# DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

## WBS: 3.4.3.501

# Scale-up of the Primary Conversion Reactor to Generate a Lignin-Derived Cyclohexane Jet Fuel

### Systems Development and Integration Session B

**Principal Investigator: Wayne Seames**

Advanced Refining Technologies

The University of North Dakota

NREL Transforming ENERGY

Washington State University

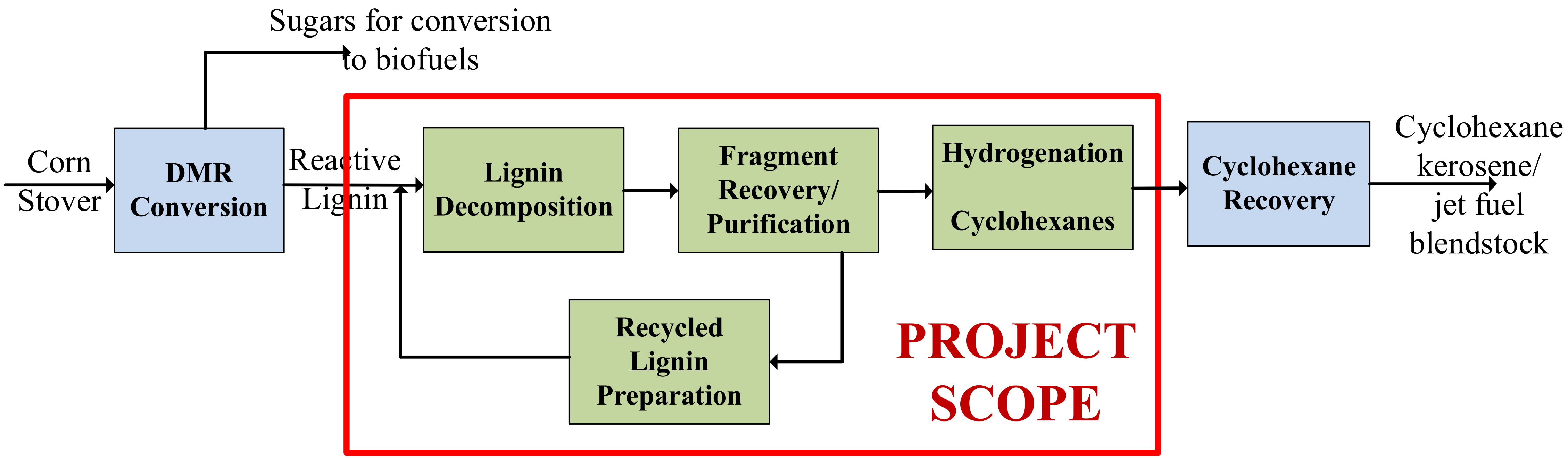
Idaho National Laboratory

**April 5, 2023**

# Project Overview

## The primary overall goals of this project are:

- **Translate lab-scale reaction technology to produce cyclohexanes from corn stover-derived reactive lignin to the engineering scale (8L/hr inlet fluid processing rate)**
- **Determine the technical, economic, and environmental feasibility of producing jet fuel and by-products from this technology.**



# Project Overview

- **These goals support EERE/BETO's overall goal to sponsor the development of technology to generate a non-aromatic sustainable jet fuel from ligno-cellulosic lignin**
- **It is one of four linked projects that use the NREL DMR system to convert corn stover into sugars and lignin streams and then process these streams into fuel and chemical products**

# Project Overview

**52 months, four budget periods:**

**BP1: Ended 8/1/20, successful verification of initial Go/No Go milestones**

**BP2: Ended 3/31/23, verification of the BP2 GNGs is in progress**

**BP3: 4/1/23 – 6/30/24,      BP4: 7/1/24 – 9/30/25**

**BETO Technology Managers: Joshua Messner and Biron Remy**

**Independent Engineer: Carol Babb, ICF**

**Project team members come from the Universities of North Dakota and Washington State, INL, NREL, and Advanced Refining Technology**

# 1 – Approach

## The project is organized into nine tasks:

**Task 1 Project Verification**

**Task 2 Production of Reactive Lignin Feed Solution:** preprocess corn stover and use DMR to generate the feed lignin solution.

