Combustion Lab

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Near-critical Fluids Treatment for Liquefaction and Extraction of Bio-Fuels

April 4, 2023

Systems Development and Integration – Emerging and Supporting Technologies

A. JAMES CLARK SCHOOL OF ENGINEERING

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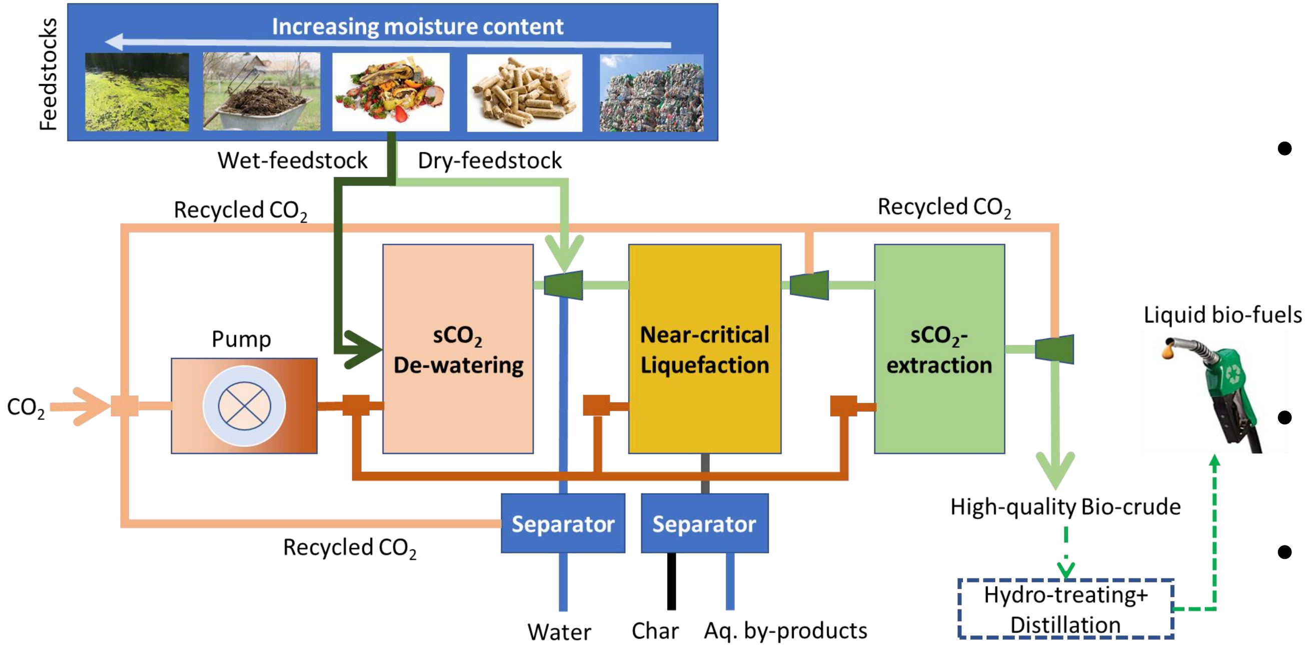
Project Overview

- **Goal:** Develop near-critical integrated liquefaction extraction (NILE) pathway to convert and fractionate various biomass, and waste components into deployable biofuels for significant GHG emission reduction

