An Experimental and Computational Approach to Investigating CO_2 Uptake of Cellulose-Producing Algae from Cellulosic Ethanol Product (FE0032207)

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2024 FECM/NETL Carbon Management Research Project Review Meeting
August 5 – 9, 2024

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Project Overview

– Funding (DOE and Cost Share): **$400,000 & $0 Cost Share**

– Overall Project Performance Dates

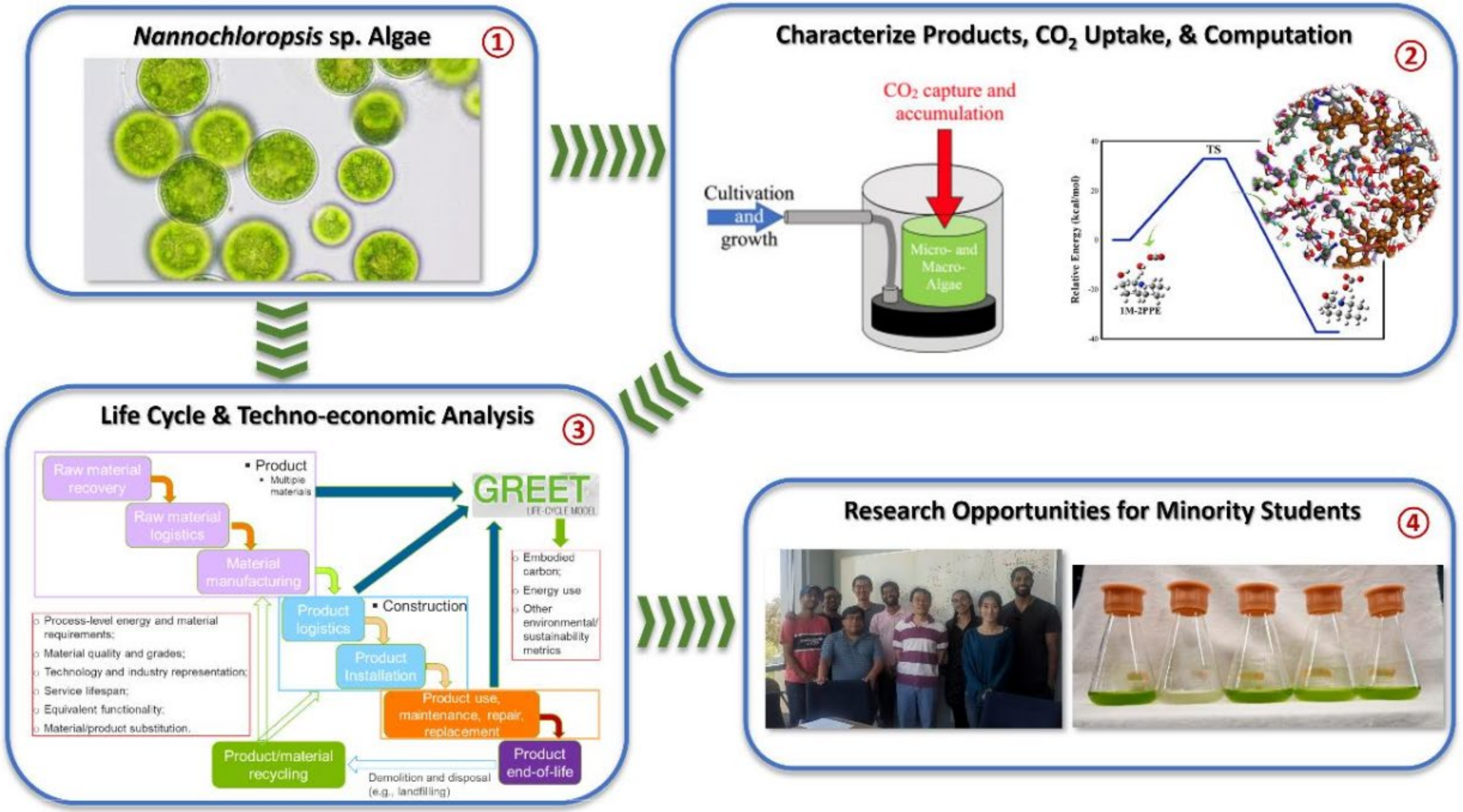
Task Number and Name (Timeline in Months)	6	12	18	24	30	36
1.0: Project Management						
Update Project Management Plan and Kick-off meeting with DOE/NETL	■					
2.0: Optimize N. salina on Effluent Gas from Cellulosic Fermentation						
2.1: Preparation of CELF-Pretreated Biomass Materials for SSF	■	■				
2.2: Culturing of N. salina and Enhancement of Biomass Density		■	■			
2.3: Co-solvent Extraction of Lipids and Recovery of Cellulose from Algae			■	■		
2.4: Quantify Cellulose/Lipid Content and Calculate Carbon Uptake Efficiency						
3.0: Model CO_2 Uptake Efficiency and Cellulose Production						
3.1: DFT Calculations of CO_2 Binding Interactions	■	■	■			
3.2: GPU-Enhanced DFTB Calculations of Cellulose Production			■	■		
4.0: Techno-economic and Life Cycle Analysis of CAPOC Integration						
4.1. Build TEA Model of CAPOC	■	■	■			
4.2: Build GREET LCA Model of CAPOC			■	■		

Project Overview

– Project Participants:

- **Prof. Bryan Wong (PI):**
  Large-scale computational simulations
- **Dr. Wafa Maftuhin (Postdoctoral associate):**
  Large-scale computational simulations
- **Dr. Charles Cai (co-PI):**
  Cellulose experiments
- **Marcus Catapang (Graduate Student):**
  Cellulose experiments
- **Aira Aquino (Undergraduate Student):**
  Cellulose experiments

