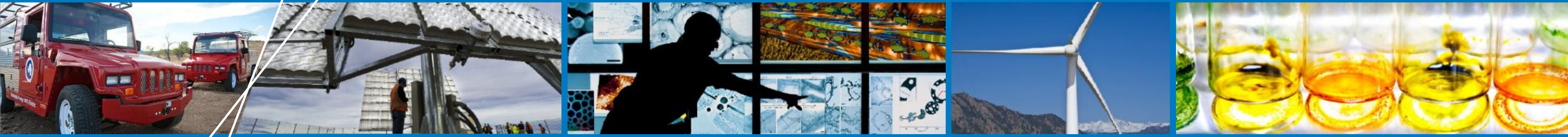
2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Integration & Scale-Up
WBS 2.4.1.301



Bio-oil Technology Area Review

Esther Wilcox

March 23rd, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Goal Statement

Integrate and scale-up pyrolysis technologies at an industrially relevant scale to demonstrate progress over the current state of technology towards meeting the BETO 2022 targets for biomass-derived fuels.

- Design and construct pilot scale unit operations to provide a flexible integrated pilot plant capable of fast pyrolysis, ex-situ, and in-situ catalytic fast pyrolysis up to 0.5 ton/day biomass feed
- Provide operational bounds, such as residence time, temperature, and catalyst regeneration capabilities, to catalyst development tasks to guide catalyst research activities
- Develop engineering designs for industrial deployment of the technology
- Provide data for techno-economic analysis (TEA) models
- Validate performance of unit operations, catalysts, and other pyrolysis technologies at the pilot scale by operating the system at steady-state during the production of at least 100 gallons of product meeting targets

Goal Statement
2017 pyrolysis demonstration targets

Ex-situ Pyrolysis Process Parameter	2014 SOT	2017 Target	2022 Target / Design Case
Vapor Products			
Non-Condensable Gases (wt%)	35	30	23
Aqueous Phase (% C Loss)	25 (2.9)	26 (2.3)	30 (1.3)
Solids (Char + Coke)	12 + 11	12 + 10.2	12 + 8.0
Organic Phase (wt%)	17.5	22.0	27.2
H/C Molar Ratio	1.1	1.3	1.6
Carbon Efficiency (%)	27	34	44
Oxygen Content (% of organic)	15.0	12.5	6.4
Hydroprocessing C Eff. (% of org.liq.)	88	90	94
Carbon Eff. to Fuel Blendstocks (%)	23.5	30.6	41.5
Energy Efficiency to Fuels (LHV basis)	30.4	40.2	56.6
Diesel-Range Product (% GGE basis)	15	14	55
Minimum Fuel Selling Price ($/GGE)	$6.47	$4.58	$3.31

2017 demonstrations:

- Produce minimum of 200 gallons of fast pyrolysis oil for hydrotreating at PNNL
- Produce minimum of 100 gallons of ex-situ catalytic fast pyrolysis oil
- Fast pyrolysis and ex-situ catalytic pyrolysis oils will meet specifications defined in the design cases, pilot plant efforts focusing on yields and catalyst lifetime

Abhijit Dutta, Thermochemical Platform Analysis Project , WBS 2.1.0.302

Quad Chart Overview

Timeline

Project start: 2010

Project end: 2017

Percent complete: 75%

Barriers

- Tt-K. Bio-oil Pathways Process Integration
- Tt-E. Liquefaction of Biomass and Bio-oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Tt-I. Sensors and Controls
- Tt-H. Bio-Oil Intermediate Stabilization and Vapor Cleanup

Budget

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding FY 15-Project End Date
DOE Funded	$2.5M	$3.3M	$3.2M	$9.5M

Partners

- Collaborations with:
  - PNNL 2.9.1.4 Feedstock, and Hydroprocessing of pyrolysis oils
  - ORNL WBS 2.12.5.1 Materials Degradation In Biomass-Derived Oils
  - INL WBS 2.9.2.1 Feedstock

1 - Project Overview
Background

- Demonstrated pyrolysis capability in TCPDU:
  - Produced > 100 gal of pyrolysis oil for a DOE FOA in 2008
  - Pyrolysis oil produced for CRADA with Petrobras
  - Constructed Hot Gas Filter and tested on pyrolysis oil[1]
- Previous use of Thermochemical Process Development Unit (TCPDU) pilot plant culminated in 2012 demonstrations of syngas upgrading pathway
  - DOW CRADA: 120 hours
  - BETO demonstration[2]: 150 hours
- BETO's focus shifted towards pyrolysis pathways. TCPDU to be used for pyrolysis demonstrations in 2017 and 2022
- Condensate drum incident[3] during Lanzatech CRADA resulted in increased focus on safety including hazard assessments and risk mitigations

1. Baldwin, R.M.; Feik, C.J., **2013** "Bio-oil Stabilization and Upgrading by Hot Gas Filtration" *Energy Fuels*, 27, p. 3224.
2. Bain, R.L.; Magrini-Bair, K.A.; Hensley, J.E.; Jablonski, W.S.; Smith, K.M; Gaston, K.R., & Yung, M.M., **2014** "Pilot Scale Production of Mixed Alcohol from Wood" *IECR*, 53, p. 2204.
3. National Renewable Energy Laboratory, "Environment, Health, and Safety Event Investigation" (INCRPT_20130208_FTLB_Drum Explosion Report, National Renewable Energy Laboratory, 2013)

