2023 FECM / NETL Carbon Management Research Project Review Meeting

August 28 - September 1, 2023

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

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University of California - Riverside

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Outline

- Short introduction
- Why use *Nannochloropsis* algae for CO_2 uptake
- Large-scale simulations for cellulose formation
- Preliminary work with density functional tight binding calculations
- What's next?

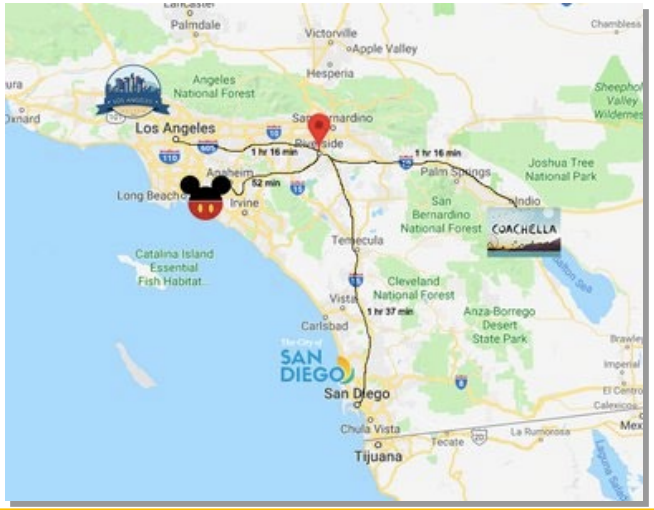
Introduction

Cai Group
(Experimental)

Center for Environmental Research and Technology (CE-CERT)

Wong Group
(Computational)

Materials Science & Engineering (MSE) Building



Cellulosic ethanol

Ethanol fermentation → traditional liquid fuel production

glucose $\xrightarrow{yeast}$ ethanol + carbon dioxide

$C_6H_{12}O_{6(aq)} \xrightarrow{yeast} 2C_2H_5OH_{(aq)} + 2CO_{2(aq)}$

Saving 50 %

CO_2 is still released

↓

several ethanol plants have invested

Challenge ↓ **Economic**

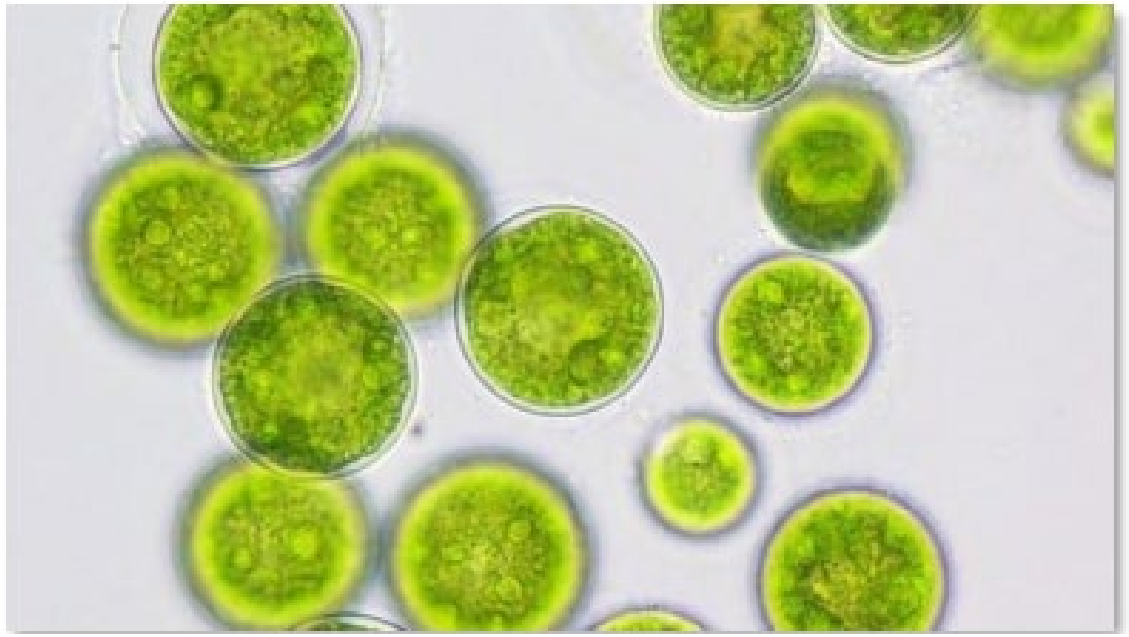
Cellulosic ethanol

Better than corn ethanol

> 20-30 gCO_2e/M

Nannochloropsis for CO_2 Uptake

- *Nannochloropsis*: cellulose-producing algae
- Can capture waste CO_2 from ethanol fermentation to produce
  - Algal lipids used for biodiesel production microcrystalline cellulose as high-value co-product



Nannochloropsis for CO_2 Uptake

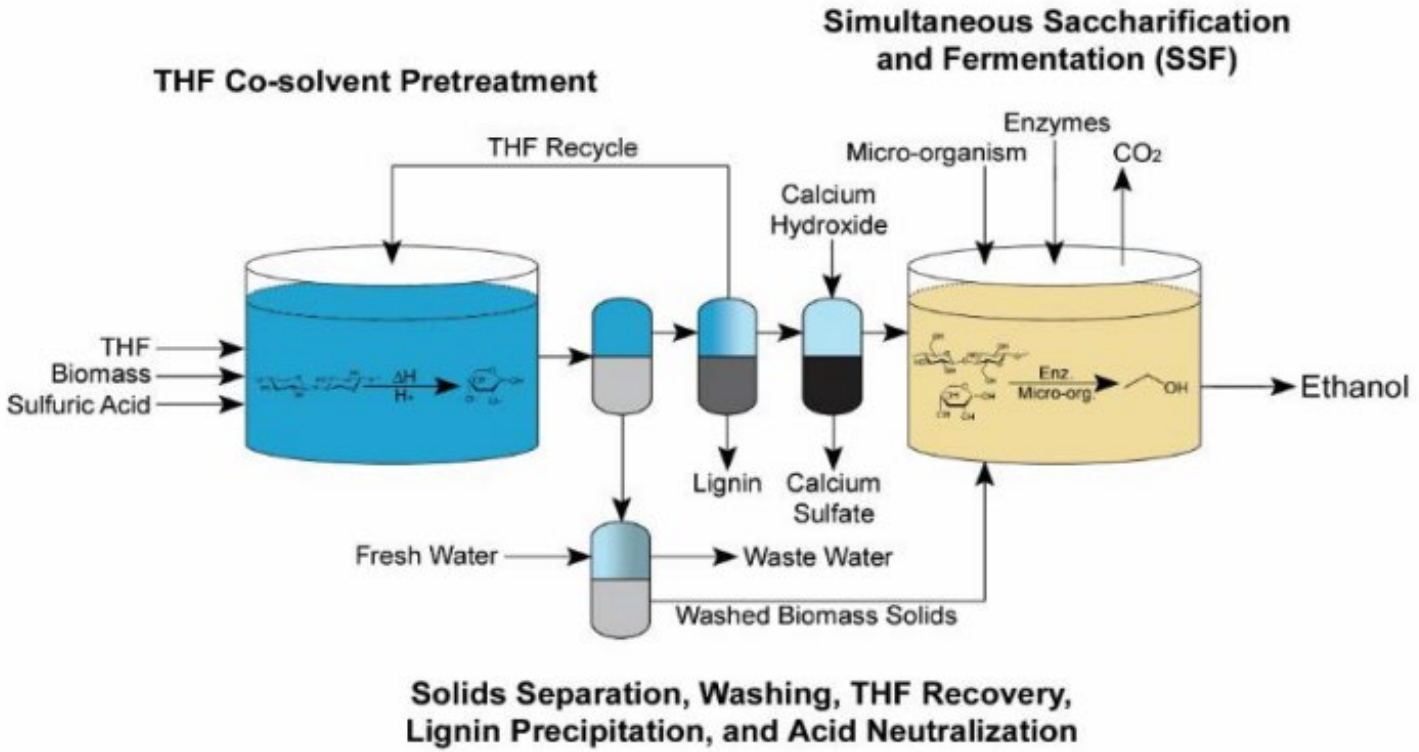
- **Economic & environmental benefits**
  - Capturing CO_2 from ethanol fermentations supports algal production and enables potential greenhouse gas savings
  - Lignin generated as byproduct can provide heating to support cellulosic ethanol production & algal cellulose production
  - Lignin is biogenic: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