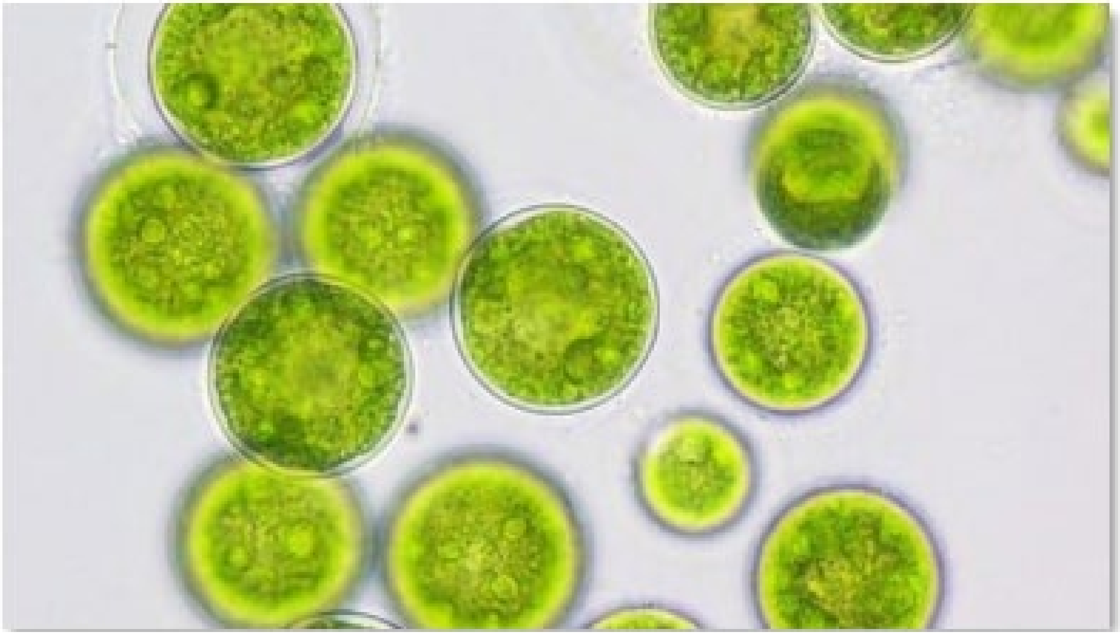
- Overall Project Objectives



Technology Background

***Nannochloropsis* Characteristics**:

- Produces both lipids and cellulose.
- Fast growth rate
- Can be cultivated in various environments
- Cellulose in *Nannochloropsis* is concentrated in the cell wall, making it recalcitrant.

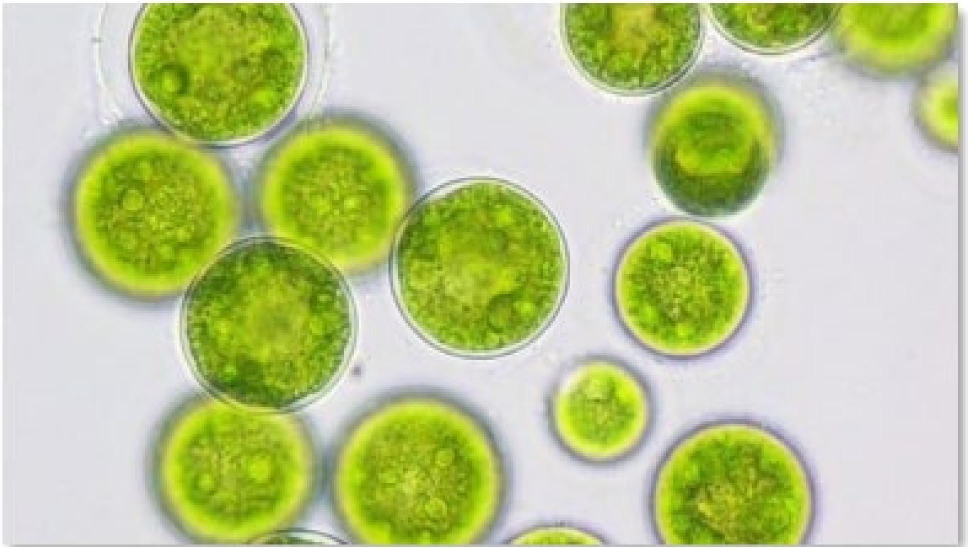


Cellulose Production:

- Cellulose is a valuable biopolymer, useful when hydrolyzed to glucose.
- Crystalline cellulose can be processed into microcrystalline cellulose for various applications.

Technology Background

- Economic & environmental benefits
  - Capturing CO_2 from ethanol fermentations supports algal production and enables potential greenhouse gas savings
  - Lignin generated as byproduct can provide heating to support cellulosic ethanol production & algal cellulose production
  - Lignin is biogenic: its combustion is carbon neutral



Technology Background

Conventional Carbon Capture:

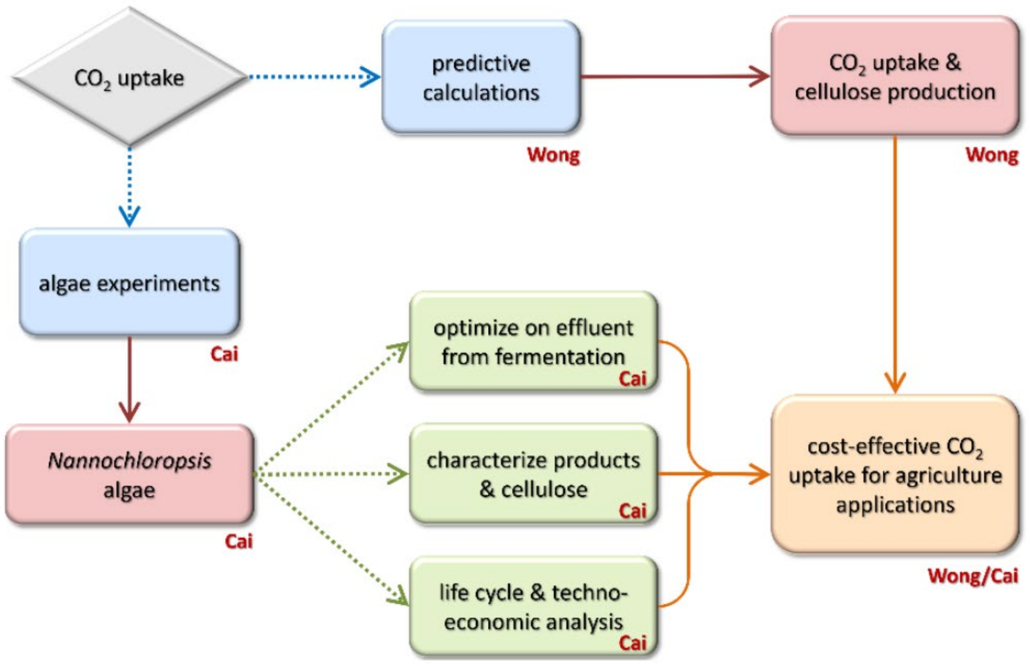
- Focuses on CO_2 storage and transportation as a commodity.
- Involves high production costs for pure and high-pressure CO_2.
- Requires expensive capture devices and complex logistics.
- Market-sensitive off-take agreements and fluctuating commodity prices.