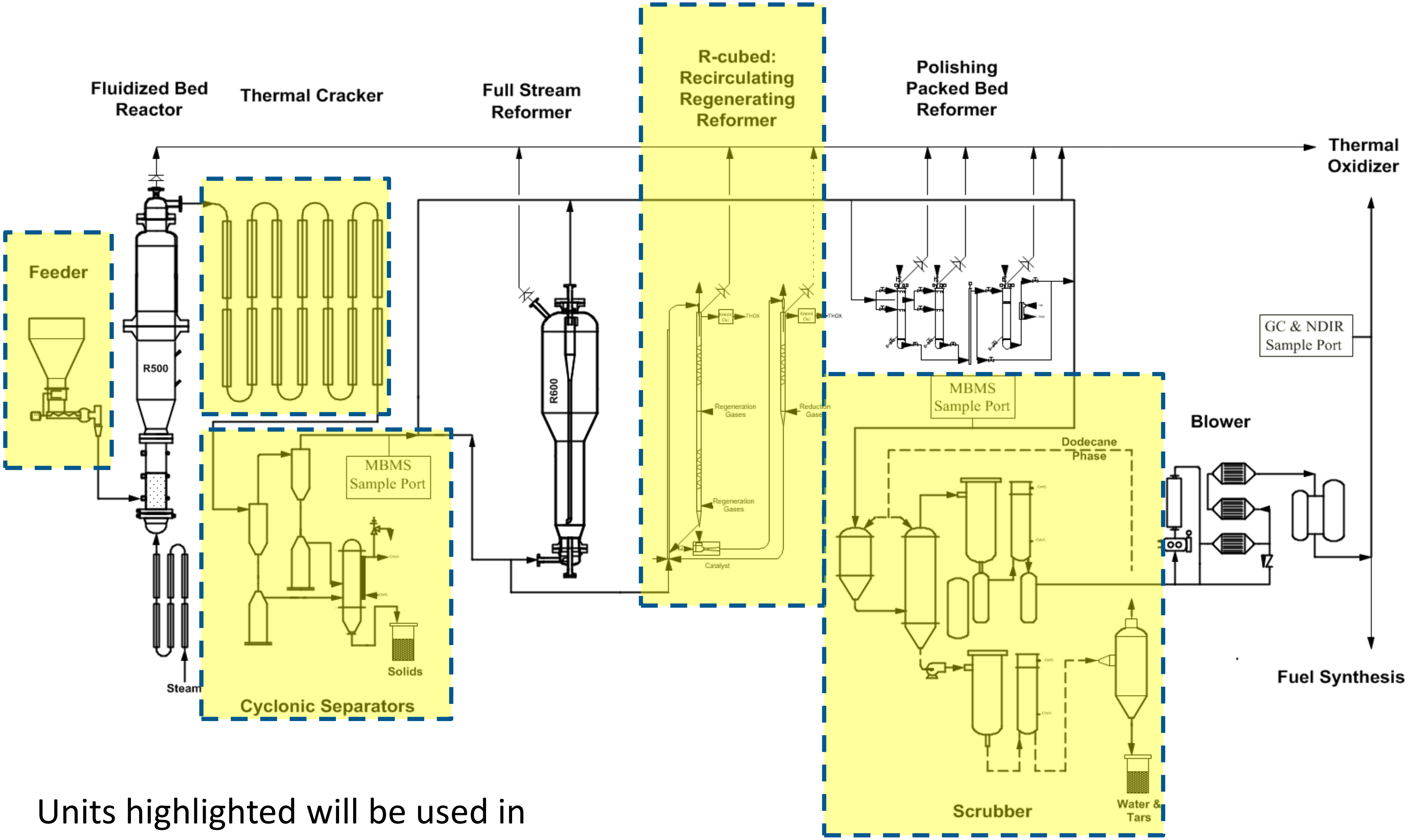
1 - Project Overview
Objectives & Timeline

Objectives:

- Upgrade the TCPDU system to improve overall operation and mitigate safety hazards
- Design, fabricate, and install additional unit operations to add ex-situ and in-situ capabilities
- Demonstrate pyrolysis pathways meeting the 2017 targets:
  - Fast pyrolysis producing at least 100 gallons under steady state conditions to be hydrotreated at PNNL
  - Ex-situ pyrolysis producing at least 200 gallons of product under steady state conditions
  - Fast pyrolysis and ex-situ oils meeting design case targets

FY13	Conduct hazard assessment on backend units, implement recommendations, and demonstrate corrective actions were successful
FY14	Conduct hazard assessment on remaining unit operations, and implement recommendations
	Design unit operations for ex-situ pyrolysis
FY15	Commission full plant to demonstrate proper functionality of improvements
	Fabricate and install unit operations for ex-situ pyrolysis capability, and perform initial commissioning of units
FY16	Complete initial evaluation of ex-situ pyrolysis operations
	Go/No-Go decision on installing in-situ capability, adding hot gas filter, or other improvements
FY17	Perform demonstration of pyrolysis pathways achieving the 2017 targets at the pilot scale
FY18 – FY22	Work with WBS 2.3.1.314 to modify pilot plant and demonstrate technology meeting 2022 targets