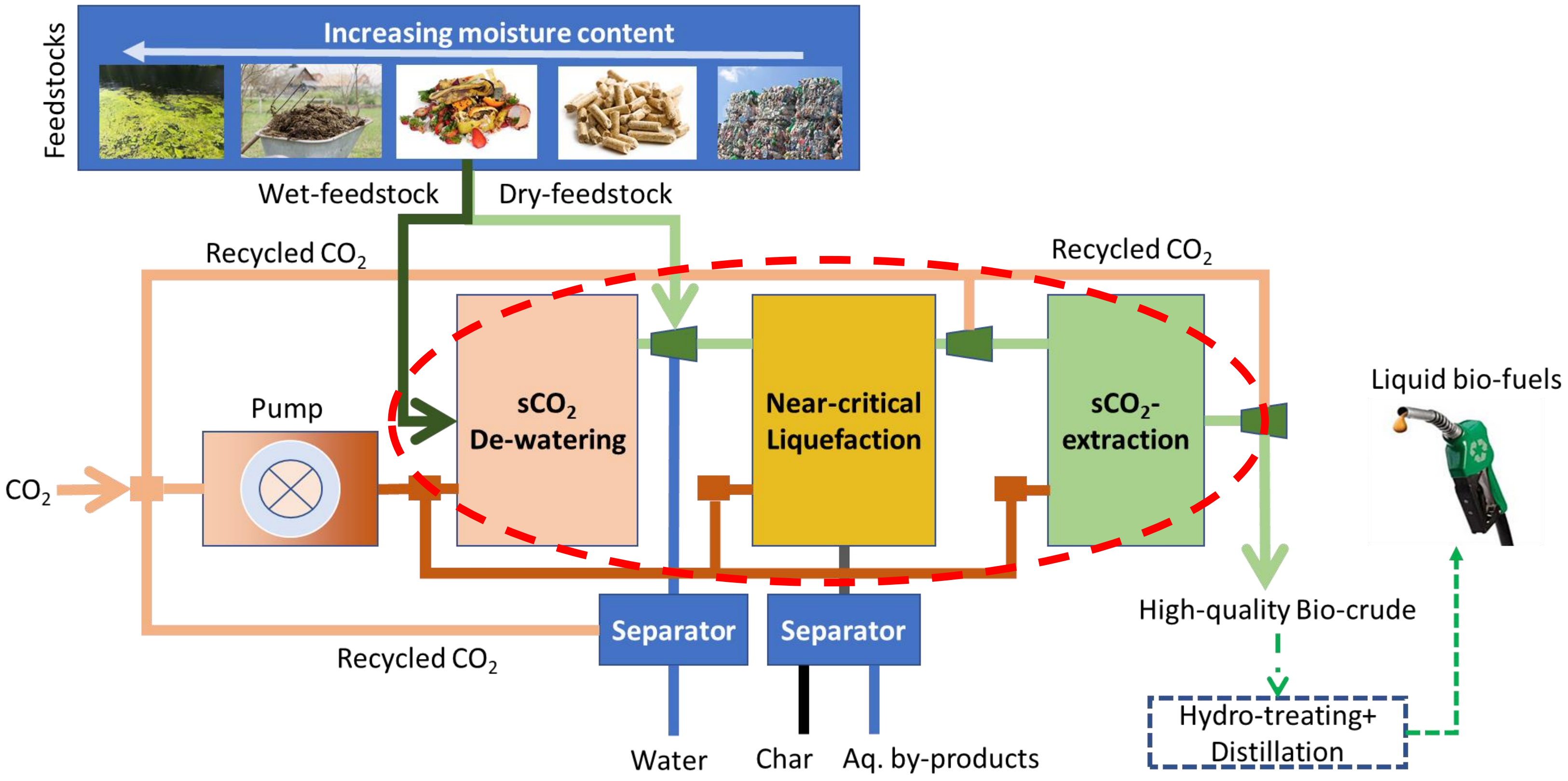


Heilmeier Catechism:

- **Aim:** Utilize supercritical CO_2 to achieve high-quality biocrude from diverse feedstocks for efficient hydrotreating
- **Today:** Processed solvent in solvothermal techniques → solvent handling, recovery issues and higher costs (ex: water→ process water)
- **Important:** Easier solvent recovery, biocrude fractionation for deployable fuels
- **Risks:** High-pressure biomass feeding, integration, and hydrotreating heavy-fractionates

Near-critical-Integrated-Liquefaction-Extraction (NILE)