**Key Milestone 2.7:** BP2, 25L of 10wt% reactive lignin solution (10+pH NaOH/water) generated (completed)

**Key Milestone 2.9**: BP3, 25+ MT of corn stover processed into 3600L of reactive lignin solution

**Task 3: Catalyst Development and Preparation:** Initial and improved pelletized catalysts.

**Key Milestone 3.3**: BP2, an effective pelletized catalyst based on WSU's original formulation produced (completed).

**Key Milestone 3.6**: BP3, an improved catalyst developed and demonstrated at the batch lab scale

# 1 – Approach

## The project is organized into nine tasks:

**Task 4: Conversion Reaction System Setup, Optimization, and Demonstration**

**4.1 Bench-scale Translation:** Used to determine if the original single step reaction scheme can convert lignin in the NaOH/water solution. Also used to optimize reaction conditions.

**Key Milestone 4.2**: BP2, 0.8L/hour bench scale continuous reaction system designed/built and a reaction scheme and conditions identified to produce at least 7.5wt% cyclohexanes (90%).

**4.2 Engineering-scale Demonstration:** Used to demonstrate the reaction technology at larger scale/longer time periods - 500 total hours total, 100 hours of continuous operation.

**Key Milestone 4.4**: BP3, A 8L/hour engineering scale continuous lignin-to-cyclohexane conversion system design, built, and commissioned/ready for demonstration testing.

**Task 5: Analytical Method Development:** A suite of methods developed for the improved characterization of decomposition products from lignin hydrogenation.

# 1 – Approach

## The project is organized into nine tasks:

**Task 6: Techno-economic Analysis:** Evaluation of the technical and economic feasibility of the proposed technology using a preliminary process design, capital and manufacturing cost estimates, and a comprehensive economic analysis.

**Task 7: Sustainability Analysis:** Life cycle models developed and compared to best available commercial technologies. Also used to determine improvements in greenhouse gas profiles versus conventional fuel and chemical product routes and to help optimize the design.

**Task 8: Prototype Jet Fuel Production and Testing:** A suite of purification unit operations designed and built to generate a prototype jet fuel. The jet fuel then tested following a CAAFI tier 1 and tier 2 prescreening protocol. After purification adjustments, improved samples will undergo ASTM D-4054 Tier One Physical Specification testing.

**Task 9: Project Management and Reporting**

# 1 – Approach

**The project has the following key Go/No Go decision points (completed, pending):**

**GNG1.1**: (BP1): Lab-scale conversion matching the proposal data = 15wt% of lignin to cyclohexanes

**GNG 1.2:** (BP2): Continuous bench-scale system conversion = >7.5wt% of lignin into cyclohexanes

**GNG 1.3:** (BP3): 25+ MT corn stover processed into >3600L of reactive lignin solution, an improved catalyst developed and demonstrated at the batch lab scale, and the engineering scale system has been commissioned.

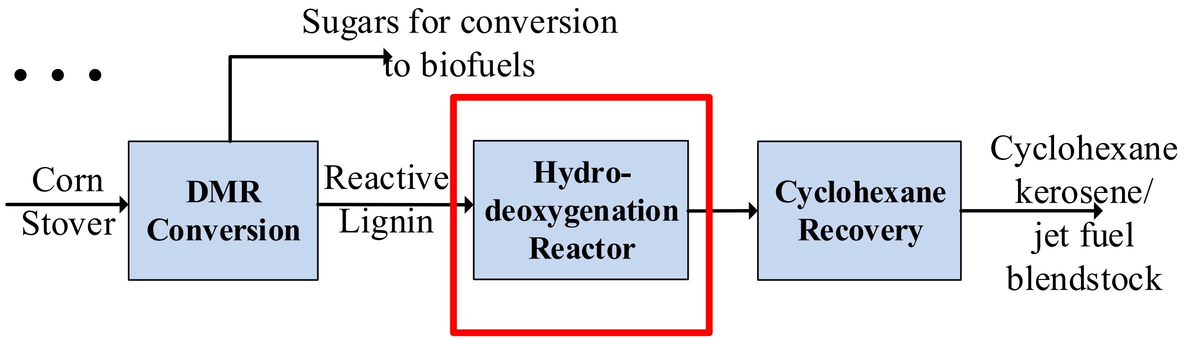
# 1 – Approach

**The BIGGEST CHALLENGE: a preliminary TEA showed that it was commercially infeasible (TCI = $100 million; NPV@20% = -$180 million) to follow the lab-scale protocol of:**

1. **Precipitate and wash the DMR-generated lignin out of solution**
2. **Dissolve the lignin in neutral water at very low concentrations**
3. **Convert into cyclohexanes in a one step reaction**

**Therefore our initial approach was to conduct the conversion reaction directly from the DMR-generated basic solution.**