1 – Project Overview
2012 Demonstration TCPDU Flow Diagram

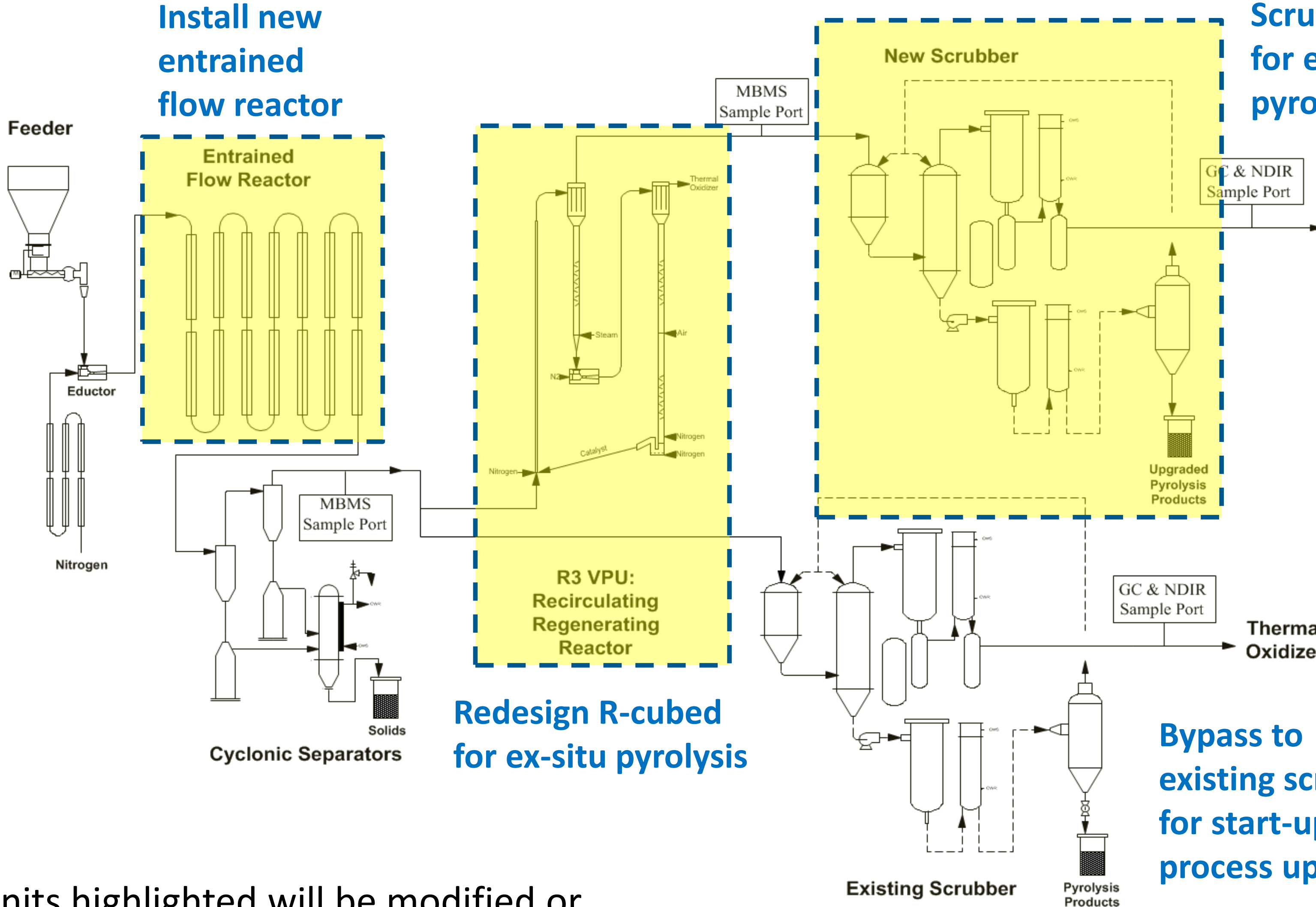


Units highlighted will be used in 2017 pyrolysis demonstration

1 – Project Overview
Ex-situ Flow Diagram for 2017 Demonstration

Install new entrained flow reactor

Scrubber system for ex-situ pyrolysis products



Redesign R-cubed for ex-situ pyrolysis

Bypass to existing scrubber for start-up & process upsets

Units highlighted will be modified or created for use in ex-situ pyrolysis

2 – Approach
Technical

Mimic commercial process model to demonstrate integrated process performance of pyrolysis pathways at the pilot scale

- Reconfigure TCPDU pilot plant for pyrolysis experiments based on unit operations identified in design reports, results of National Advanced Bioenergy Center (NABC), and catalyst research from other tasks
- Final integrated demonstration based on downselection of pathway, catalyst, and feedstock formulation
- Collaboration with catalyst design and TEA tasks to ensure proper reactor designs and integration. Feedback to catalyst design tasks regarding operational bounds

WBS: 2.3.1.313	2.3.1.315	2.3.1.314	2.4.1.301	2.1.0.302
Catalytic Pyrolysis Sciences **Pyrolysis science fundamentals, catalyst modeling** **Lab scale**	**Biomass Upgrading: Catalyst Development/Testing** ***Ex-, in-situ* Catalyst development/evaluation** **Lab scale**	**Biomass Deconstruction: Catalyst Development /Testing** ***Ex-situ* catalyst evaluation/ characterization** **Lab-small pilot**	**Engineering Integration and Scale-up** ***Ex-, in-situ* TCPDU pilot scale demonstration** **Pilot scale**	**Technoeconomic Analysis of Integrated VPU Process** ***Ex-, in-situ*, product/process costs at pilot scale**

mg-g → g-kg → 100's kg

2 – Approach: Success Factors & Challenges

- **Critical success factors:**
  - Demonstration of proper functionality of operability and safety upgrades through steady state operation (less than 5% change in key process parameters) producing 25 gallons of pyrolysis oil (FY15)
  - Design of new pyrolysis units operate within design parameters (e.g. residence time, proper solids flow control, temperature) determined by establishing the actual operating bounds of the units during commissioning (FY15)
  - Optimize performance of ex-situ pyrolysis unit operations through feedback and input from feedstock and catalysts tasks (FY16)
  - Demonstration of selected pyrolysis pathway using chosen feedstock and catalyst at the pilot scale by producing at least 100 gallons of product under steady state conditions that meet the 2017 targets (FY17)
  - Provide process data for techno-economic analysis (WBS 2.1.0.302) that are commercially relevant
  - Provide engineering designs through publications and patents that can be adopted by industry
- **Challenges:**
  - Design of new unit operations had to be completed prior to full understanding of catalysts and expected product composition
  - Accurately measure mass/energy balances
  - Maintaining flexibility of the pilot plant in order to demonstrate different pathways, including fast pyrolysis and ex-situ pyrolysis