Project Overview

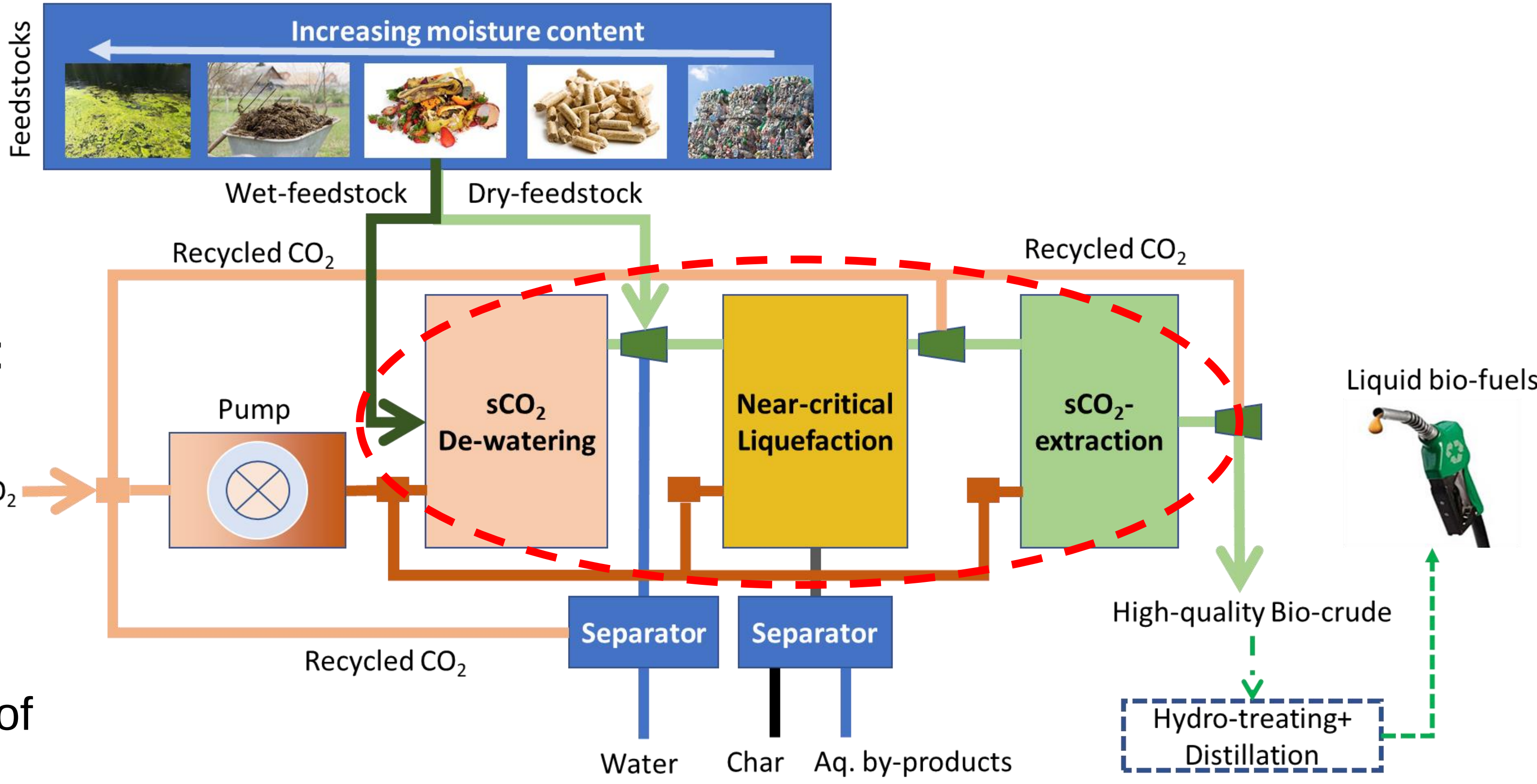


3 key steps in feedstock conversion

- **Utilize supercritical CO_2**
- GHG reduction via:
  - ✓ Efficient feedstock moisture handling
  - ✓ Improved liquefaction yields
  - ✓ Clean by-product separation
  - ✓ CO_2-led quality improvement in bio-crude
- Fuel cost reduction via:
  - ✓ Energy reduction
  - ✓ GHG reduction
  - ✓ Feed flexibility
  - ✓ Efficient hydrotreating
  - ✓ Process optimization

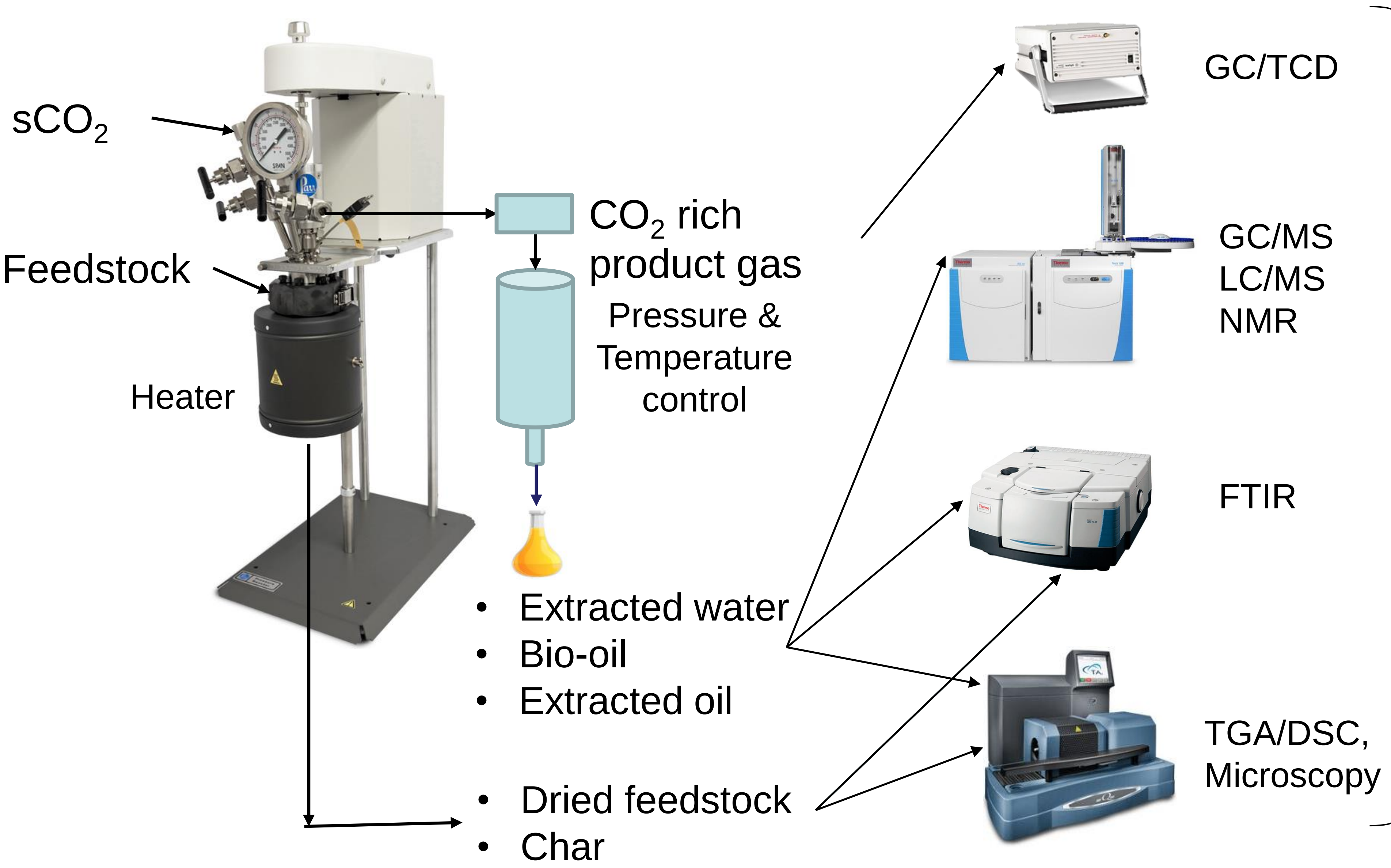
Technical Approach

- 3 key processes to improve bio-crude production:
  - sCO2 dewatering process:
    - ➢ High throughput;
    - ➢ Low water cleaning requirement.
  - Near-critical liquefaction with sCO_2:
    - ➢ Low energy needs;
    - ➢ High bio-crude yield;
    - ➢ High solvent tunability.
  - sCO2 extraction:
    - ➢ Low Oxygen/Carbon content of bio-crude produced;
    - ➢ Less hydrotreatment requirement.