Proposed Method:

- Use highly pure CO_2 effluent from ethanol fermentation as direct feed for algal cultures.
- Ethanol fermentation effluent can reach up to 39% CO_2 concentration in bioreactor headspace.
- Direct feeding of moist CO_2 effluent to algal cultures avoids drying and concentration costs.
- Eliminates the need for exogenous CO_2 capture, drying, and storage, reducing overall costs.

Technical Approach/Project Scope

a. Project steps and work plan



Project schedule

Milestone	Milestone Title and Description	Date	Status (%)	Success Criteria
M1	Kick-off meeting with DOE/NETL Project Officer/Manager	09/01/22	100%	Kickoff meeting attended
M2	Preparation of CELFPretreated Biomass Materials for SSF	06/15/23	100%	Produce up to 1 kg of CELF-pretreated poplar wood for SSF
M3	Culturing of N. Salina and Enhancement of Biomass Density	12/31/23	100%	Achieve 1 g/L DW algae broth density using CO_2 effluent from SSF of biomass
M4	Co-solvent Extraction of Lipids and Recovery of Cellulose fromAlgae	09/30/24	50%	Achieve >90% recovery of cellulose and lipids
M5	Quantify Cellulose/Lipid Content and Calculate Carbon Uptake Efficiency	11/31/24		Achieve >20% cellulose content in algal cell wall and 30 wt% lipid content
M6	DFT Calculations of CO_2 Binding Interactions	06/31/24	50%	Binding energies calculated and verified with experiment
M7	GPU-Enhanced DFTB Calculations of Cellulose Production	11/30/24		DFTB calculations used to explore microcrystalline cellulose production
M8	Build TEA model of CAPOC	12/31/23	80%	Successfully develop and run TEA model in AspenOne environment
M9	Build GREET LCA model of CAPOC	02/28/25		Demonstrate GHG savings of >85% compared to conventional petroleum processing to fuels

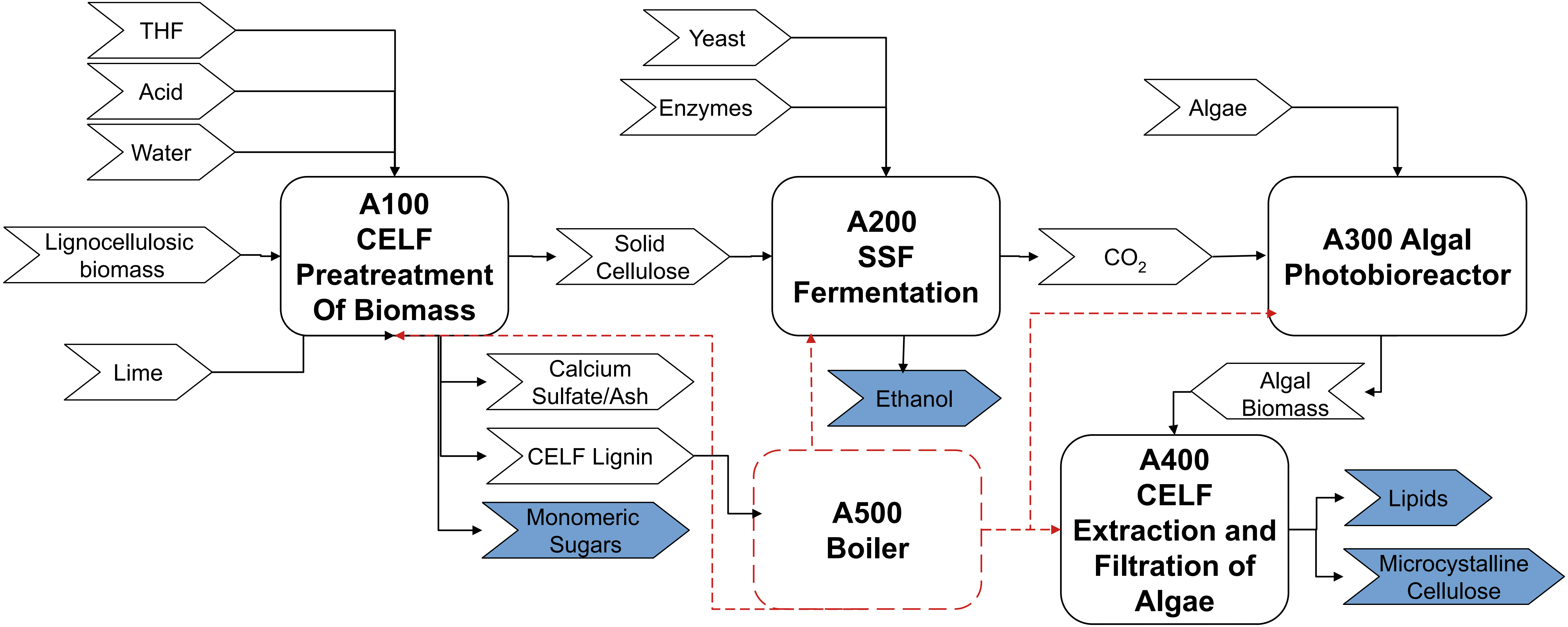
Technical Approach/Project Scope

Project risks and mitigation strategies

Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
Expenses may not be adequate	Low	Medium	Low	The PI and co-PI have monthly meeting
Cost/Schedule Risks:				
Proposed schedule may not be adequate	Low	Medium	Low	The PI and co-PI have weekly meetings
Technical/Scope Risks:				
The various life cycle and quantum calculations in this project may require several iterations to converge.	Low	Medium	Low	The PI and co-PI have over 18 years of experience
Management, Planning, and Oversight Risks:				
Unanticipated delays may occur during the project	Low	Medium	Low	The PI contact the DOE/NETL Program Officer to discuss options and agree on a course of action.
ES&H Risks				
Safety issues may arise during the assessment.	Low	Low	Low	All safety equipment is regularly monitored per regulations by the university.
External Factor Risks:				
Unanticipated external factors (such as the COVID-19 pandemic) may delay progress	Low	Medium	Low	The PI and co-PI have already ramped up their laboratories to nearly full speed

Progress and Current Status of Project

co-locating cellulosic ethanol fermentation with algal lipid and cellulose production