2 - Approach
Management

- **DOE approved:**
  - AOP with SMART quarterly milestones
  - Go/No-Go decisions
  - Project management plan with schedule, budget, and risk abatements
- Quarterly progress and milestone reports submitted to DOE
- 3-year merit review of project in 2014 with Go/No-Go decisions
- Weekly task meetings with research team to monitor progress and mitigate potential risks early
- Fabrication subcontracts with clear statement of work including progress update requirements and critical progress completion dates

Examples:

FY15 Q2 Milestone: Shakedown and validate the FY14 changes for fast pyrolysis. Run the TCPDU system in fast pyrolysis mode to produce 25 gallons of pyrolysis oil from oak, during which the system is at steady state (key process parameters, such as feed rate, temperature, pressure, do not deviate more than 5%).

FY16 Q1 Go/No-Go Decision: Continue with ex-situ pyrolysis without further TCPDU modifications for the FY17 demonstration. Decision will be based on TCPDU commissioning of ex-situ operations in the TCPDU, ex-situ data from other systems (DCR), and input from catalyst development tasks.

3 - Technical Accomplishments
Operational & safety assessments and upgrades

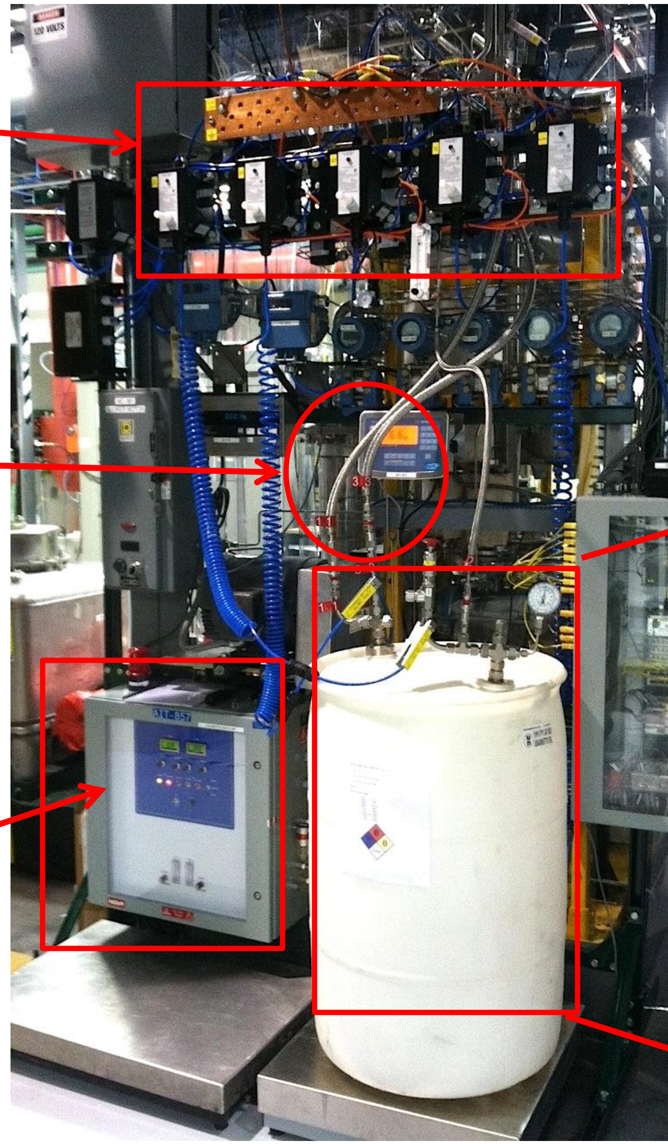
- **Hazard and operability assessments conducted on entire system, including new designs, control system gap analysis, and fire triangle analysis**
  - > 800 scenarios evaluated
  - > 500 unique recommendations made for improvements
  - Recommendations prioritized based on risk, code compliance, and impact on improved operation
  - ~170 recommendations determined to be required before restart of TCPDU
- **All required changes made to system including:**
  - New char passivation station
  - New condensate drum purging station
  - Redesign of thermal oxidizer system
  - Upgraded control system and user interface
  - Updated or created ~50 procedures
- **Full NEC electrical code compliance inspection**
- **Inspection of all pressure relief devices**
- **Calibration and testing of all safety systems**
- **Training of new operators**

3 - Technical Accomplishments
Drum design eliminates all legs of fire triangle

Ground indicator lights assure proper grounding of system necessary to eliminate static build-up

Continuous N_2 flow maintains inert headspace

LEL/O_2 detector monitors headspace and stops system if flammables or oxygen detected