Pretreatment Approaches

Co-Solvent Enhanced Lignincellulosic Fractionation (CELF) developed by experimental collaborator (Dr. Cai) to pretreat lignincellulosic biomass

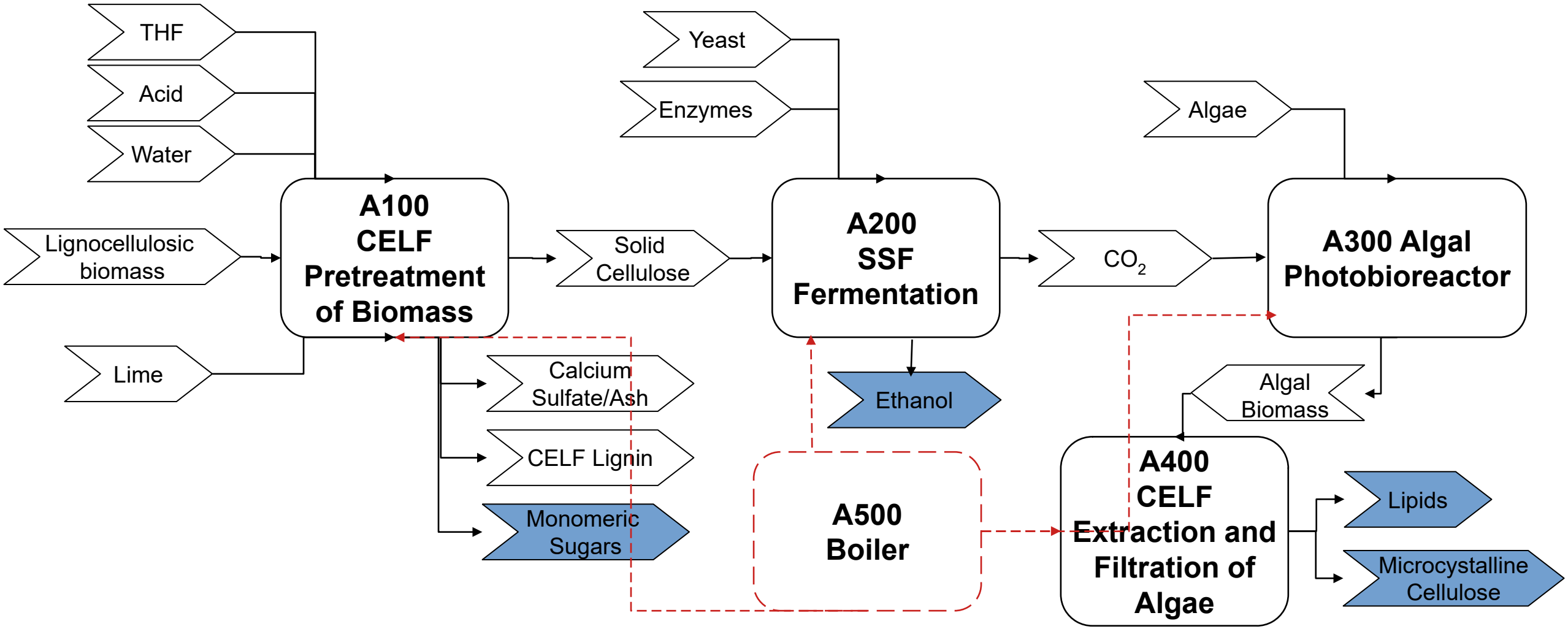
CELF nondestructively fractionates lignin, oleic, & protein in any plant-based