**This led to the project's biggest risk . . .**



# 1 – Approach

**The BIGGEST RISK: could we convert the lignin directly from a 10wt% lignin in pH10+ NaOH/water solution?**

**Our strategy: first translate the WSU one step, bi-functional catalyst technology to the bench scale to determine if this is possible prior to scaling to the engineering scale.**

**If this wasn’t possible, adopt an alternative conversion strategy.**

**Bottom line: unable to get the hydro-deoxygenation reactions to occur, so we pivoted to the best alternative strategy (more on this in the progress section)**

# 1 – Approach

**The SECOND CHALLENGE: tight coordination/execution of the upfront work activities to allow bench-scale testing to occur no later than the 5th month of BP2 despite the constraints due to the pandemic and subsequent supply-chain issues.**

1. **INL must acquire and preprocess corn stover**
2. **NREL must process the corn stover into the lignin solution**
3. **WSU/ART must produce pelletized catalyst**
4. **UND must design and build the bench-scale system**

# 1 – Approach

**The SECOND CHALLENGE: tight coordination and execution of the upfront work activities to allow bench-scale testing as soon as possible**

**STRATEGY:**

- **Approval for INL to start work in BP1**
- **Monthly coordination meetings**
- **Working to an overall coordinated schedule**

**SUCCESS!**

| | | BP2 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Subtask** | **Project Months - SOPO ==>** | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| **Number** | **Description** | Sept | Oct | Nov | Dec | Jan | Feb | Mar | Apr |
| 1.1 | Initial Project Verification | M1.1 | | | | | | | |
| 2.1 | Preprocess Corn Stover - 15MT | M2.2 | | | | | M2.4 | | |
| 2.2a | Generate Lignin Solution - 50 L | | | | | | | | M2.3 |
| 3.1 | Bench-scale Pelletized Catalyst - 500g | | | | | | | | M3.1 |
| 4.1a | Design & Build Bench-scale system | | | | | | | M4.1a | |
| | | Completed | | | Planned | | | Milestone met | |
| | | | | | Delayed | | | | |

# 2 – Progress and Outcomes

**A no-cost extension was processed and approved to extend BP2 by four months to 3/31/23 (due to the need to pivot to the alternative conversion strategy).**

**The BP2 Verification Meeting was held on January 23-24, 2023**

**The BP2 verification report is currently being finalized.**

**BP3 currently scheduled to start on May 1st, pending EERE final approval.**

# 2 – Progress and Outcomes

**The BIGGEST RISK: could we convert the lignin directly from a 10wt% lignin in pH10+ NaOH/H2O solution?**

**The conversion of lignin to cyclohexanes occurs in two steps over a bi-functional catalyst developed at Washington State University:**

1) **Fragmentation of the lignin – mostly producing guiacol, phenol, and syringol**

   **Successful from 10wt% lignin in pH13 NaOH/water solution**

2) **Hydro-deoxygenation of these compounds to form cyclic compounds – mostly higher order cyclohexanes**

   **Unsuccessful from 10wt% lignin in pH13 NaOH/water solution**

# 2 – Progress and Outcomes

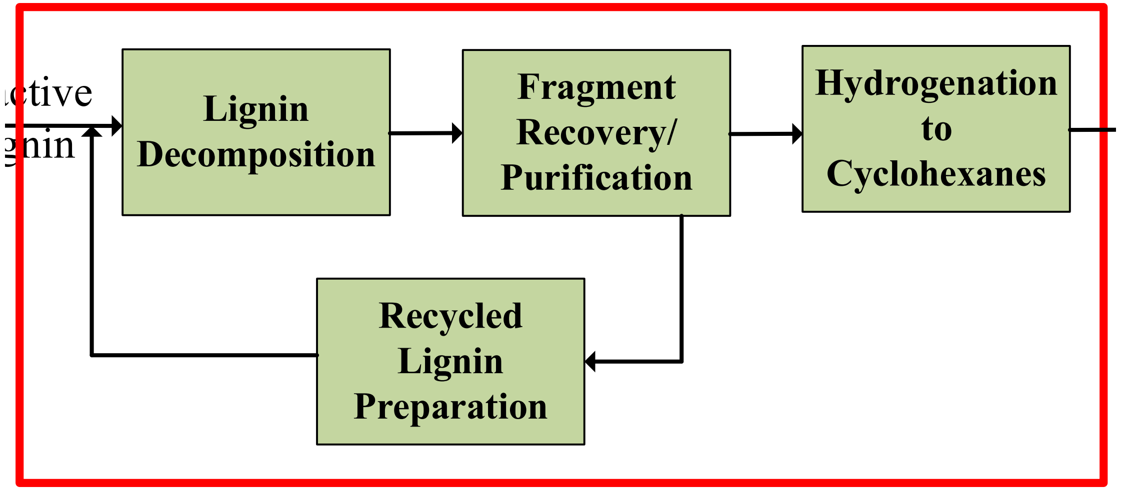
## An alternative strategy developed and approved by EERE/BETO:

1 Non-catalytically decompose the lignin (in the NREL solution) into the fragments

2 Extract the guiacol, phenol, syringol, and other organic compounds out of the reaction product solution with ethyl acetate (concentrate and recycle the unreacted lignin)

3 Separate the target compounds out of the solvent, which can then be reused

4 Convert the phenol, guiacol, syringol, etc. into cyclohexanes using the existing Ru catalyst.

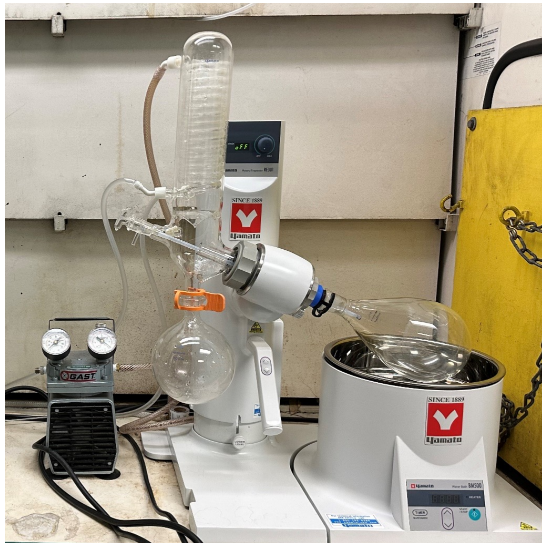


# BENCH-SCALE EQUIPMENT USED IN BP2

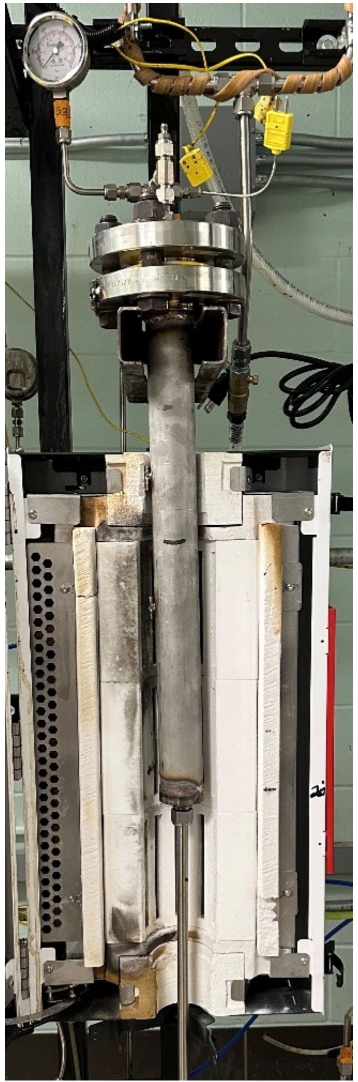
### STEP 1 - Non-Catalytic Decomposition

### STEP 2- Extraction in Ethyl Acetate

### STEP 3- Recovery out of EA



### STEP 4- Catalytic Hydrogenation



# 2 – Progress and Outcomes: RESULTS

1 Non-catalytically decompose the lignin (in the NREL solution) into the fragments

Single pass: ~50wt% lignin fragmented; 9.1wt% of lignin carbon into usable monomers

Overall: ~99+% lignin fragmented; ~18wt% usable monomers

2 Extract the organic compounds out of the reaction product solution with ethyl acetate

>96% recovery in multi-stage extraction

3 Separate the target compounds out of the solvent, which can then be reused

>99% recovery out of solvent; >99% solvent recovery from target compounds

4 Convert the phenol, guiacol, syringol, etc. into cyclohexanes using the existing Ru catalyst.

Results for this step are still pending. Literature and lab-scale tests suggest >80% conversion of phenol and guiacol and >60% conversion of syringol into cyclohexanes.