3 key steps in feedstock conversion

Technical Approach



Key features:

- Feedstock characterization
- Compositional analysis and quality-assessment for bio-crude
- Thermal stability
- Kinetics and calorific analysis
- Carbon conversion

Challenges:

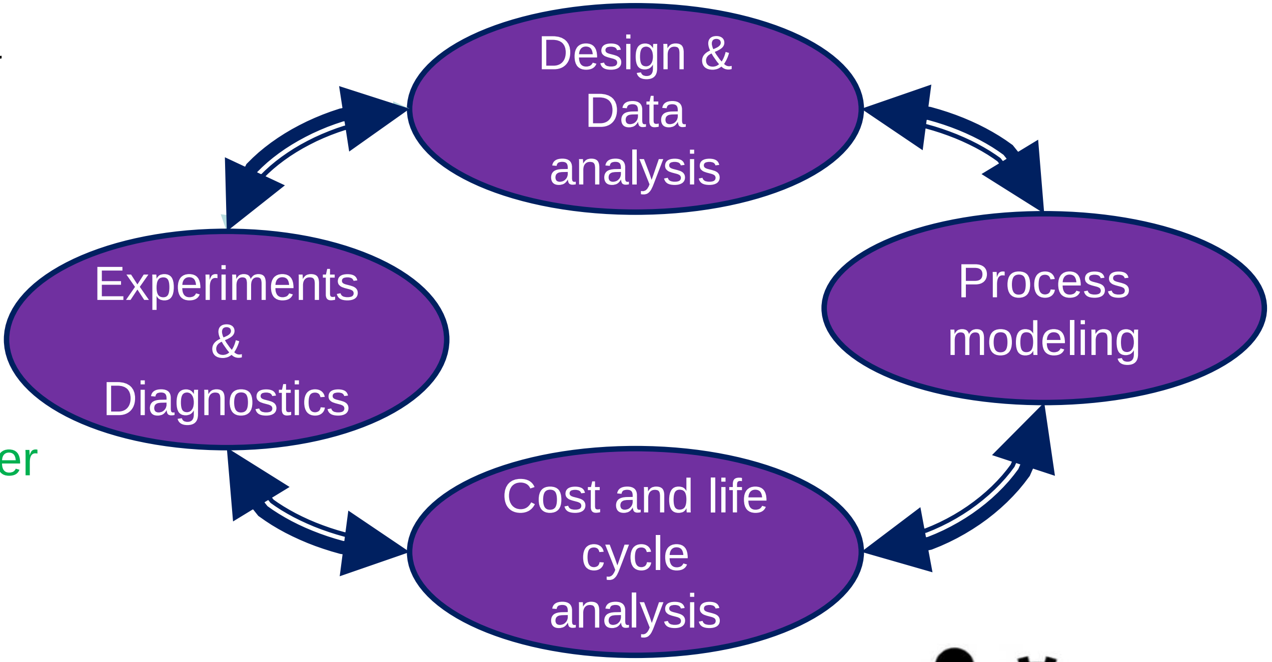
- Waste stream (chars) handling
- Complex chemistry and co-solvent behavior

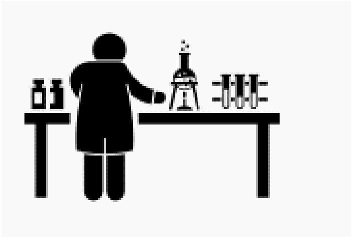
Management Approach

Prof. Ashwani K. Gupta

Prof. Peter Sandborn

1 postdoctoral researcher
1 undergrad. Intern*





1 postdoctoral researcher
1 graduate research assistant
1 undergrad. Intern*

1 graduate research assistant
1 undergrad. Intern*

1 graduate research assistant
1 undergrad. Intern †

*MSI/HBCU interns
(McNair scholars)
†UG team

Cost and LCA Modeling Approach

- Create a model based on the cost of ownership of equipment/facilities.
  - The model proposed will be stochastic.
  - Inputs:
    - Process/equipment/facilities procurement and operation costs
    - **Optimization for GHG reduction (Go/No-go decision point)**
    - Weighted average cost of capital (WACC)
    - Material and labor costs
    - Equipment/facilities operational life
    - Yield
    - Reliability (and maintenance costs)
    - Cost of disposal of unusable byproducts

Risks Analysis and Mitigation Strategies

Scale-up

- ❖ High-pressure biomass feeding, thermochemical uniformity
- ✓ Multiple scale 1-6 L batch reactors and semi-continuous operation
- ✓ Moisture control and CO_2 for biomass handling

Process integration

- ❖ By-product (char) separation, pressurization, Reactor CapEx
- ✓ Bio-crude extraction directly from liquefaction, P and T optimized
- ✓ Process intensification, continued components' compatibility tests

Hydrotreatment

- ❖ Heavy fractionates hydrotreatment failure
- ✓ High biocrude to crude ratio mixtures in hydrotreating for light fractionates
- ✓ Low biocrude to crude ratio mixtures in hydrotreating for heavy fractionates
- ✓ Process optimization (H_2, catalyst, and carbon conversion)

DEI and Outreach Approach

- Mentoring UMD Center for Minorities in Science & Engineering undergraduate students' research; **Univ. Texas, El Paso** underrepresented Hispanic minorities **student research internship** at UMD & faculty seminars at UTEP;
- Community impact from direct to Prince George's public school, high school student research interns (during years 1-4), and The Maryland Day - community outreach (annual event).
- Diversity training: ADVANCE TERP Allies bias training (in year 1) and diversity awareness training (during years 2-4 held annually);