Could be extended to algae fractionating & extract *nannochloropsis*



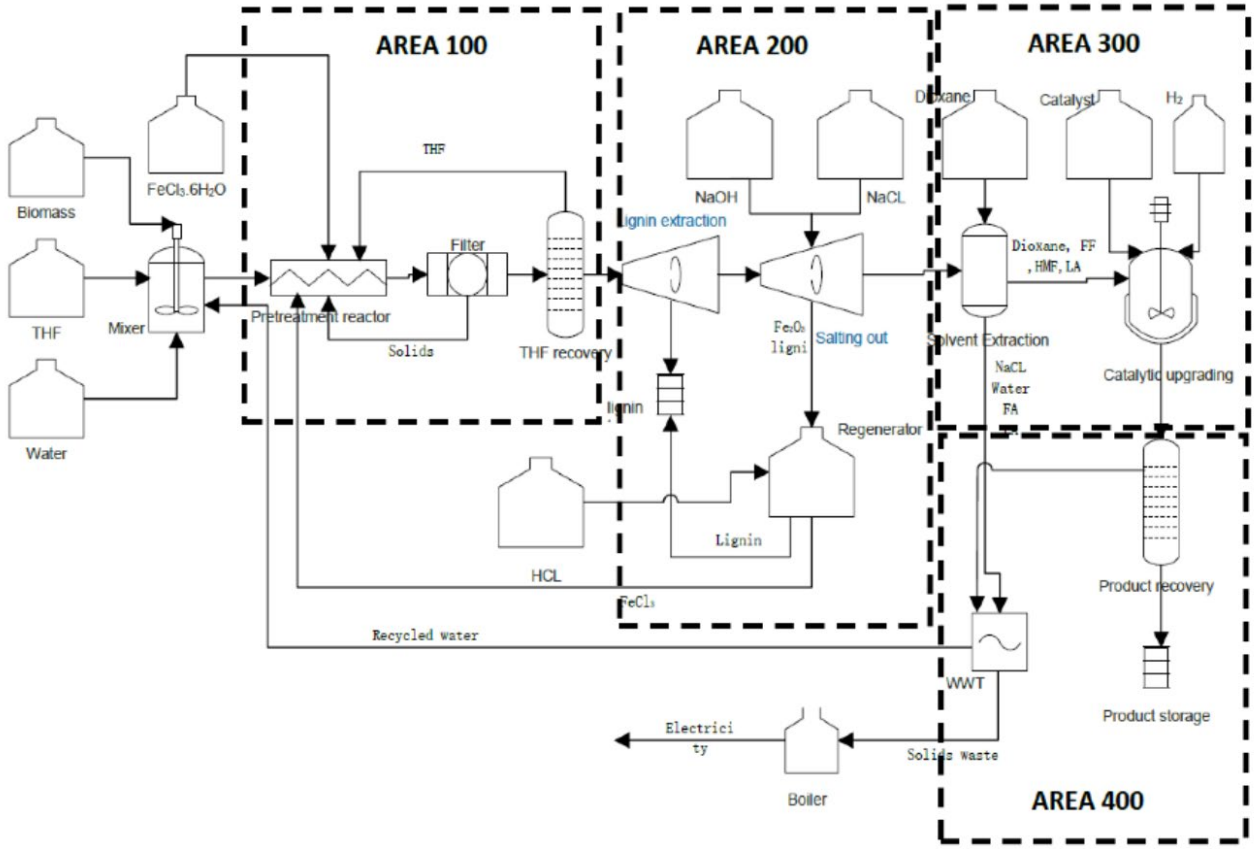
Process diagram flow

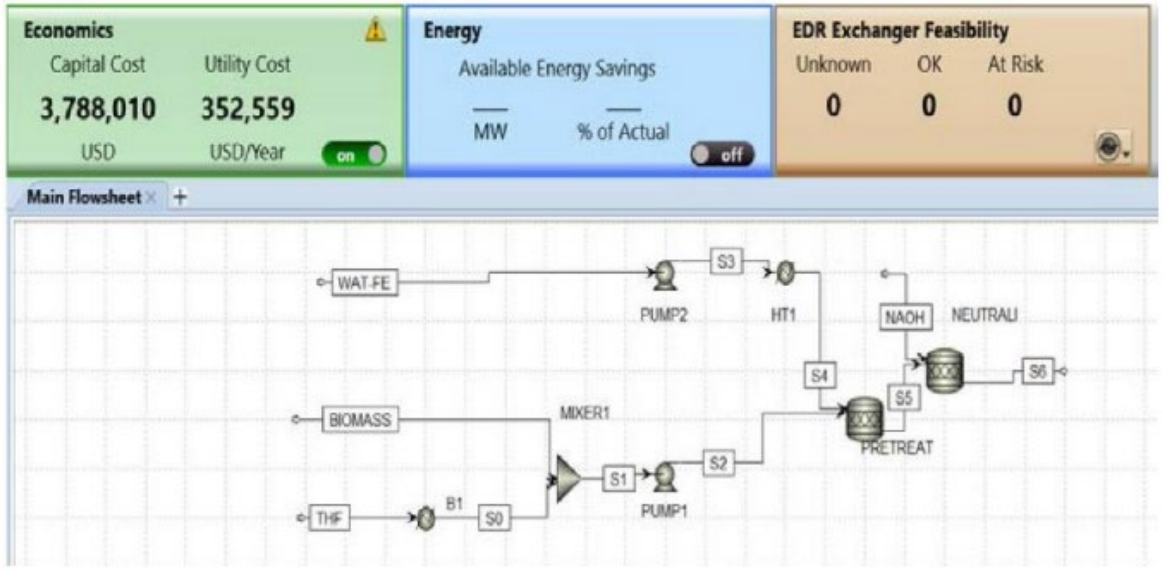
co-locating cellulosic ethanol fermentation with algal lipid and cellulose production



Life cycle analysis

Techno-economic & life cycle analysis will support quantitative outcomes





AspenOne software using modified GREET model for cellulosic ethanol will be used

Preliminary work with CELF

- Performed CELF pretreatment of industrial hemp and corn stover to prepare glucan-rich material for digestion by SSF (simultaneous saccharification and fermentation).

- CELF pretreated corn stover achieved >80% glucan, however, CELF pretreated industrial hemp only reached 75% (target 80%).

- We have begun to optimize CELF conditions to further improve glucan composition for industrial hemp. Once we have obtained similar glucan concentrations in both feedstock types, we can begin to measure CO_2 emission from fermentation.

- Our modeling team has successfully integrated CELF pretreatment, solids filtration, solvent recovery, and neutralization processes in AspenOne. We are currently optimizing heat recovery to calculate initial energy balance Our goal is to target total heat utilization of 4.5kwh/tonne biomass input.