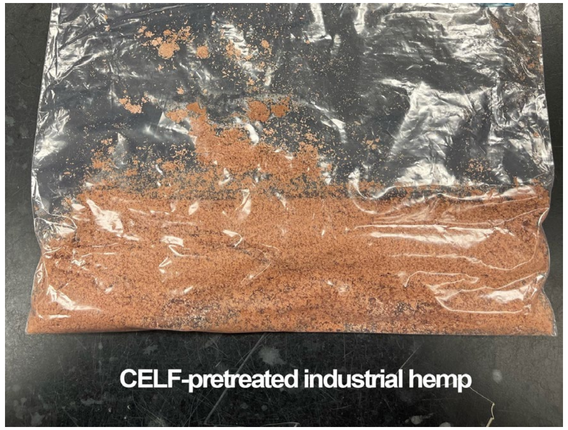


Optimize N. Salina on Effluent Gas from Cellulosic Fermentation

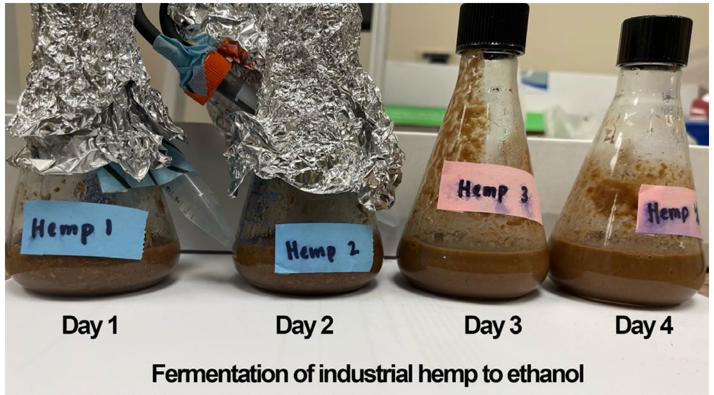
- Performed CELF pretreatment on industrial hemp and corn stover.
- Target: 80% glucan concentration in pretreated solids.

Results:

- Corn stover: >80% glucan achieved.
- Industrial hemp: 75% glucan achieved.
- Optimization underway to improve glucan content in industrial hemp.
- Next step: Measure CO_2 emission from fermentation.



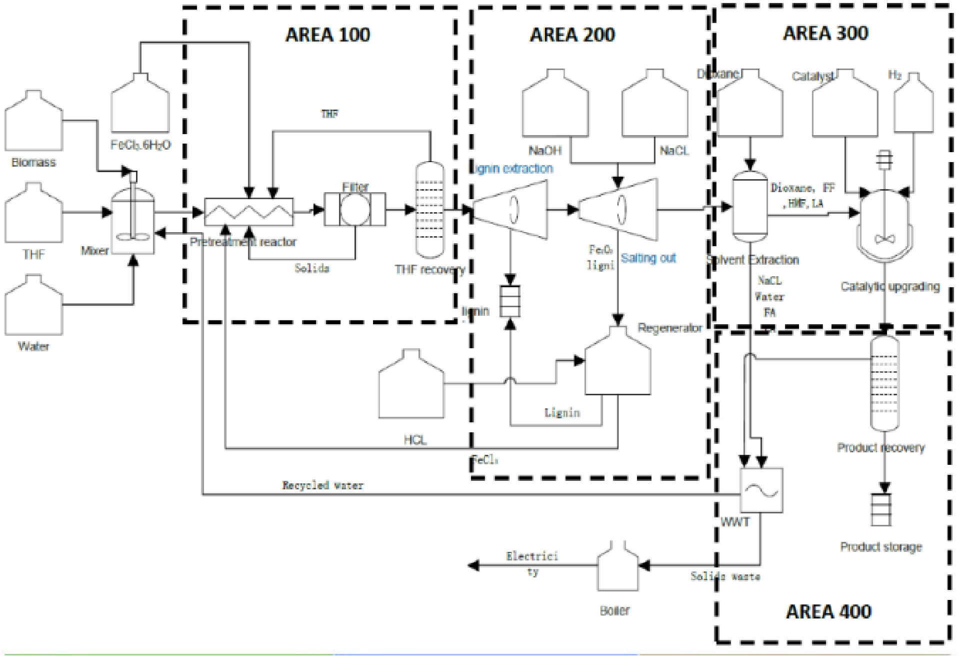
Knife-milled industrial hemp stalk subjected to mild CELF pretreatment



SSF of CELF-pretreated industrial hemp at 100 g/L initial loading. Observed rapid solubilization of solids over first four days. Ethanol analysis under way.

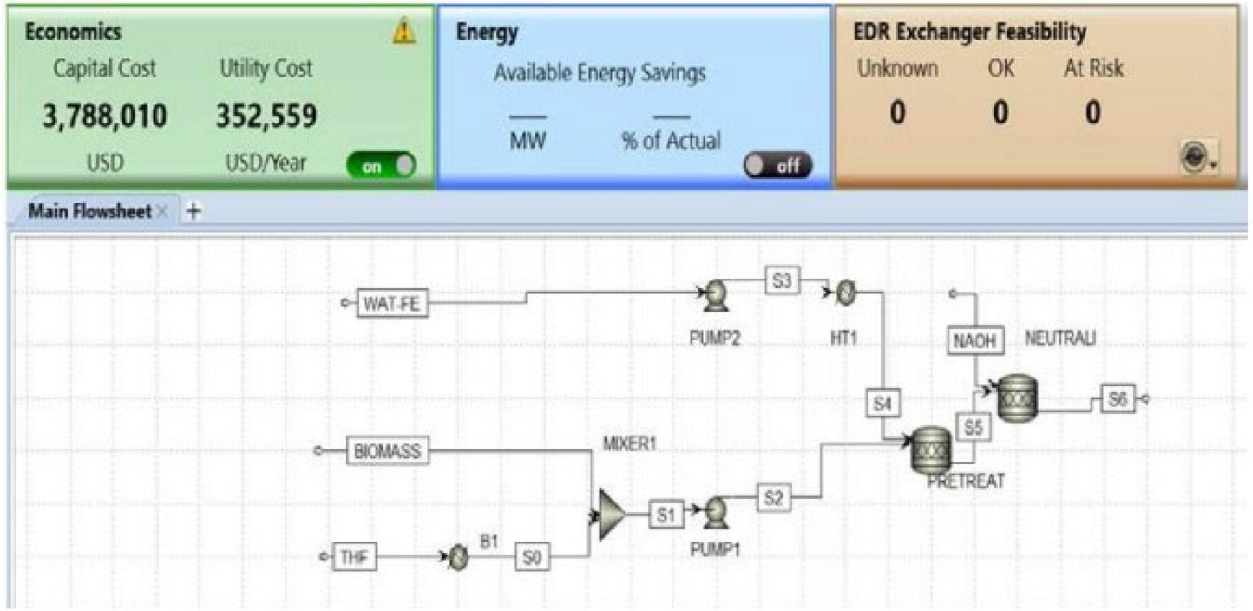
Life cycle analysis

Techno-economic & life cycle analysis will support quantitative outcomes



- Integrated CELF pretreatment, solids filtration, solvent recovery, and neutralization in AspenOne.
- Optimizing heat recovery to calculate initial energy balance.
- Target: 4.5 kWh/tonne biomass input for total heat utilization.