Table 1. Diversity objective and milestones	FY1			FY2			FY3			FY4		
	Fall	Sp	Su	Fall	Sp	Su	Fall	Sp	Su	Fall	Sp	Su
Objective 1. Diversity training												
Milestone 1.1 ADVANCE TERP Allies bias training		■										
Milestone 1.2 Diversity awareness training					■			■			■	
Milestone 1.3 Participant climate questionnaires		■			■			■			■	
Objective 2. Fostering diversity in future workforce												
Milestone 2.1 CMSE undergraduate student research	■	■	■	■	■	■	■	■	■	■	■	■
Milestone 2.2 McNair Scholars research projects			■			■			■			■
Milestone 2.3 UTEP UMR graduate students research		■	■		■	■		■	■		■	■
Milestone 2.4 Participant climate questionnaires			■			■			■			■
Objective 3. Community impact												
Milestone 3.1 PGCPS high school research projects			■			■			■			■
Milestone 3.2 Maryland Day-Renewable energy booth		■			■			■			■	
Milestone 3.3 Participant feedback via PGCPS teacher			■			■			■			■

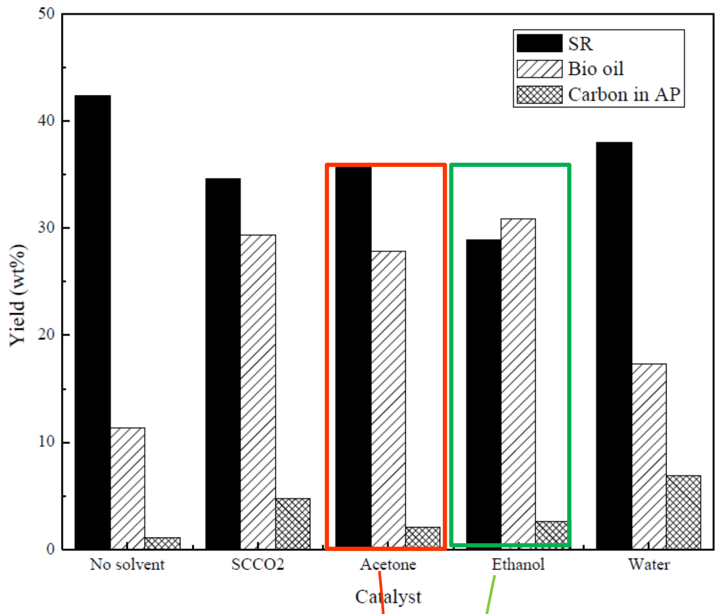
Progress and Outcomes

- **Project Schedule:**
- **Task 1.0: Initial Verification**
- **Task 2.0:** Test-rig design, parts acquisition and building scaled test components (M4-M6)
- **Task 3.0:** Development of sCO_2-based dewatering of bio-feedstocks (M4-M30)
- **Task 4.0:** Development of near-critical liquefaction of bio-feedstocks (M4-M36)
- **Task 5.0:** Development of sCO_2 fractionation of bio-crude (M13-M36)
- **Task 6.0:** Continuous demonstration of process components (M31-M48)
- **Task 7.0:** Process modeling and optimization for life-cycle and cost-analysis (M7-M48)

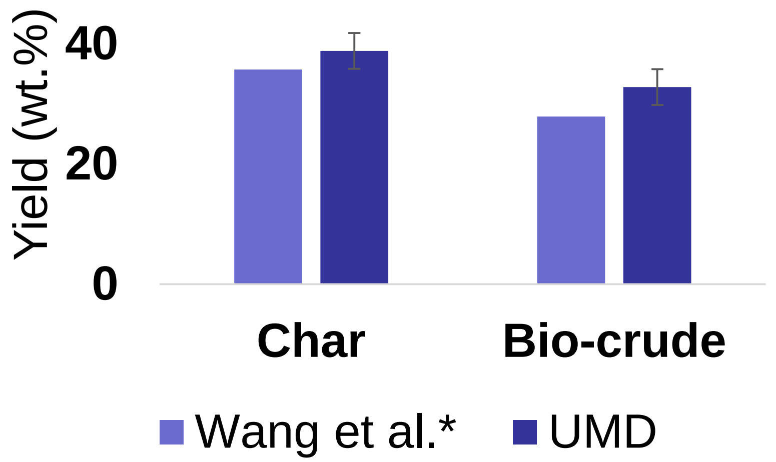
- **Go/No-Go Decisions:**
- **GNG#1:** Initial verification
- **GNG#2:** Moisture control, yield improvement, heating value>30 MJ/kg, water content<1% [M18]
- **GNG#3:** GHG reduction>70%, biocrude compatibility with crude [M36]
- **End goal:** 100/500 hrs operation, cost reduction [M48]

Progress and Outcomes

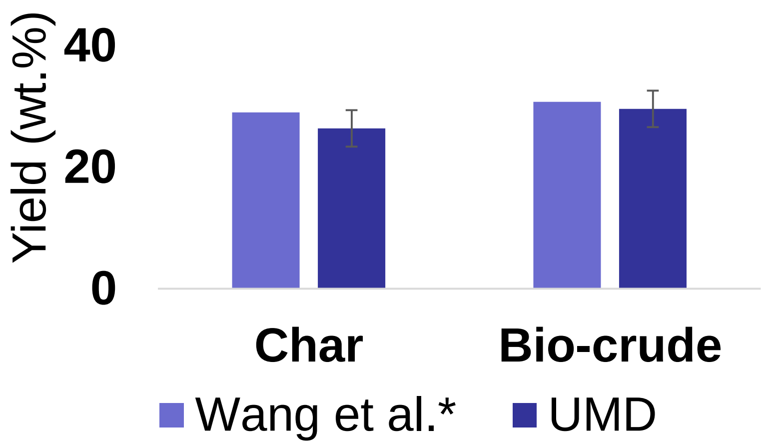
Initial verification process:



Acetone: 300 °C for 2 hr, 10% K_2CO_3



Ethanol: 300 °C for 2 hr, 10% K_2CO_3



*Wang Y, Wang H, Lin H, Zheng Y, Zhao J, Pelletier A, et al. Biomass and Bioenergy 2013;59:158–67.