Preliminary work with CELF

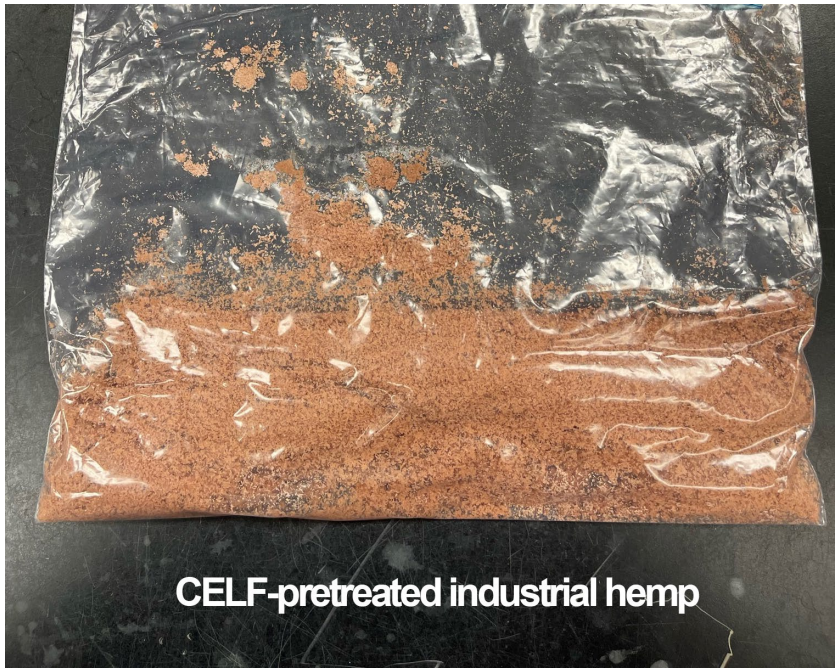


Figure 1. Knife-milled industrial hemp stalk subjected to mild CELF pretreatment

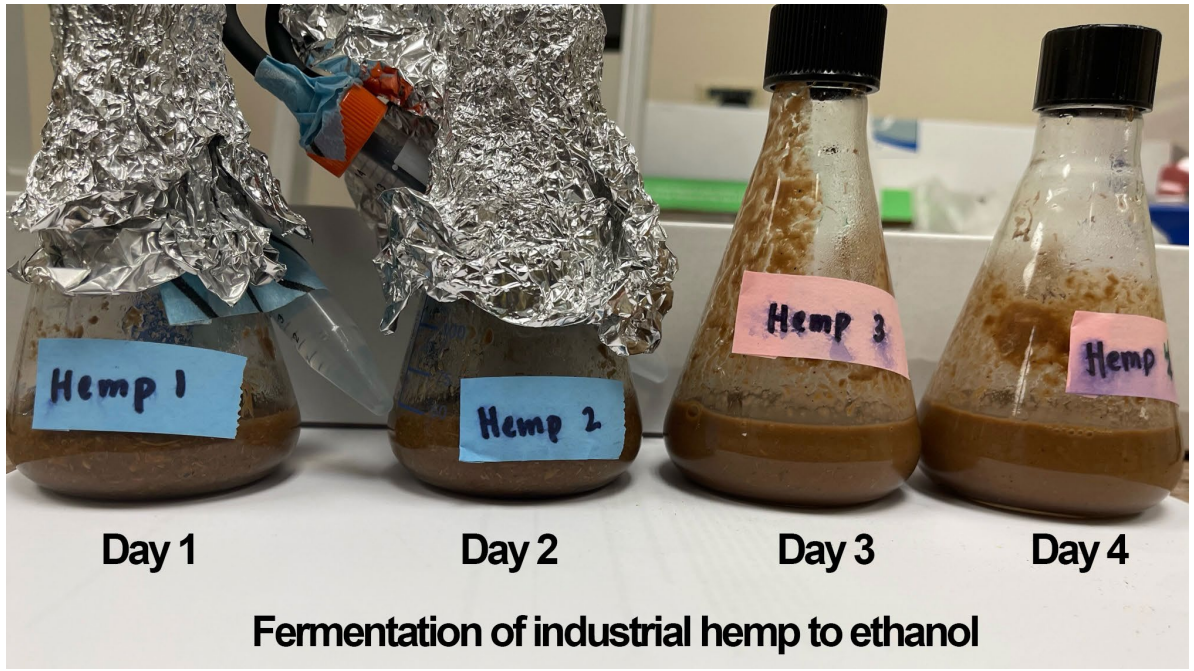
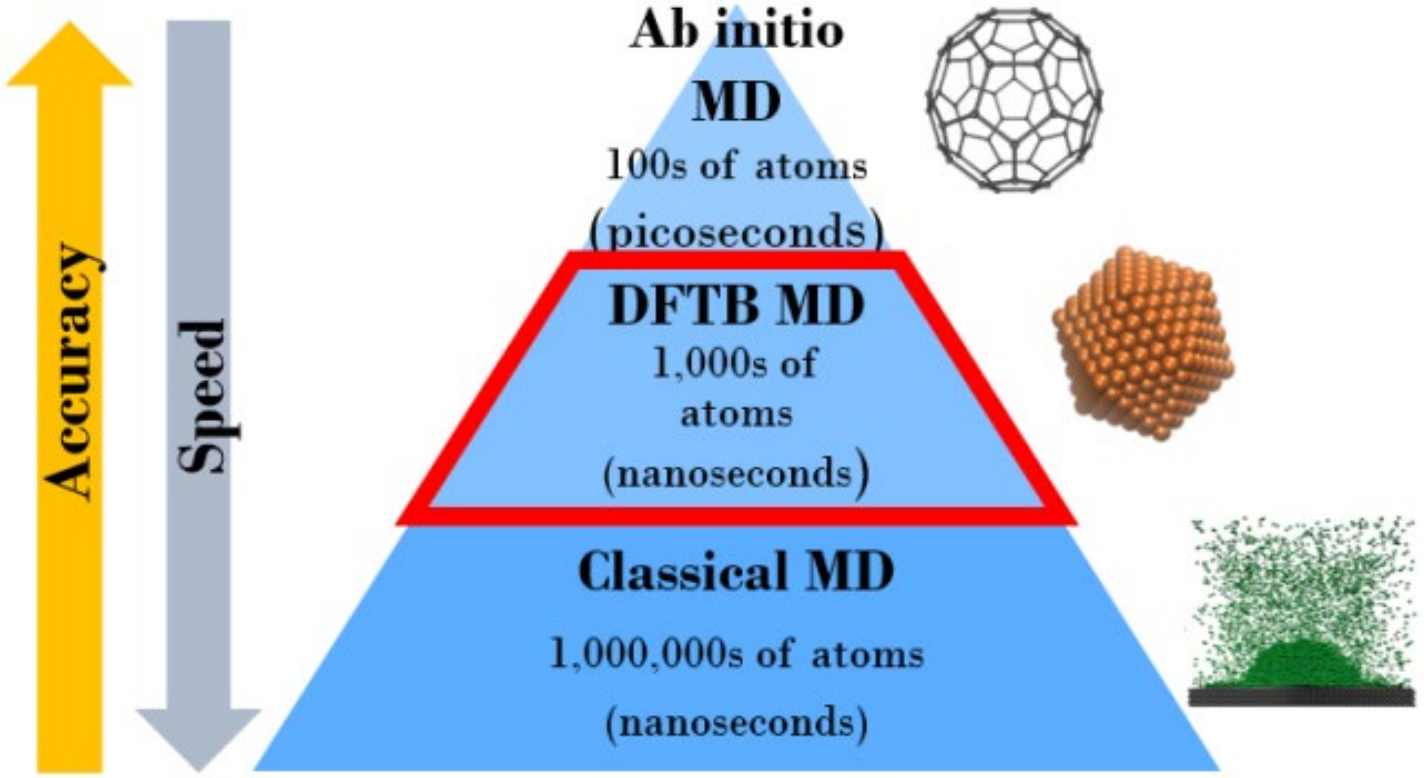


Figure 2. SSF of CELF-pretreated industrial hemp at 100 g/L initial loading. Observed rapid solubilization of solids over first four days. Ethanol analysis under way.

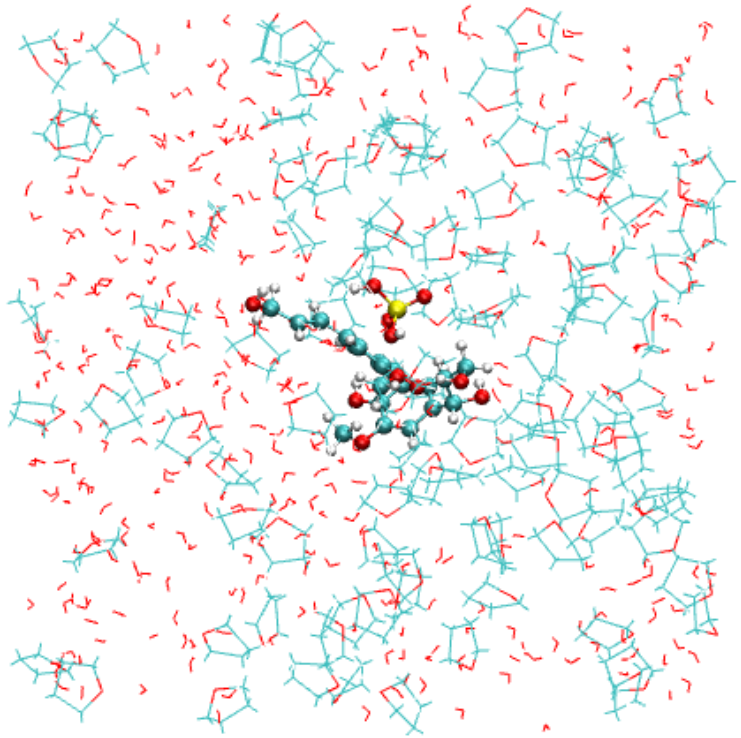
Molecular modelling

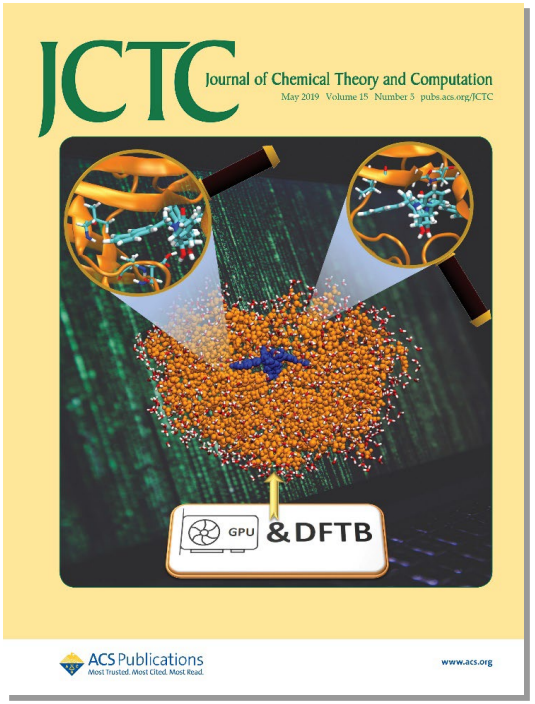
- DFT good for small systems
- Classical molecular dynamics can handle large systems but are missing the quantum part
- DFTB merges reliability of DFT with computational efficiency of tight binding