# 2 – Progress and Outcomes

## Other BP2 (9/1/21 – 3/23) accomplishments:

**Task 2. Sufficient corn stover preprocessed and adequate lignin solution produced for small scale optimization testing and for initial engineering scale testing.**

**Task 3. Pelletized catalyst using the existing formulation generated for the small scale continuous system and engineering-scale testing.**

**Task 5. New analytical equipment installed and improved analytical method development is in progress.**

**Task 6. Initial preliminary design developed.**

**Task 7. Initial baseline lifecycle analysis (LCA) model is in progress using model inputs.**

# 3 – Impact

## EERE funding used to:

- **Derisk this technology - developing pre-commercialization data**
- **Provide technical data at a scale that can be used to assess the attractiveness of this process for potential commercial applications.**
  - **Demonstration at realistic process conditions for a novel conversion system to generate a cyclohexanes jet fuel/fuel blendstock from a reactive lignin solution generated from corn stover.**
- **Extends the existing NREL-WSU partnership to exploit LC derived lignin to include UND. The team’s areas of expertise are highly complementary.**

# 3 – Impact

- **Renewably-derived cyclohexanes jet fuel/blendstock eliminates the need for aromatics to provide seal swell capabilities**
  - **Could be a key component in an overall strategy to increase the renewable content of U.S. jet fuels.**
- **Energy density is an important parameter affecting aircraft range and fuel consumption (due to fuel weight in the aircraft).**
  - **Removing aromatics increases energy density which is also attractive to commercial airplane operators.**

# Summary

- **Despite the need to pivot late in BP2 to a more complex, multi-step processing scheme, the project is close to achieving its intermediate objectives and has shown that the lignin generated by the deacetylation of corn stover in the DMR process can be converted out of a 10wt% lignin in pH10$^{+}$ NaOH/water solution into cyclohexanes.**
- **Successful early coordination between four separate groups was achieved to allow bench-scale testing early in BP2.**
- **The project is currently on budget but approximately one month behind schedule (with the extension).**
- **The key next steps are to design, build, and operate an engineer scale system, to finish the TEA and LCA, and develop an assessment of the commercialization potential of this technology.**

# EE0009257: SCALE-UP OF THE PRIMARY CONVERSION REACTOR TO GENERATE A LIGNIN-DERIVED CYCLOHEXANE JET FUEL

**Technical POC Name: Wayne Seames / University of North Dakota**

Funding Mechanism
2020 DE-FOA-0002203

## Timeline

- Project start date: 10/1/20
- Project end date: 9/30/25

| | FY22 Costed | Total Award |
|---|---|---|
| **DOE Funding** | $558,232 | $3,085,000 |
| **Project Cost Share** | $233,701 | $1,019,315 |

TRL at Project Start: 3
TRL at Project End: 4

## Project Partners

- Washington State University
- National Renewable Energy Laboratory
- Idaho National Laboratory
- Advanced Refining Technology

## Project Goal

- The goal of this project is to scale-up the conversion steps of a process (RED highlighted area in figure below) to generate a jet fuel/fuel blendstock from the lignin contained in corn stover. Corn stover is preprocessed then converted into a 10 wt% reactive lignin in a 10+ pH NaOH/water solution. This reactive lignin slurry will be transformed into alkylmono-cyclohexanes. The reaction product streams will be analyzed to completely characterize the products using improved methods developed during the project.
- The technology will be demonstrated at a processing rate of 8L/hr (50 TPH corn stover equivalent) for 100 continuous and 500 total hours. An improved catalyst will also be developed and tested. The remainder of the process will be modeled using process simulation and preliminary engineering design techniques. Techno-economic and sustainability analyses will be completed to define the technology's commercial potential.

## End of Project Milestones

- Engineering scale demonstration of a method to convert at least 7.5% (inlet carbon basis) of corn stover-derived lignin into cyclohexanes for use as jet fuel blendstock.
- Techno-economic and Sustainability analyses for commercial facilities using this technology.
- Advanced analytical methods to completely characterize lignin decomposition products.
- Development/demonstration using a non-REE catalyst for hydrogenation.

# Additional Slides

**(Not a template slide – for information purposes only)**

- *The following slides are to be included in your submission for evaluation purposes, but will **not** be part of your oral presentation –*
- *You may refer to them during the Q&A period if they are helpful to you in explaining certain points.*

# Responses to Previous Reviewers' Comments

- This project has NOT been peer reviewed previously

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# Publications, Patents, Presentations, Awards, and Commercialization

- No publications have been submitted to date
- No commercialization efforts have been made to date

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