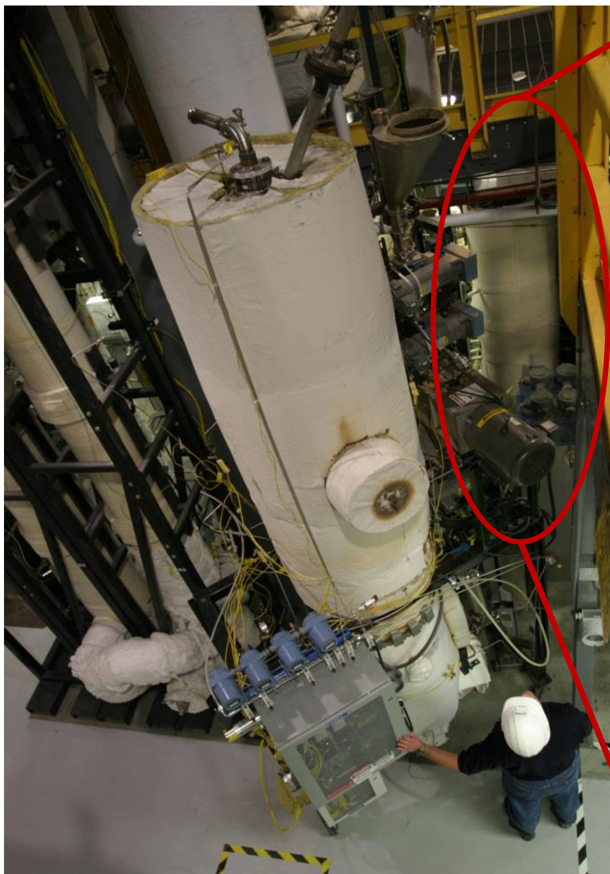


Before placing in service, drum is purged with nitrogen to eliminate oxygen from empty drum

Liquid fills from bottom of drum at 45° angle to minimize splash and thus static buildup

3 - Technical Accomplishments
New entrained flow reactor installed

- **New design allows for:**
  - Consistent temperature profile and control across reactor
  - Inspection of pipes without disassembly

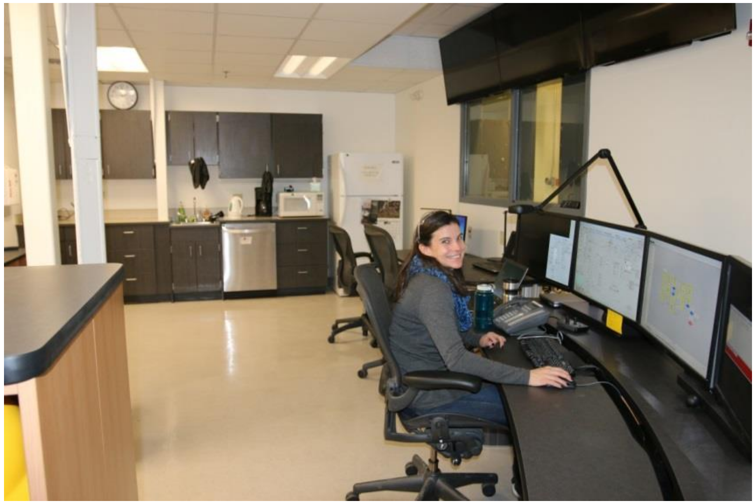


- **Corrosion testing:**
  - Old reactor pipes sent to ORNL for corrosion testing
  - Material test samples from ORNL installed for future analysis

3 - Technical Accomplishments
Analytical system upgrades & new control room

- **Analytical capabilities assessed and updated to:**
  - Simplify sampling and data
  - Improve TCPDU operation by changing real-time gas composition sample locations
  - Improve mass balances
  - Maintain flexibility of system by adding sample ports for future experiments

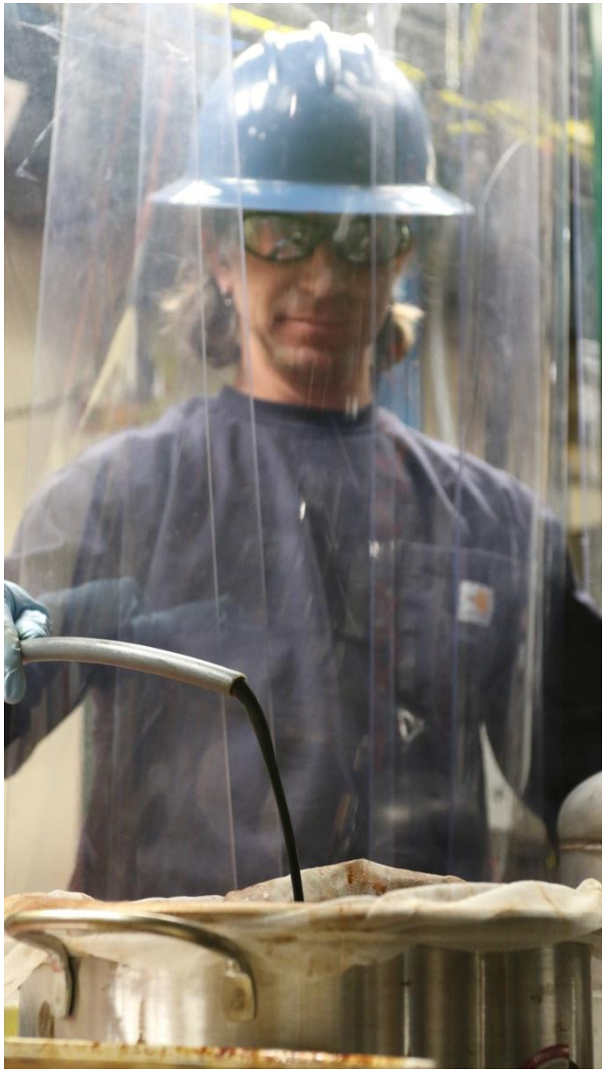
- **Relocation of analytical equipment to climate controlled room provides:**
  - Improved life and reduce maintenance on equipment
  - Consolidates and reduces sampling thereby improving representative sampling



