024

BP	Success Criteria	Milestone
BP3	Solvent recovery (>95%) validated by using solvent recovery strategies focused on breaking the carboxylic acid/solvent acid/base pairs on the surface of the particles.*	**Milestone 8.2**
BP3	Synthesize 5 kg of carboxylated lignin or lignite using the down selected solvent	**Met Milestone 8.3**
	Complete LCA/TEA analysis confirming the production of carbon-negative materials.	**Met Milestone 8.3**

* CO_2BOLs did not have adequate basicity for carboxylation, therefore we used NaOH for carboxylation.



Comparing CO_2LIG *vs.* DAC

CO_2LIG is a potentially profitable CDR approach at a reasonable scale with potential to expand to other markets and materials.

- CO_2 sequestration for decking market in US

  ~250 thousand metric tons/year
- Equivalent emissions of 54,000 US cars/year

  ~1.86 M cars globally

	DAC	CO_2LIG
Reactive CDR?	**No**	**Yes**
Global Scale	**Gtonne/yr**	**0.0046 Gtonne/yr**
45Q Credit	**$180**	**$60**
Cost	**>$100/tonne**	**+$130/tonne**

Adaptable to: fencing, siding, furniture, structural materials

Conclusions

Reactive CDR can produce economically-viable CO_2-negative composites from lignin or lignite and recycled HDPE.

- Lignin and lignite carboxylation at Kg scale with ~2-4.2 wt. % CO_2
- Shear assisted processing and extrusion (ShAPE^{TM}) enables:
    - Composites with 50-80 wt.% lignin filler
    - Composites with 80-90 wt.% lignite filler
    - Recycling and re-extrusion of old decking improving product lifetime
- CO_2LIG composites meet IBC metrics for flooring or decking
- Lignite CO_2LIG composites have 63% lower GWP than WPC
- Lignin CO_2LIG composites have a net-negative GWP after 20-54 years assuming:
    - 100% renewable electricity, recycled HDPE
    - CO_2 sequestered in CO_2LIG, and excess CO_2 stored in the ground
- Adaptable to other composite markets to increase CO_2 sequestration potential

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Thank you

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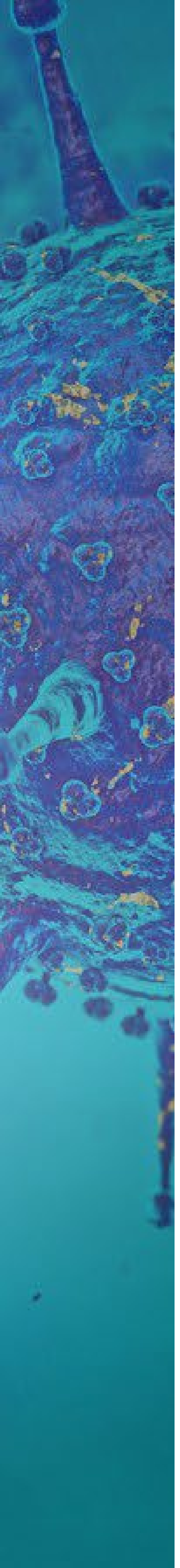
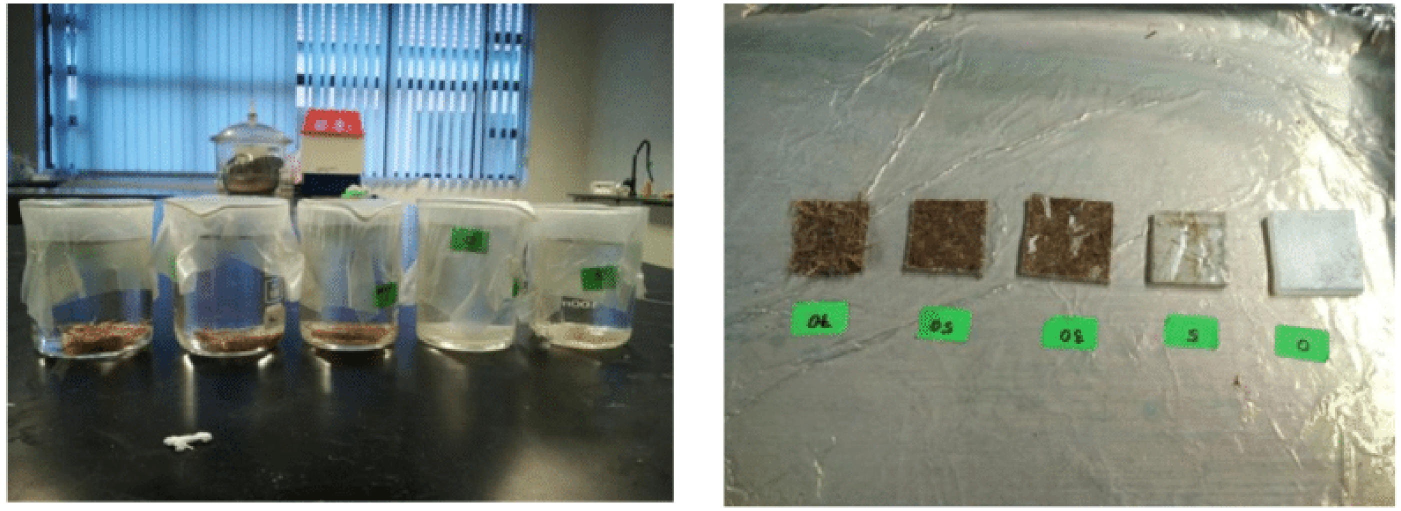


Next Steps: Environmental Performance Testing

Testing CO_2LIG-plastic composite for durability and flammability.



Water absorption testing

Lab-scale freeze-thaw testing

ASTME659
Lab-scale self-ignition and auto-ignition temperature testing

ASTM E84 Flammability spread index
To determine flammability class (A, B, C) of material