Molecular modelling

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





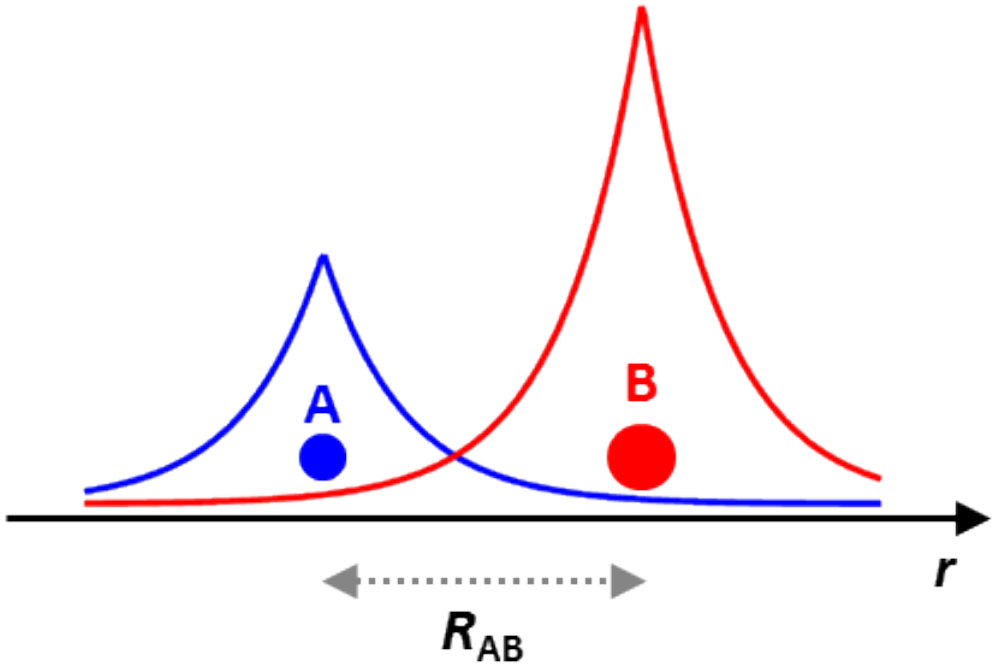
Cover of May 2019 issue (NETL Project DE-FE0030582)

S. I. Allec, Y. Sun, C.-en A. Chang, B.M. Wong
J. Chem. Theory Comput. **15**, 2807 (2019)

DFTB Primer

DFTB: coarse-grained, parameterized DFT with atomic-centered basis functions

Computational savings: pre-parameterized “basis” functions



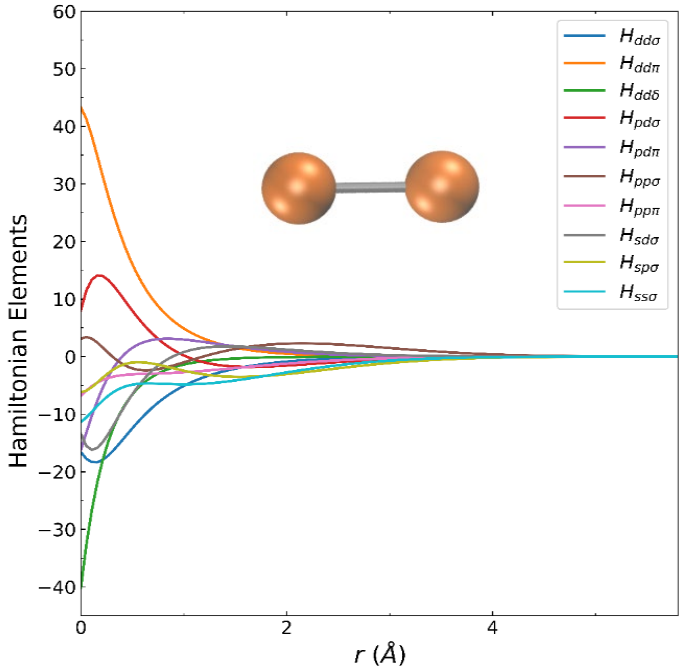
pre-tabulated as function of R_{AB}

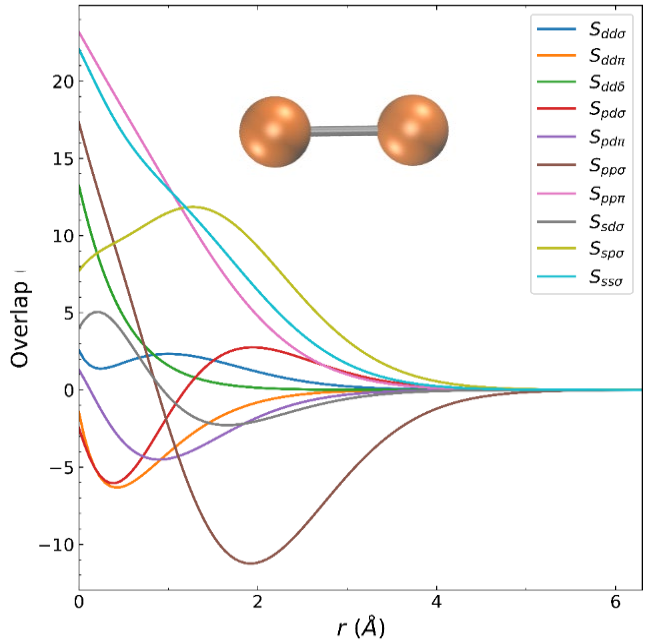
simplifies integrals in SCF procedure

DFTB Primer

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

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





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

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

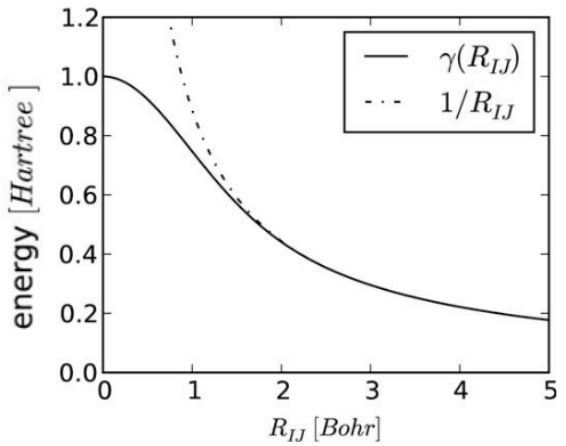
parametrized beforehand from DFT calculations

DFTB Primer

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

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

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



Computational Materials Science 47 (2009) 237–253

3ob-3-1 skf parameter

param	e_d	e_p	e_s	U_d	U_p	U_s	f_d	f_p	f_s
C	0.0	-0.194	-0.505	0.365	0.365	0.365	0.0	2.0	2.0
H	0.0	0.0	-0.239	0.419	0.419	0.419	0.0	0.0	1.0
O	0.0	-0.332	-0.879	0.236	0.236	0.236	0.0	4.0	2.0
S	0.321	-0.258	-0.630	0.328	0.328	0.328	0.0	4.0	2.0