New control room built:

- Camera feeds from process areas provide line-of-sight
- New location, fire rating, and ventilation ensures safety of operators from process hazards

3 – Technical Accomplishments
Commissioning of general TCPDU changes

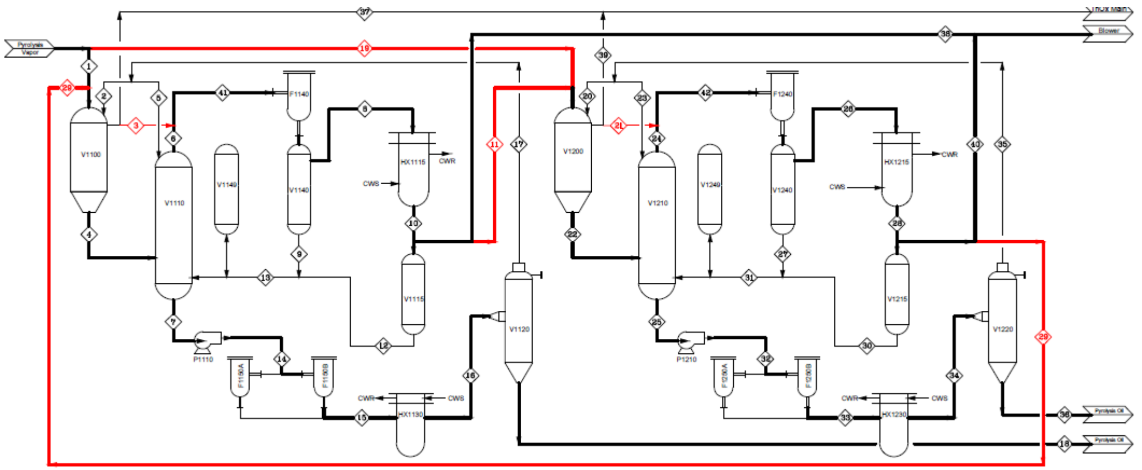


- **Initial commissioning:**
  - System run for 3 days, kept in hot-standby overnight
  - Steady-state achieved quickly and easily maintained
  - Recommendations were made by operators for further improvement and were implemented
- **Condensate drum:**
  - LEL and LOC levels of headspace while online were below alarm levels during operation and remained below LEL & LOC for 4 weeks after removal from system
- **Char collection & passivation:**
  - Oxygen intrusion in char collection below LOC
  - Char successfully passivated on new passivation station
- **Fast pyrolysis oil production commissioning:**
  - System run for 5 days, kept in hot-standby overnight
  - Steady-state achieved quickly and maintained
  - Over 25 gallons of oil produced
  - Mass balances and oil analysis in progress

3 – Technical Accomplishments
New scrubber designed for ex-situ pyrolysis

- **Collaborated with Process Engineering Associates on design**
- **5 designs evaluated, including distillation**
- **Design elements allow for:**
  - Collection of flammable products, such as BTX
  - Ability to collect 2 dew point fractions with a wide temperature range for first fraction
  - Ability to use variety of scrubbing fluids, including dodecane, isopar, water, and recycled pyrolysis products
  - Higher probability of successful 2017 demonstration by using a modification of existing design known to work for pyrolysis
  - Flexibility to run new dual scrubber units in series, parallel, or individually, and use existing scrubber for start-up or bypass around ex-situ reactor
  - Easier operation and maintenance

Existing scrubber



New dual scrubber unit design flow diagram

3 – Technical Accomplishments
R-Cubed design modifications for use in pyrolysis

- **Collaborated with Particulate Solids Research, Inc., experts in solids flow, on design**
- **Changes based on learnings from 2012 demonstration and input from catalyst development tasks**
- **Design parameters defined with catalyst development tasks:**
  - Usable for modified HZSM-5 catalyst (70 – 80 µm, 900 g/L density)
  - Solids loading range of 0.5 to 3 $mass_{catalyst} : mass_{py\ vapor}$ ratio
  - Controllable solids flow over 100 hrs of operation
  - Minimize attrition and solids carry-over
  - Steam stripping and air regeneration of catalyst

Add/replace pressure transducers for faster sampling & better control of fluid beds