AspenOne software using modified GREET model

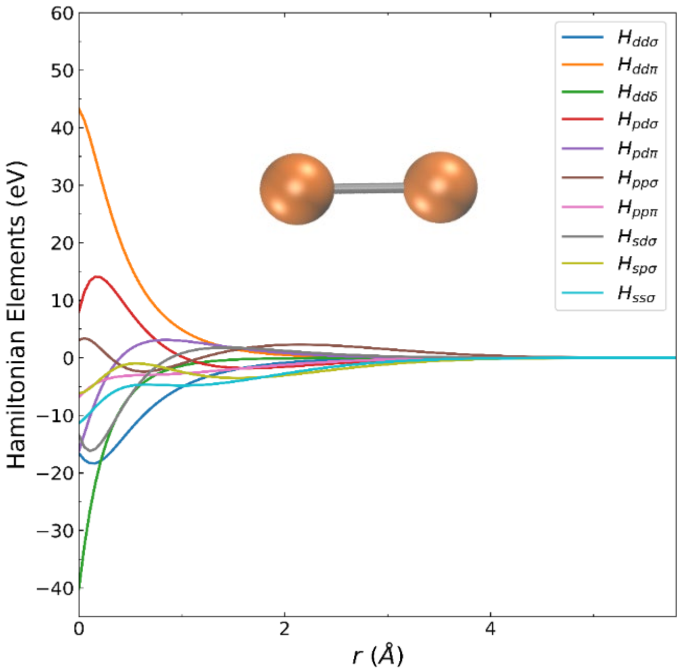


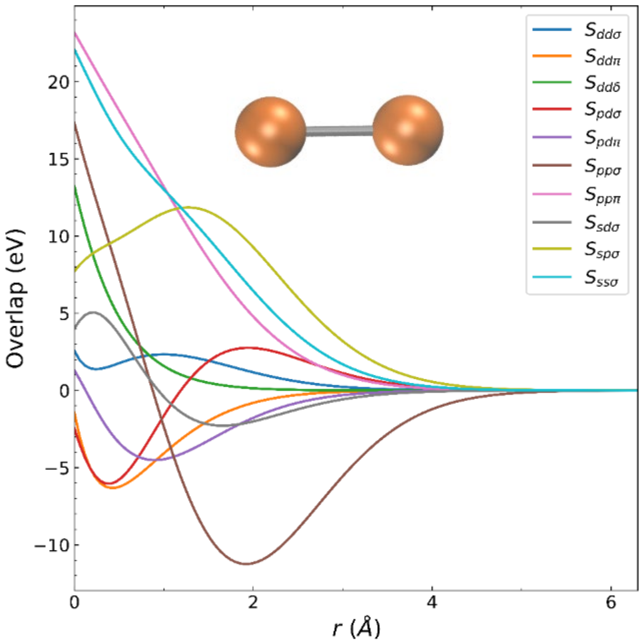
DFTB Primer

Large-scale Density Functional Tight Binding (DFTB) calculations will probe cellulose formation

$$E_{DFTB} = E_{BS} + E_{Coul} + E_{rep}$$

$$\boldsymbol{E_{BS}} = \sum_{i}^{occ} \sum_{\mu\nu} c_{\mu}^{a*} c_{\nu}^{a} H_{\mu\nu}^{0}$$





$$H_{\mu\nu}^{0} = \langle \phi_{\mu} | H^{0} | \phi_{\nu} \rangle$$

$$S_{\mu\nu} = \int \phi_{\mu}(r) \phi_{\nu}(r) d^{3}r$$

parametrized beforehand from DFT calculations

DFTB Primer

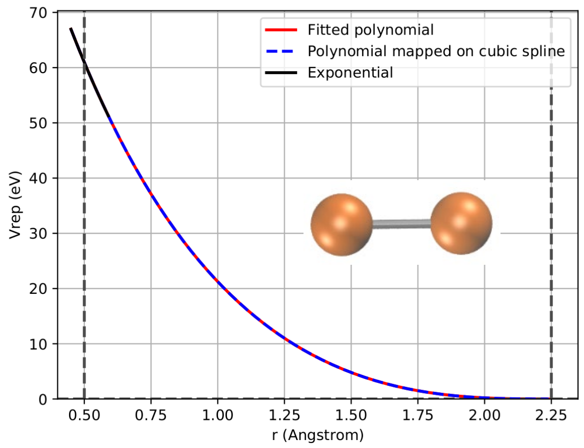
$$E_{DFTB} = E_{BS} + E_{Coul} + E_{rep}$$

$$E_{Coul} = \frac{1}{2}\sum_{IJ} \gamma_{IJ}\left(R_{IJ}\right)\Delta q_I \Delta q_J$$

$$\boldsymbol{\gamma_{IJ}(R_{IJ}) = \begin{cases} U_I, & I = J \\ \dfrac{erf(C_{IJ}R_{IJ})}{R_{IJ}}, & I \neq J \end{cases}}$$

parametrized beforehand from DFT calculations

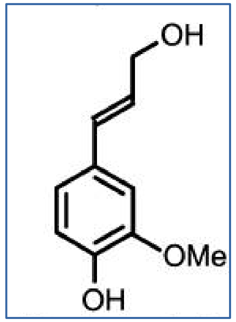
$$E_{rep} = \sum_{I<J} V_{rep}^{IJ}\left(R_{IJ}\right)$$



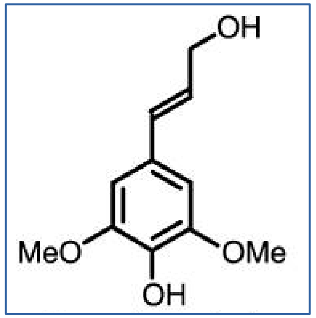
Pre-parameterization allows fast calculations of large systems

Lignin model

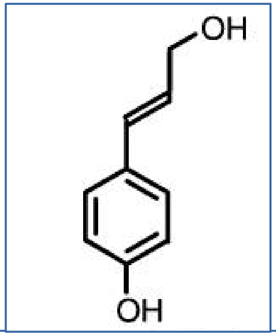
Lignin subunits:



guaiacyl (G)



syringyl (S)