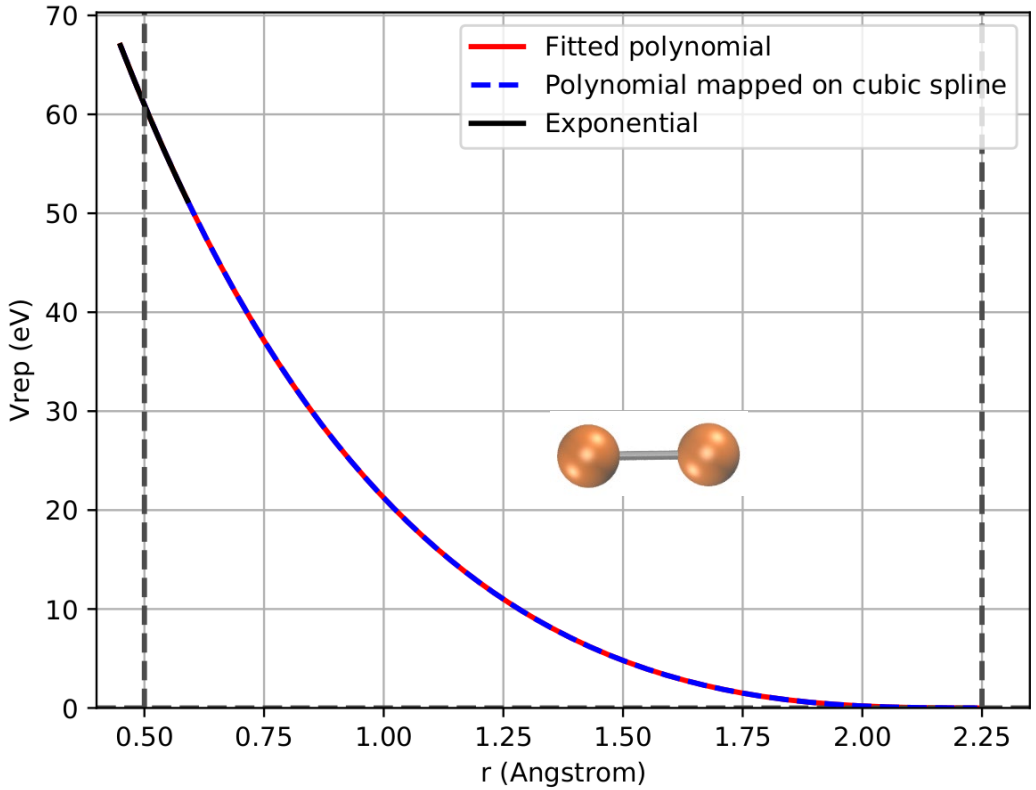
e = onsite energy, U = Hubbard U, f = occupation number

parametrized beforehand from DFT calculations

DFTB Primer

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

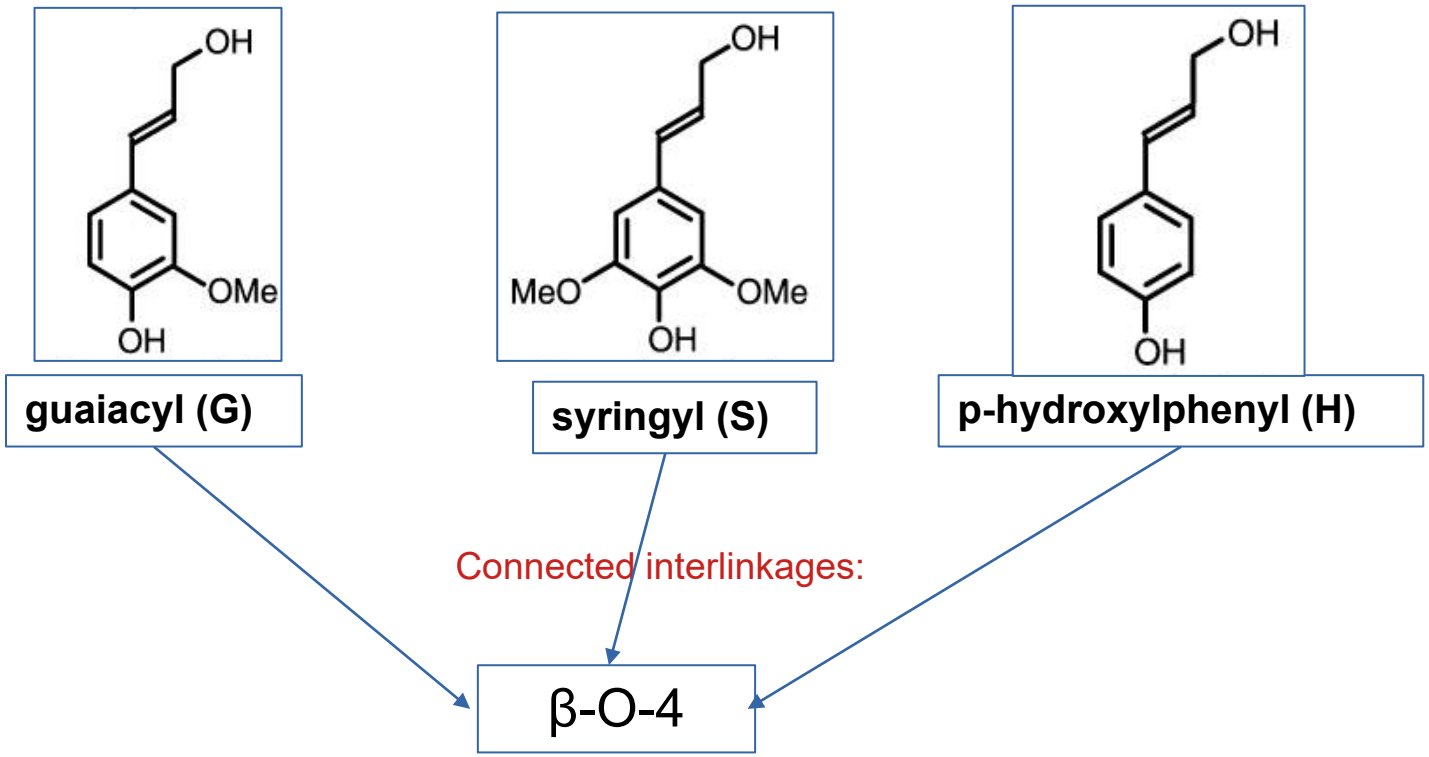
$$E_{rep} = \sum_{I<J} V_{rep}^{IJ}\left(R_{IJ}\right)$$