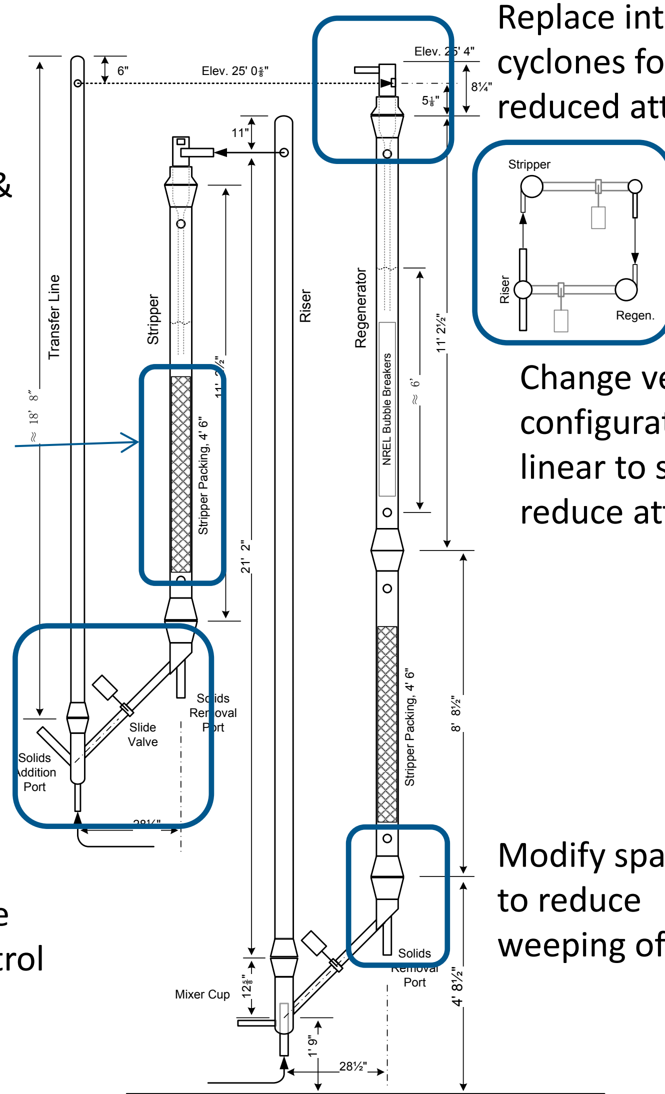
Replace baffles with packing for increased steam stripping efficiency

Use of slide valves improve solid flow control

Replace internal cyclones for reduced attrition

Change vessel configuration from linear to square to reduce attrition

Modify spargers to reduce weeping of solids



Redesigned R-cubed system

4 - Relevance

- **Addresses BETO's strategic goal for thermochemical conversion:**
  "Develop technologies for converting feedstocks into cost-competitive commodity liquid fuels such as renewable gasoline, jet fuel, and diesel and achieve a minimum fuel selling price of $3/gallon of gasoline equivalent."
  - Validates unit operations and engineering designs, integrates processes, and demonstrates technologies required to convert biomass to hydrocarbon fuels
  - Performance targets guided by techno-economic analysis of R&D results and data from runs used to validate techno-economics

- **Project addresses biomass conversion pathways in the MYPP:**
  "M X.17: Demonstrate and validate bio-oil production to a stable intermediate."
  - TCPDU pilot plant will be used to demonstrate pyrolysis pathways in 2017 at industrially relevant scale

- **Maintains & operates a BETO core capability for Technology Demonstration & Deployment:**
  "To develop emerging production technologies beyond bench-scale to pre-commercial demonstration scale, culminating in the construction of pioneer biofuels production plants."
  - Condensate collection and char passivation designs address technology needs beyond bench-scale

5 - Future Work

Remainder of FY15

- Compare bio-oils produced from TCPDU using entrained flow reactor to those produced from smaller systems using fluid bed reactor (DCR)
- Fabricate, install, and shake-down new scrubber system, and upgraded R-cubed reactor for ex-situ pyrolysis

FY16 – FY17

- Go/No-Go decision on additional upgrades for ex-situ pyrolysis, such as hot gas filtration
- Commission and initial testing of TCPDU for ex-situ pyrolysis
- Demonstrate ex-situ and fast pyrolysis with hydrotreating pathways, producing at least 100 gallons of final product under steady state operation meeting the 2017 design case targets

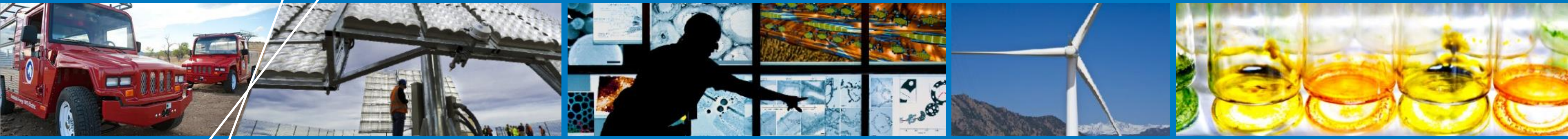
Summary

- **Overview:** BETO’s focus shifted to pyrolysis, requiring changes to the TCPDU for pyrolysis pathway demonstrations
- **Approach:** Upgrade the TCPDU system for improved operation and safety, and for ex-situ pyrolysis, while maintaining flexibility. Commission changes to ensure proper operation and functionality prior to 2017 demonstration.
- **Relevance:** This task maintains and operates a core BETO capability *“To develop emerging production technologies beyond bench-scale to pre-commercial demonstration scale, culminating in the construction of pioneer biofuels production plants”*
- **Progress since FY13 review:**
  - Hazard assessments completed for entire plant
  - Improvements implemented and tested through demonstrations
  - Ex-situ unit operations designed
- **Future work:**
  - Install and commission ex-situ unit operations
  - Demonstrate pyrolysis pathways meeting the 2017 targets

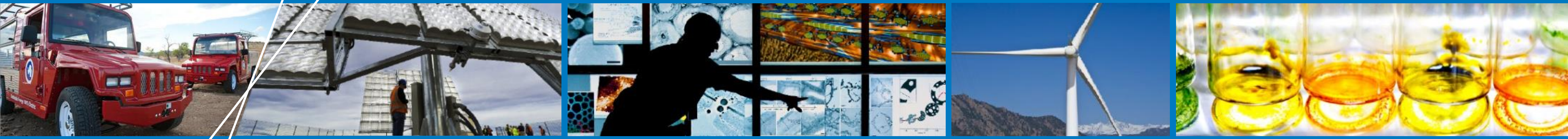
Acknowledgements

- **Thermochemical Process R&D Section:**
  - Tim Dunning
  - Dan Dupuis
  - Katie Gaston
  - Chris Golubieski
  - Ray Hansen
  - Marc Oddo
  - Matt Oliver
  - Marc Pomeroy
  - Kristin Smith

DOE BETO



Questions?