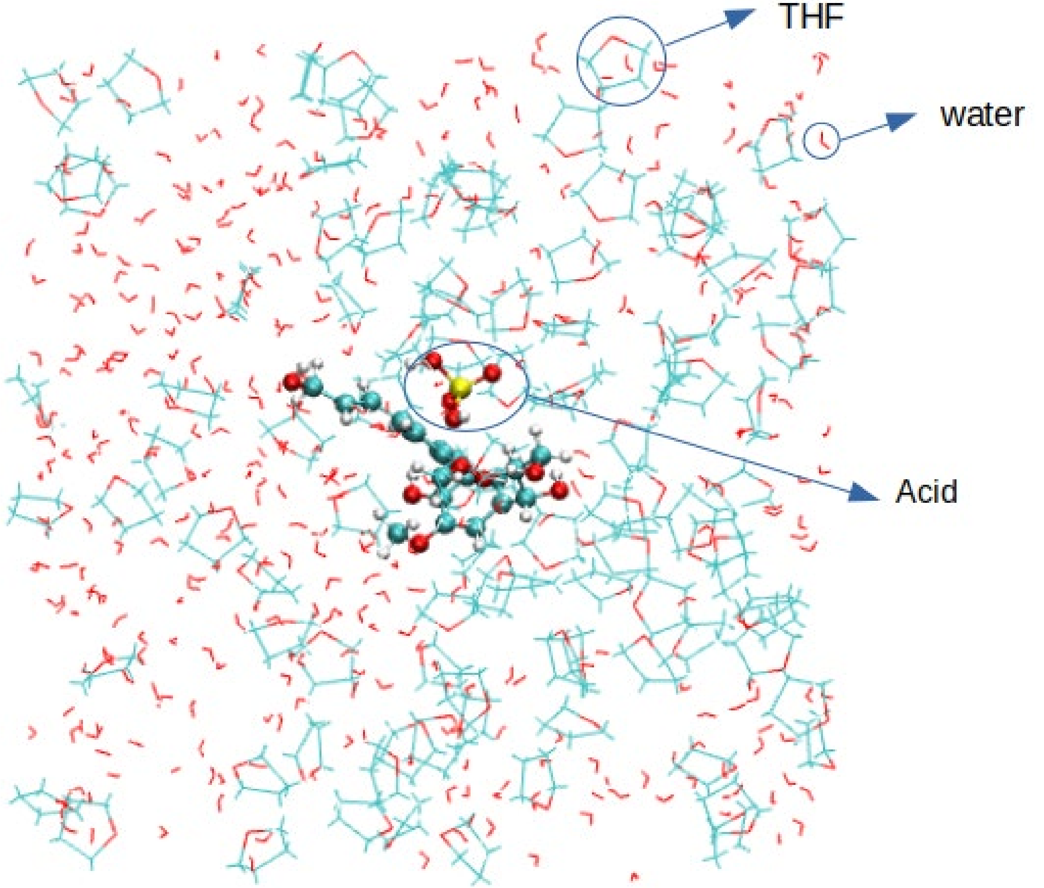
p-hydroxylphenyl (H)

Connected interlinkages:

β-O-4

Model of lignin dimer β-O-4:

- G-G
- S-S
- H-H
- G-S
- S-H
- S-H
- S-G
- H-S

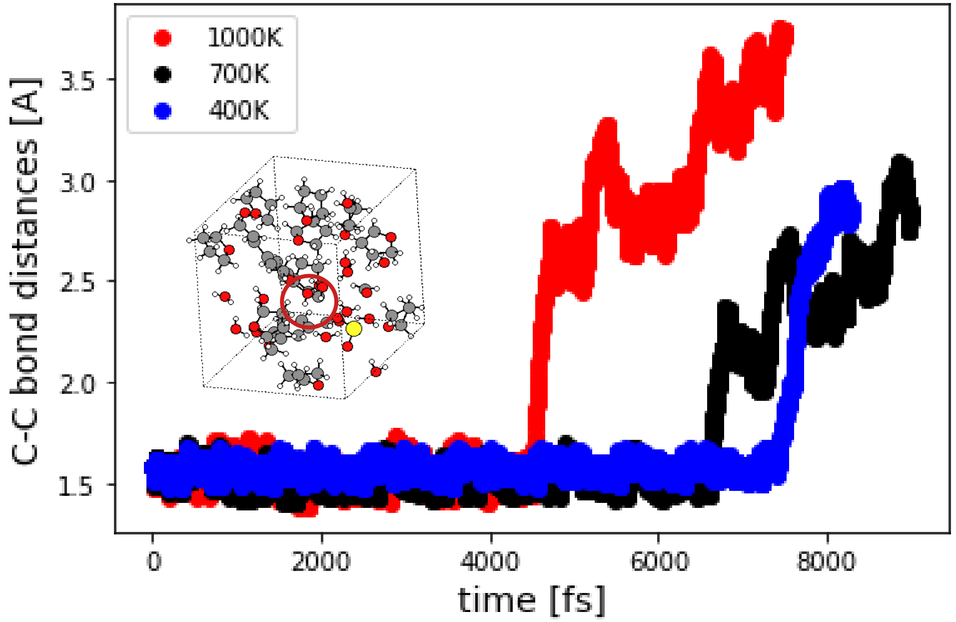


GG dimer β-O4 (2560 atoms)

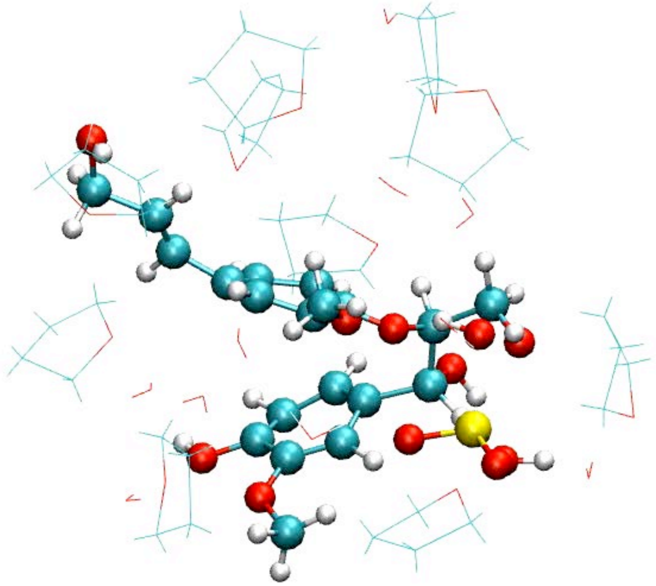
Small scale simulations

NVT (1000 K): Nose-Hoover Thermostat

Temperature effect: fractionation of lignin dimer β-O-4



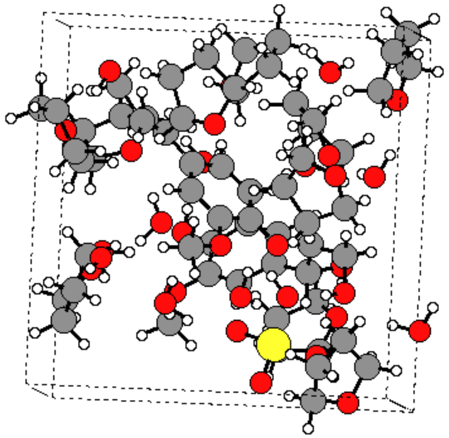
Fractionation shown by increasing bond distances