Pre-parameterization allows fast calculations of large systems

Simulated CELF Pretreatment

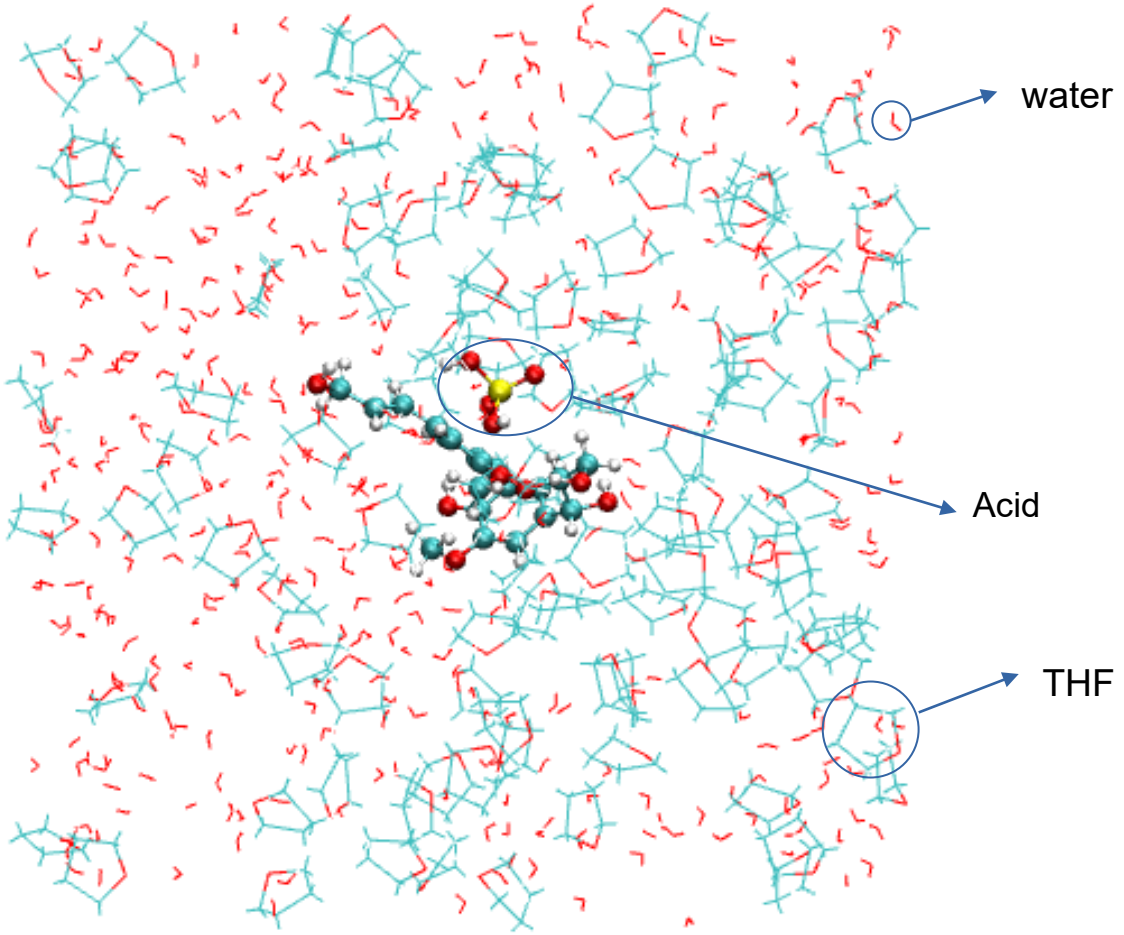
Lignin subunits:



Model of lignin dimer β-O-4:

- G-G
- G-S
- S-G

DFTB



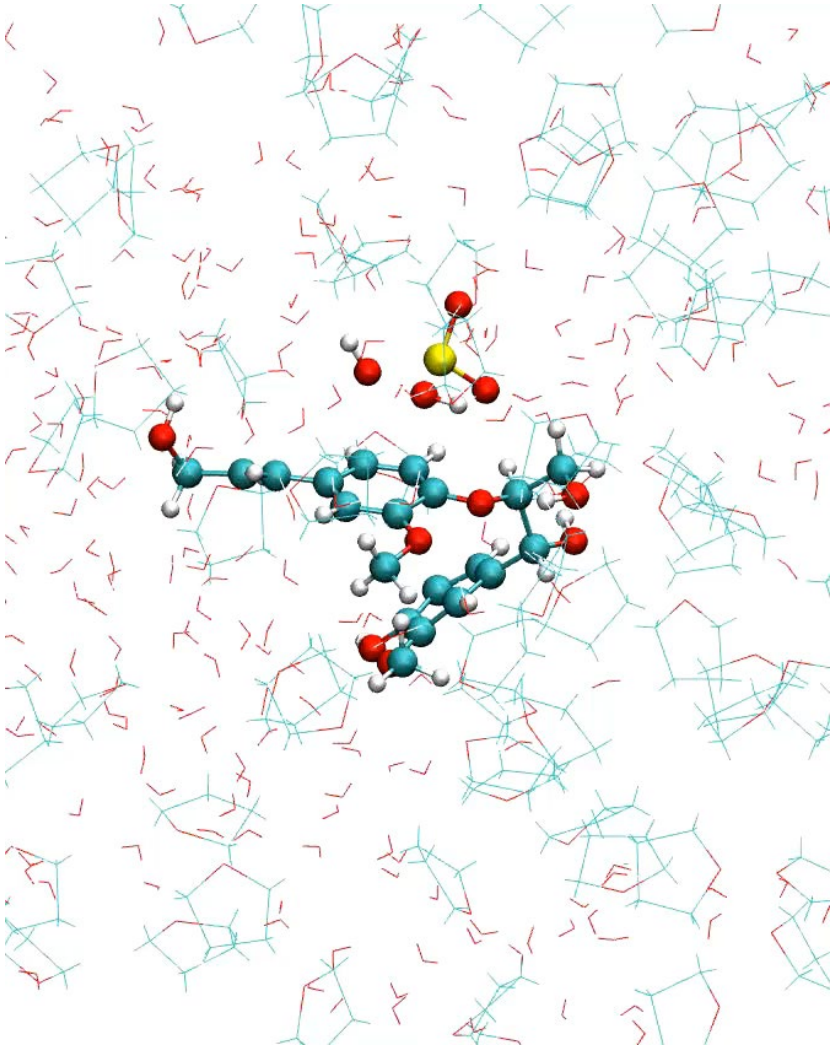
GG dimer β-O-4 (2560 atoms)

- DFTB3 (3ob-3-1) + DFT-D3 disp effect
- PBC (mimic periodicity)
- DFTB relaxation (Force < 0.07 eV/A)
- Co-solvent:

  - 1:1 THF:Water v/v ratio

  - Acid (H_2SO_4)

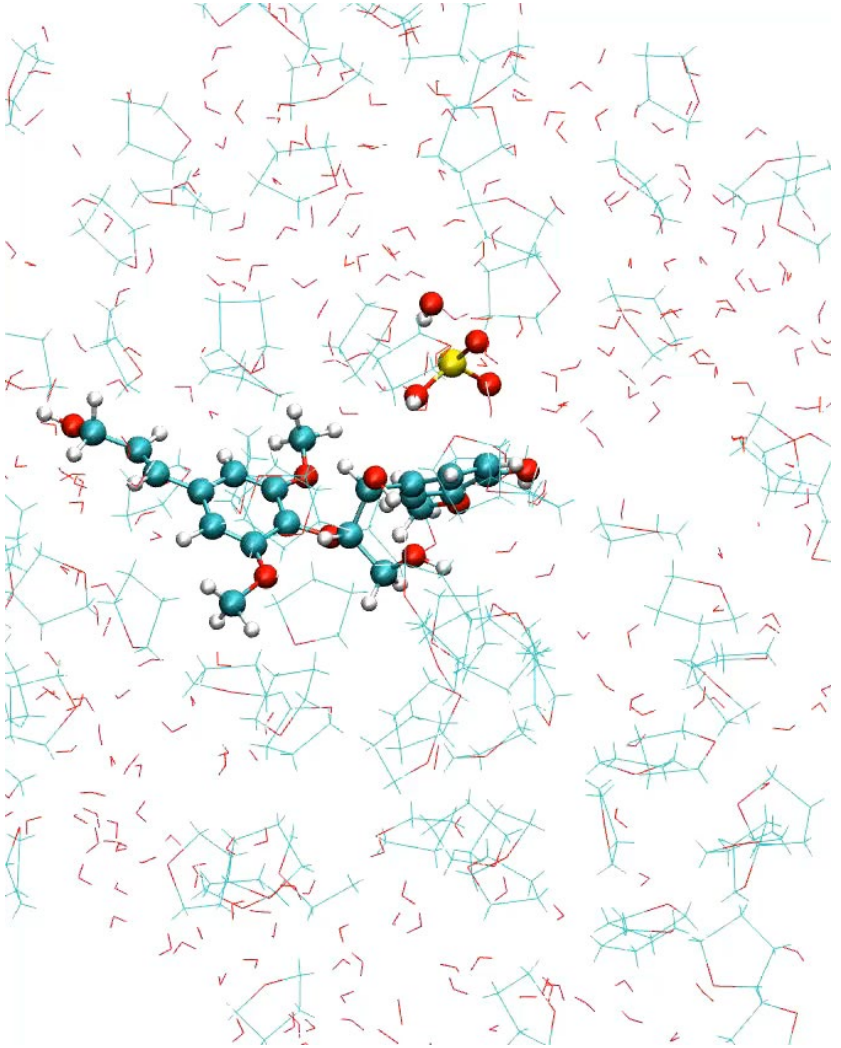
Preliminary work with DFTB-MD



- GG dimers
- NVT (423 K): Nose-Hoover Thermostat
- @NERSC (National Energy Research Scientific Computing)