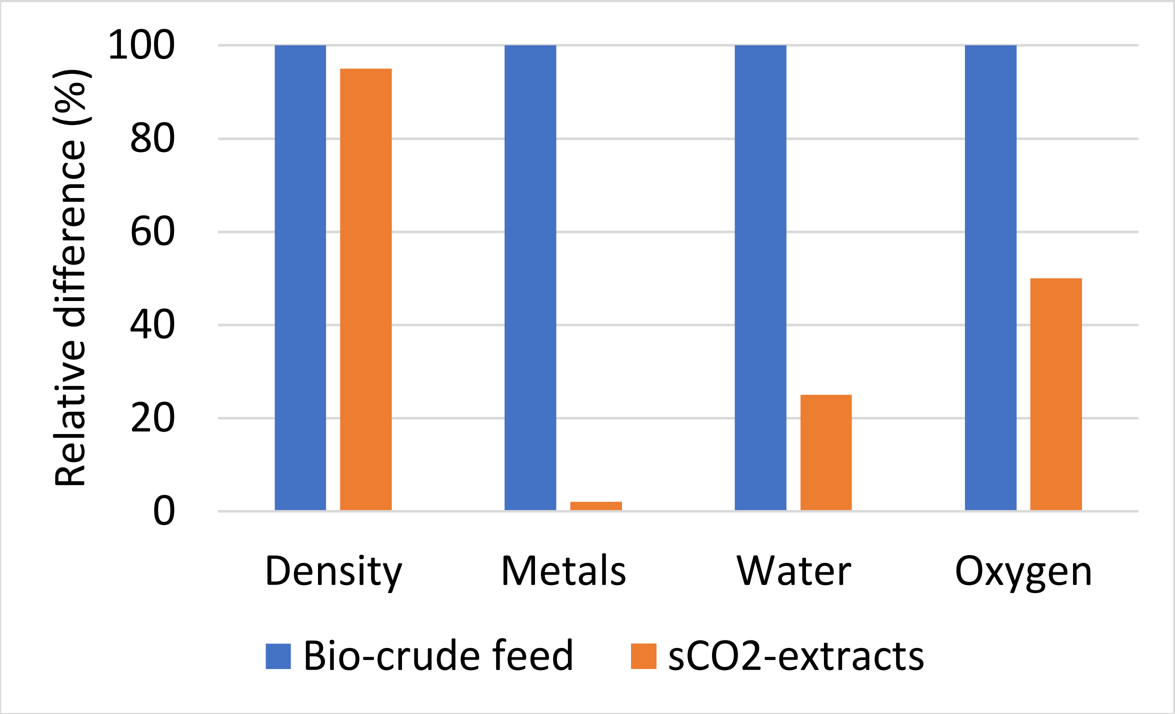
Impact

- Improve bio-carbon penetration (higher biocarbon in refining) in aviation and long-haul fuel needs compared to conventional technologies.
- NILE processes utility and their incorporation into existing petroleum refining, and emerging sCO_2-power-cycle technologies.

Features	NILE	Fast-pyrolysis	HTL
Temperature	150-350 ^oC	500-600 ^oC	250-450 ^oC
Pressure	100-275 bar	Atmospheric	100-350 bar
Water residue	Fresh and separated	~20-30% in oil as azeotrope	4-15% in oil & rest contaminated
Metal content	Separated in residue	In char	Contaminated HTL oil from catalysts
Acidity	Lowered phenolic acids	pH=2-3 (oil can precipitate when adjusted)	pH=8-9 (oil can precipitate when adjusted)
Viscosity increase while ageing	Only by 4 cSt from sCO_2 extracts of bio-oil over 60 days	22 cSt increase over 60 days	Increase by >5 times over 60 days

Impact

- sCO_2-led quality improvement in bio-crude:
  - reduction in the metal, water and oxygenate content
    - ➢ These reductions help to improve bio-crude ageing stability, heating value and lower viscosity
  - Improvement in hydrotreatment process:
    - ➢ No coke formation;
    - ➢ Low oxygen content (down to 1.6 wt.% compared to 3.1 wt.% from conventional hydrotreated bio-crude).
    - ➢ Better boiling point distribution, with no fractions above the diesel fuel range and larger amount of the low boiling fractions (gasoline and jet fuel).