Additional Slides for Peer Evaluation

Glossary of Terms

AOP	annual operating plan		**MYPP**	Multi-Year Program Plan
BETO	Bioenegy Technology Office		**NABC**	National Advanced Bioenergy Center
BTX	Benzene, Toluene, Xylene		**NREL**	National Renewable Energy Laboratory
DOE	Department of Energy		**ORNL**	Oakridge National Laboratory
FY	fiscal year		**PNNL**	Pacific Northwest National Laboratory
gge	gallons of gasoline equivalent		**PFD**	Process flow diagram
HC/HCs	hydrocarbons		**PHA**	Process hazard analysis
HZSM-5	Zeolite Socony Mobil–5		**P&ID**	Piping & instrumentation diagram
INL	Idaho National Lab		**R&D**	research and development
LEL	Lower explosion limit		**SOT**	state of technology, always relative to an indicated date
LOC	Limiting oxygen content		**TEA**	technoeconomic analysis - includes a process design and associated economics based on economic assumptions in BETO-sponsored design reports
LHV	lower heating value - energy released to yield carbon dioxide and steam		**TCPDU**	Thermochemical Process Development Unit – a pilot scale system used for demonstration of thermochemical pathways
MFSP	minimum fuel selling price, based on economic assumptions in BETO-sponsored design reports		**SOT**	state of technology, always relative to an indicated date

Response to 2013 Reviewer comments

Comment – On overall impressions: *"Effort seems a bit premature and also appears to be the justification for continuing to modify and operate an existing pilot plant. Experience suggests that this is costly and inefficient."*

The TCPDU system is a robust and flexible pilot plant. The current design allows for relatively easy design and implementation of additional unit operations to add capabilities.

Comment – On overall impressions: *"This is difficult work with many impediments to success, but it needs to be done. Due to the immature nature of the supporting R&D work, it may be too early in the technology development cycle to implement a pilot plant of this scale."*

We worked closely with the catalyst development tasks to define design criteria ranges. They have provided us with information about their current catalysts, as well as potential future catalysts. In addition, we built in as much flexibility beyond those ranges as possible. The design limitations are then provided back to the catalyst development tasks in order to help direct the catalyst research such that the catalyst for the demonstrations will be able to be run in the TCPDU.

Comment – On overall impressions: *"NREL appears to be effectively dealing with safety issues that have caused delays. The uncertainty about the final pyrolysis pathway makes it unclear what the present facility should include. BETO may want to focus the effort on present needs, such as providing reasonable quantities of liquid bio-oil and postponing other decisions until later."*

You are correct that the final pathway has not been decided on. It is also uncertain whether the 2022 pathway will be the same as the 2017. Therefore, our design efforts have been to add the capability of as many pyrolysis pathways as possible to the TCPDU. We currently have the ability to produce fast pyrolysis oil, which can then be sent to other labs, such as PNNL, for further processing. We have designed unit operations (new scrubber and modified R-cubed) to add the capability of ex-situ pyrolysis. With the ex-situ modifications, only a change in the feeder system would be required to also add in-situ capability. It is important to us not to lose any of the previous capabilities of the TCPDU system, therefore all designs also maintain core functionality.

Comment – On overall impressions: **"**There is some learning potential from scale-up, and some benefit from capability to produce larger quantities of pyrolysis oil, but not very innovative, and value-for-money is questionable."

This task maintains and operates a core BETO capability for the Technology Demonstration & Deployment: "To develop emerging production technologies beyond bench-scale to pre-commercial demonstration scale, culminating in the construction of pioneer biofuels production plants." This pilot plant is used to evaluate early TRL stage technologies at a large scale, including testing newly developed catalysts for robustness and lifetime. Through our efforts in the past year, we have designed novel systems to address safety hazards associated with thermochemical pathways. Engineering designs and research from the TCPDU will be made available to the public and industry through peer reviewed publications and patents, which can then lead to further advances in the field.

Publications, Patents, & Presentations (FY13 – current)

- Baldwin, R.M.; Feik, C.J., 2013 “Bio-oil Stabilization and Upgrading by Hot Gas Filtration” *Energy Fuels*, 27, p. 3224.
- Dutta, A.; Hensley, J.; Bain, R.; Magrini, K.; Tan, E. C. D.; Apanel, G.; Barton, D.; Groenendijk, P.; Ferrari, D.; Jablonski, W.; Carpenter, D., 2014 “Technoeconomic Analysis for the Production of Mixed Alcohols via Indirect Gasification of Biomass Based on Demonstration Experiments.” IECR, 53, p. 12149.
- Bain, R.L.; Magrini-Bair, K.A.; Hensley, J.E.; Jablonski, W.S.; Smith, K.M; Gaston, K.R., & Yung, M.M., 2014 “Pilot Scale Production of Mixed Alcohol from Wood” *IECR*, 53, p. 2204.
- Wilcox, EM; Pomeroy, MD, “Hazard Mitigation for Biomass Gasification Condensate Collection.” Presented by EM Wilcox at *Thermochemical Science for Biofuels biannual meeting*, **September 2, 2014,** Denver CO.

- Patent Record of Invention in progress: “Controllable biochar passivation method using oxygen”