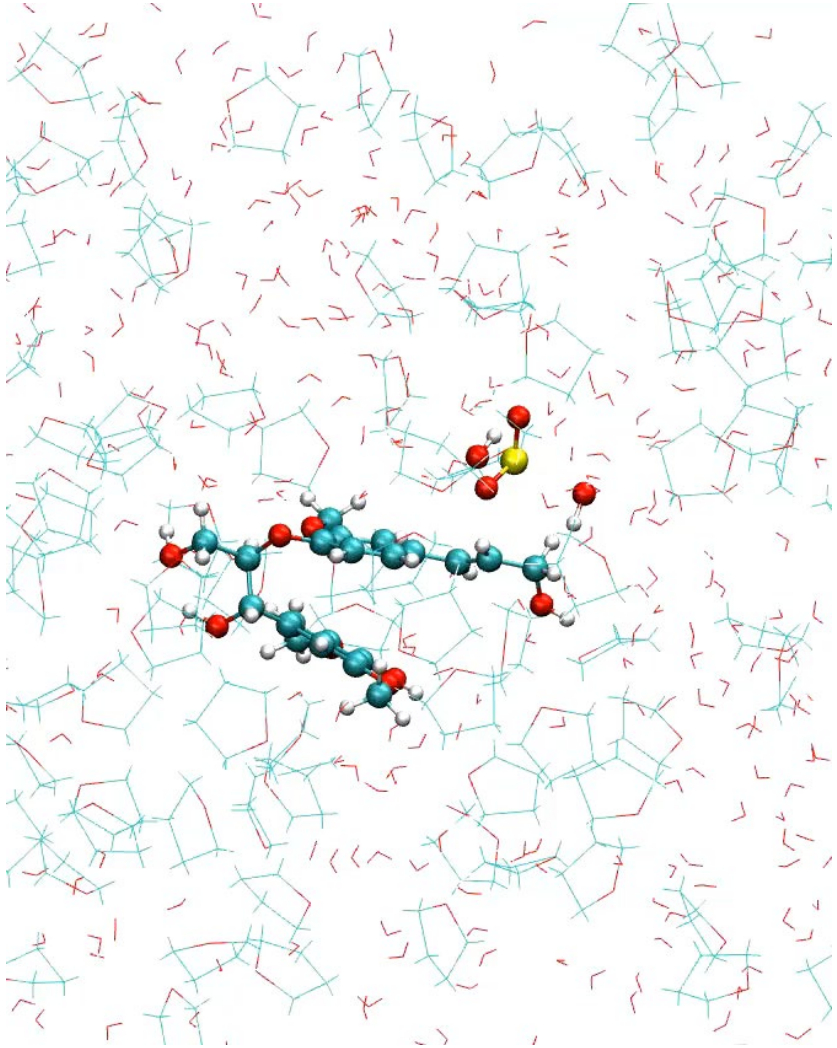
Preliminary work with DFTB-MD

- GS dimer



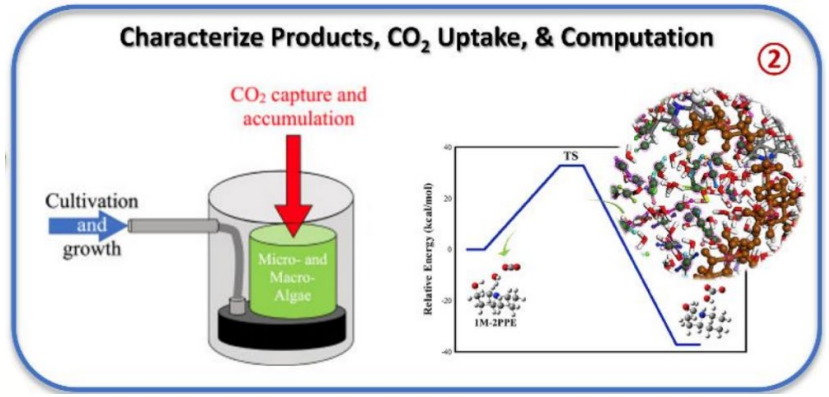
Preliminary work with DFTB-MD

- SG dimer

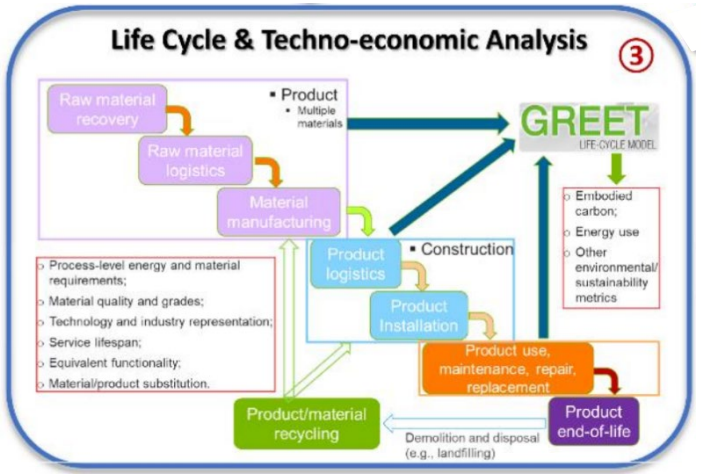


Summary

CELF



DFTB enables fast predictions of cellulose formation



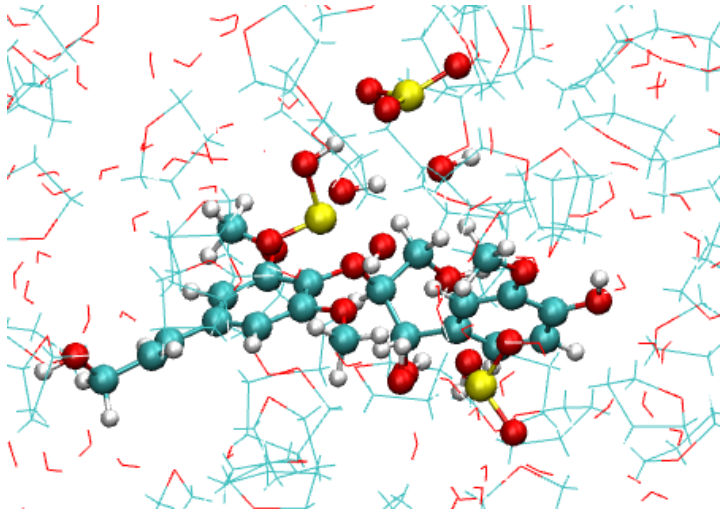
Outlook

CELF Pretreatment

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

DFTB-MD calculations for cellulose formations:

- Longer time scale
- Other dimer structures →
  - G-H
  - H-G
  - H-H
  - H-S
  - S-H
  - S-S
- Vary temperature
- Add more acid (SO_4H_2)



Acknowledgements

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Thank You
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