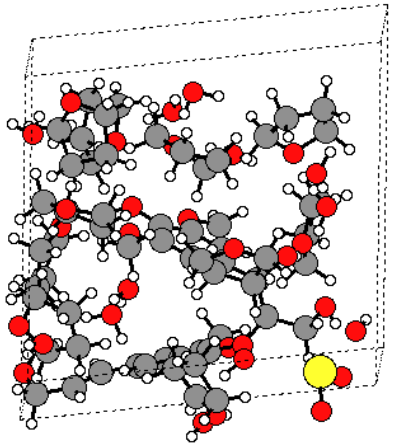
Small scale simulations

Fractionation observed

G-G

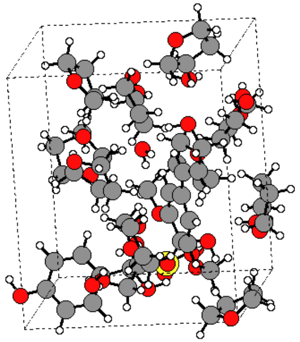


S-G

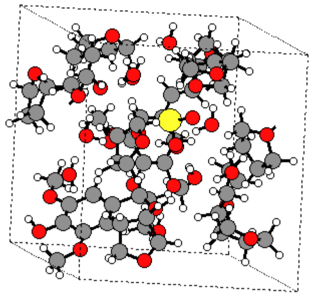


No fractionation observed

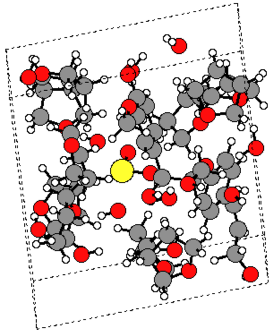
H-S



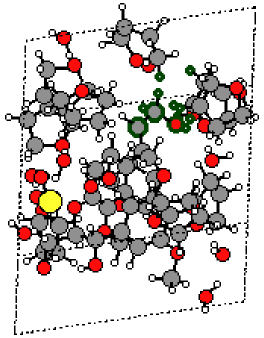
S-S



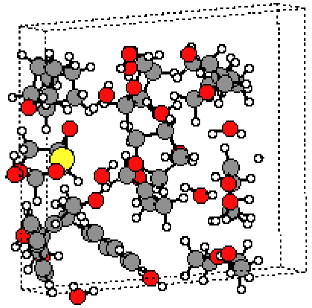
G-H



G-S



H-H

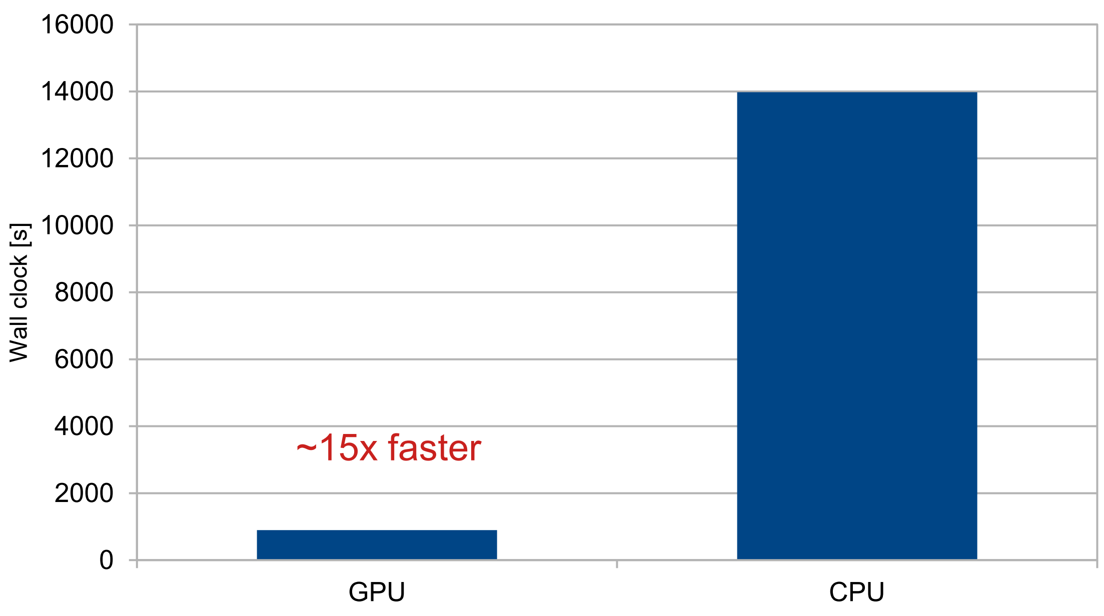


GPU-Enhanced DFTB Calculations

list of libraries:

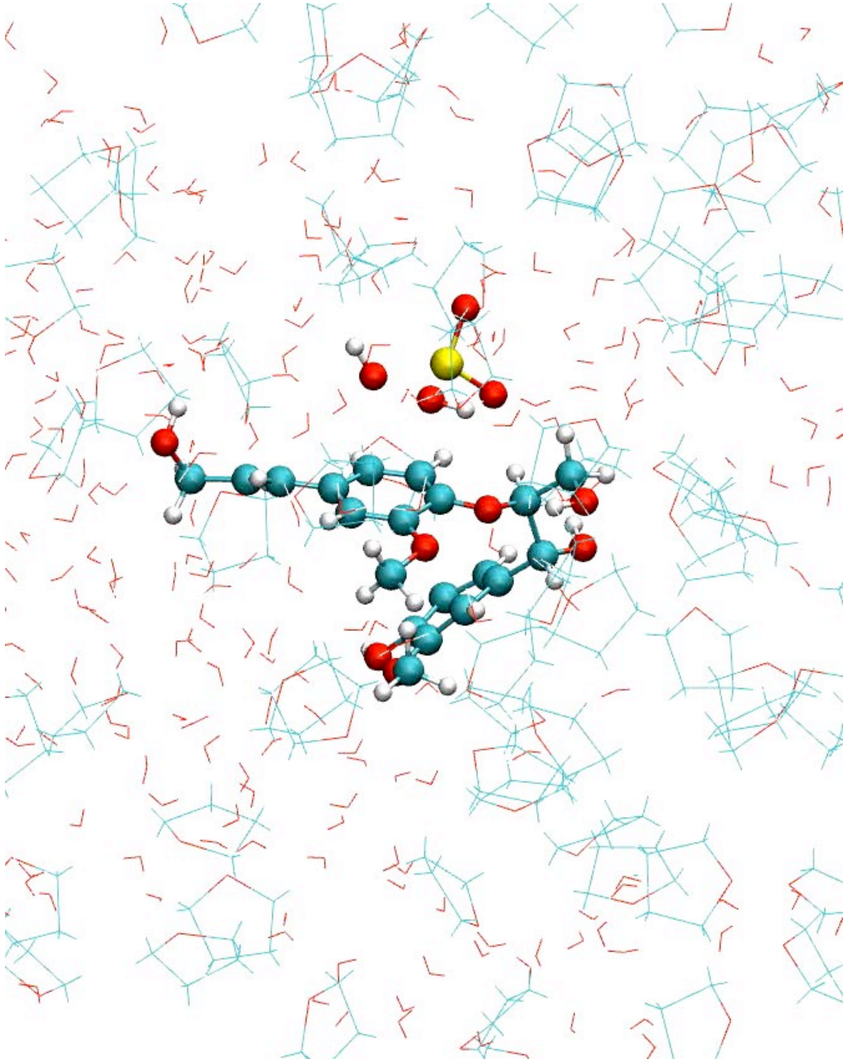
- Eigenvalue SoLvers for Petaflop-Applications (ELPA)
- Matrix Algebra on GPU and Multicore Architectures (MAGMA)
- ELectronic Structure Infrastructure (ELSI)

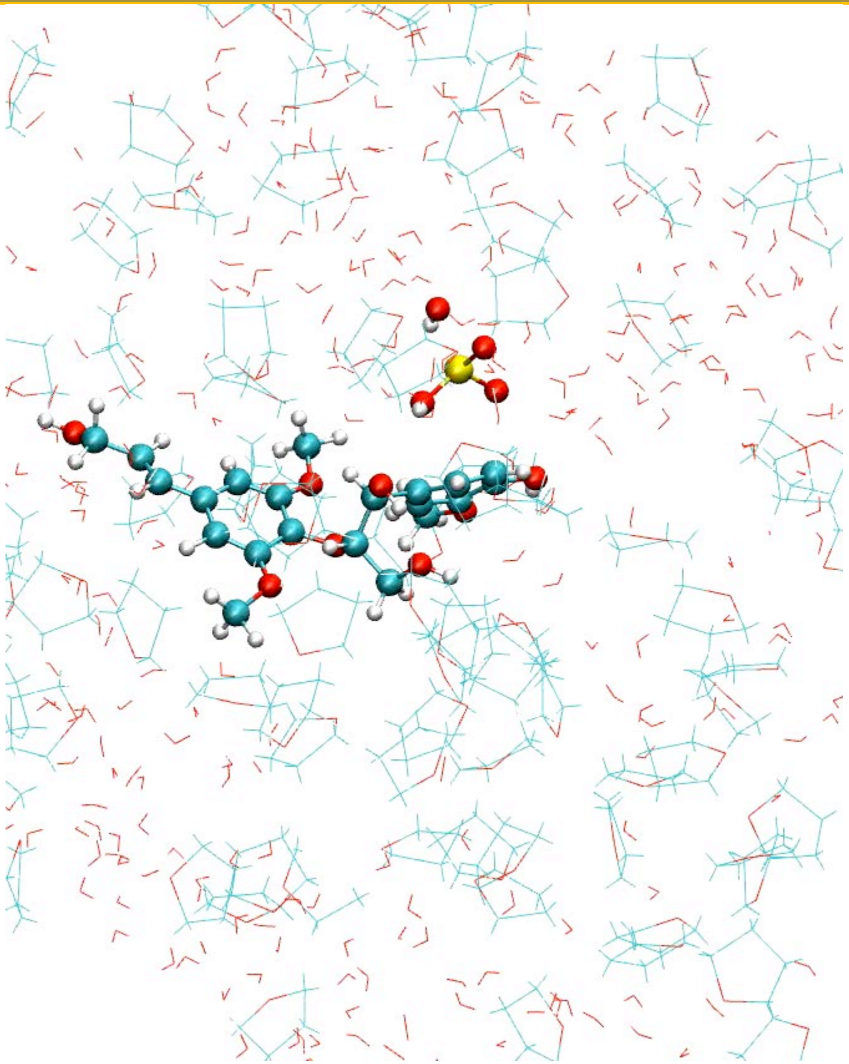
DFTB performace: CPU vs GPU



Comparison of CPU vs GPU (1 node) for geometry optimization of Lignin dimer (Smaller is Better)

Large scale DFTB-MD





Lessons Learned

- The difference in glucan concentration achieved between corn stover and industrial hemp highlighted the need for continuous optimization. Tailoring CELF pretreatment conditions is crucial to maximize efficiency and yield.
- Combining experimental methods with large-scale DFTB simulations proved essential. This synergy aids in accurately representing and understanding chemical reactions, thus enhancing the predictive power of our models.
- Supports two students and a postdoctoral associate.
- Promotes diversity by involving underrepresented minority students.
- Enhances hands-on learning in CO_2 conversion and agriculture.
- The PI and co-PI continue to work together on the large-scale DFTB calculations that would be used to complement the experimental efforts

Plans for future testing

- Continue advancing experimental aspects of the project.
- Explore new molecular configurations in large-scale DFTB simulations to understand reactivity of large biomolecular systems.
- Aim to observe chemical reactions that align more closely with experimental conditions.
- Investigate combined experimental and computational approaches.

Summary

Summary

CELF Pretreatment

- Corn stover: >80% glucan achieved.
- Industrial hemp: 75% glucan achieved.

Molecular Simulations for cellulose formations:

- Increased temperatures can speed up the fractionation of lignin dimers
- a single-node GPU can remarkably speed up DFTB calculations by up to 15 times compared to a single-node CPU.

Future plans

- Improve glucan composition for industrial hemp
- Measure CO_2 emission from fermentation
- AspenOne: optimizing heat recovery

- Large-scale simulation based on DFTB-GPU for both G-G and S-G lignin dimers at 1000K

Combining experimental and computational approaches in optimizing CELF pretreatment and utilizing CO_2 from ethanol fermentation for algal production is essential for advancing cost-effective and efficient CO_2 uptake methods


Thank You
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Acknowledgements

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Acknowledgment: This material is based upon work supported by the Department of Energy Award Number DE-FE0032207.

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