Improved crude properties via sCO_2-extraction*

*Nikolaos Montesantos, Rudi P. Nielsen, and Marco Maschietti
Industrial & Engineering Chemistry Research **2020** *59* (13), 6141-6153

Summary

- Near-critical-integrated-liquefaction-extraction (NILE) route to convert different biomass, sorted wastes and wet-wastes into high-quality bio-crude with capabilities to replace petroleum crude.
- Development of the 3 key NILE components for an equivalent throughput of 0.5 dry tons/day
- Key components:
  - sCO2-dewatering;
  - near-critical liquefaction;
  - sCO_2-extraction of bio-crude.
- About to complete Task 1.0: Initial verification:
  - ✓ Process information and data supporting the technology readiness level of the overall process.
- Project target: Achieve GHG emission reduction beyond 70% and for fuel costs to reach the $2.5/GGE mark.
- Process modeling, lifecycle assessment (LCA) and technoeconomic analysis (TEA)

Quad Chart Overview

Timeline
- *10/1/2021*
- *10/31/2026*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)*	$3,101,362
Project Cost Share *	$775,340	

TRL at Project Start: TRL of 3
TRL at Project End: TRL of 5

Project Goal
Develop a near-critical-integrated-liquefaction-extraction (NILE) pathway to convert various biomass, and waste components into deployable biofuels for aviation and long-haul transportation applications using supercritical carbon dioxide (sCO_2) as solvent.

End of Project Milestone
Our end of project goal is to achieve optimized conditions for the tested feedstocks where the bio-crude extract can replace the petroleum crude while achieving GHG emission reduction greater than 70% and fuel costs of $2.5/GGE. Integration capability of the components developed in this project.

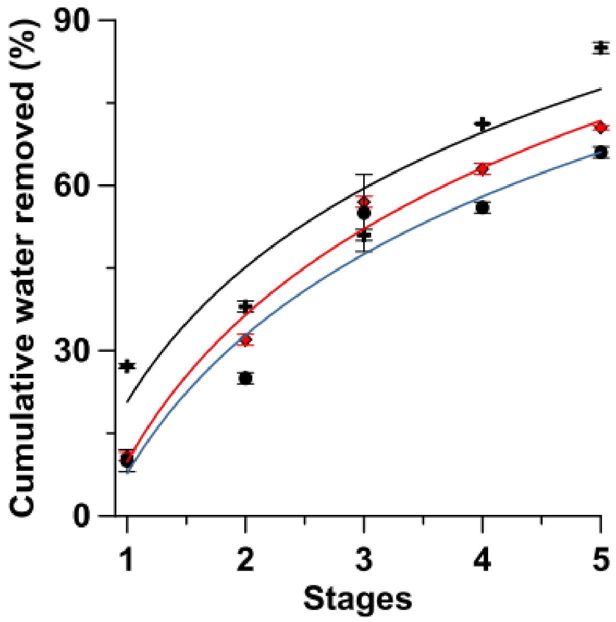
Funding Mechanism
Scale-up of biotechnologies – pre-pilot for biofuels and bioproducts.

Project Partners
- Electronic Systems Cost Modeling Laboratory.

Additional Slides

Dewatering

- Removing moisture content of biomass leads to a reduction of the processing costs, as well as of the costs for storage and transport.
- Biomass drying is a critical parameter when using biomass for energy purposes since moisture content has a marked effect on the conversion efficiency and heating value.
- sCO_2 dewatering reduces capillary-induced tensile stresses, observed during air-drying, allowing CO2 to penetrate into the pores of biomass, preserving its structure while removing water levels.
- CO2 low critical temperature (31.1°C) allows drying process to occur at relatively low temperatures, lower than in a conventional drying.

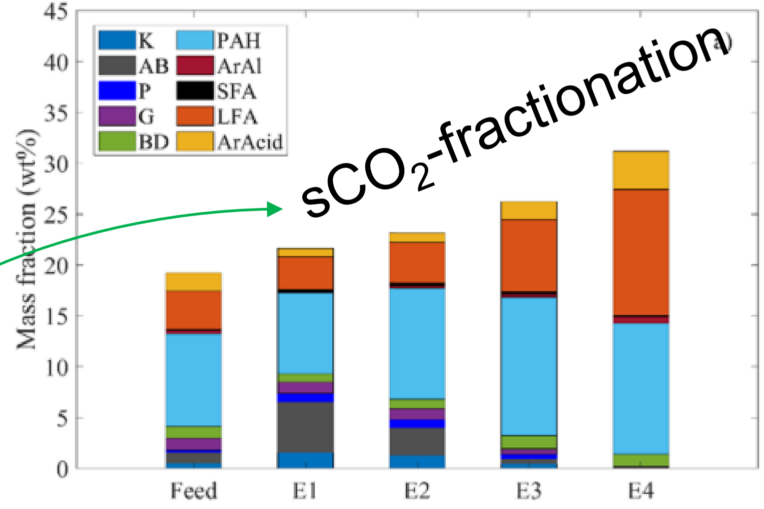


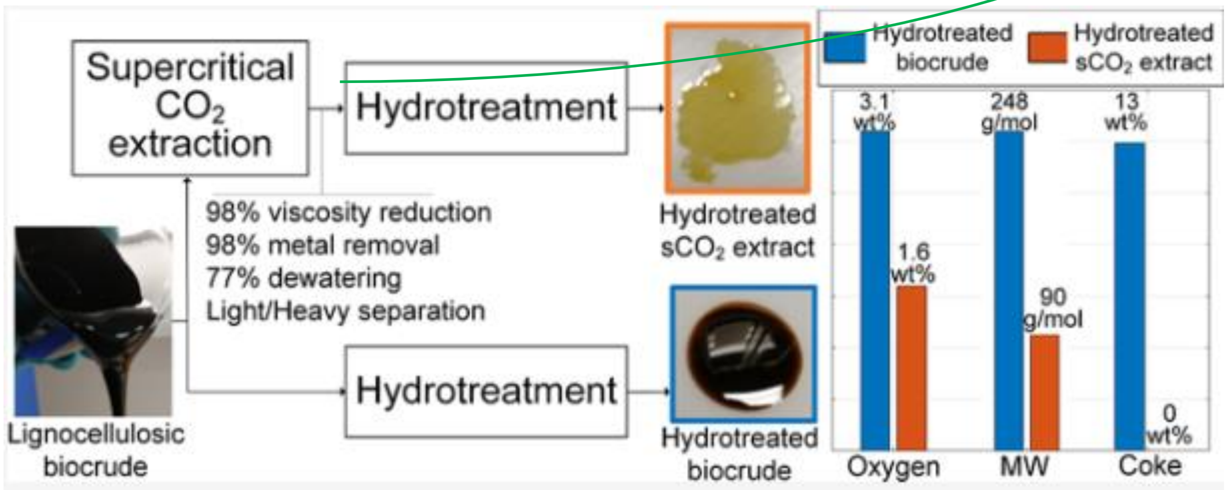
Dewatering of wet-organic wastes using sCO_2 via water displacement.

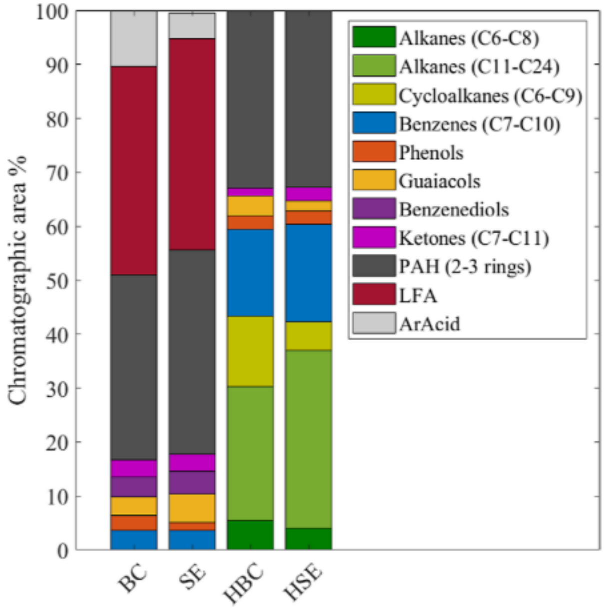
*Asafu-Adjaye O, Via B, Sastri B, Banerjee S. Water Research. 2021, 190, 116764.

Hydrotreating sCO_2 Extracted Biocrude

- **Absence of coke in hydrotreating sCO_2 extract –**
  - Reduce the H_2 consumption (milder hydrotreatment)
  - Maintained catalyst performance
- **Large reduction of the molecular weight –**
  - limiting less desirable cracking reactions
- **Low viscosity and low metal content**







Supercritical carbon dioxide hydrotreatment extraction utilizing commercial CoMo and NiMo catalysts*.

*Montesantos N, Kohli K, Brajendra K, Maschietti M. Ind. Eng. Chem. Res. 2022, 61, 15114−15124.

*Montesantos N, Nielsen R.P, and Maschietti M. Ind. Eng. Chem. Res. 2020 *59* (13), 6141-6153

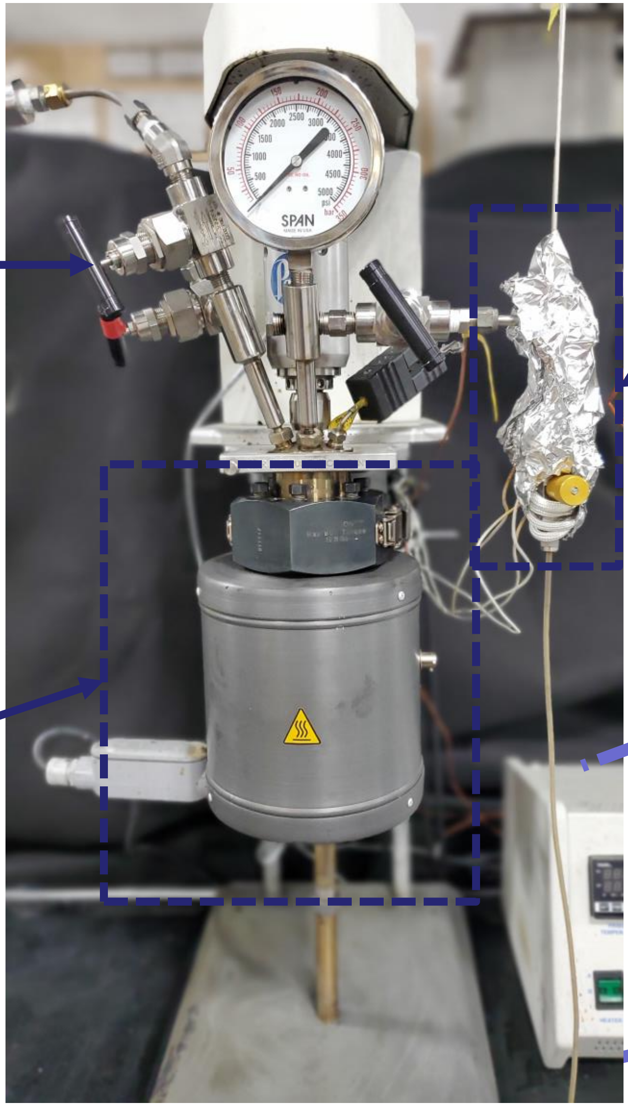
Approach

- Reactor

Siphon tubed CO_2 cylinder

High pressure CO_2 inlet

High pressure reactor in furnace



Heated sCO_2 outlet valve

Temperature & Stirring controller