THE OHIO STATE UNIVERSITY

Biomass Gasification for Chemicals Production Using Chemical Looping Techniques

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Department of Chemical and Biomolecular Engineering

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DOE Bioenergy Technologies Office (BETO)

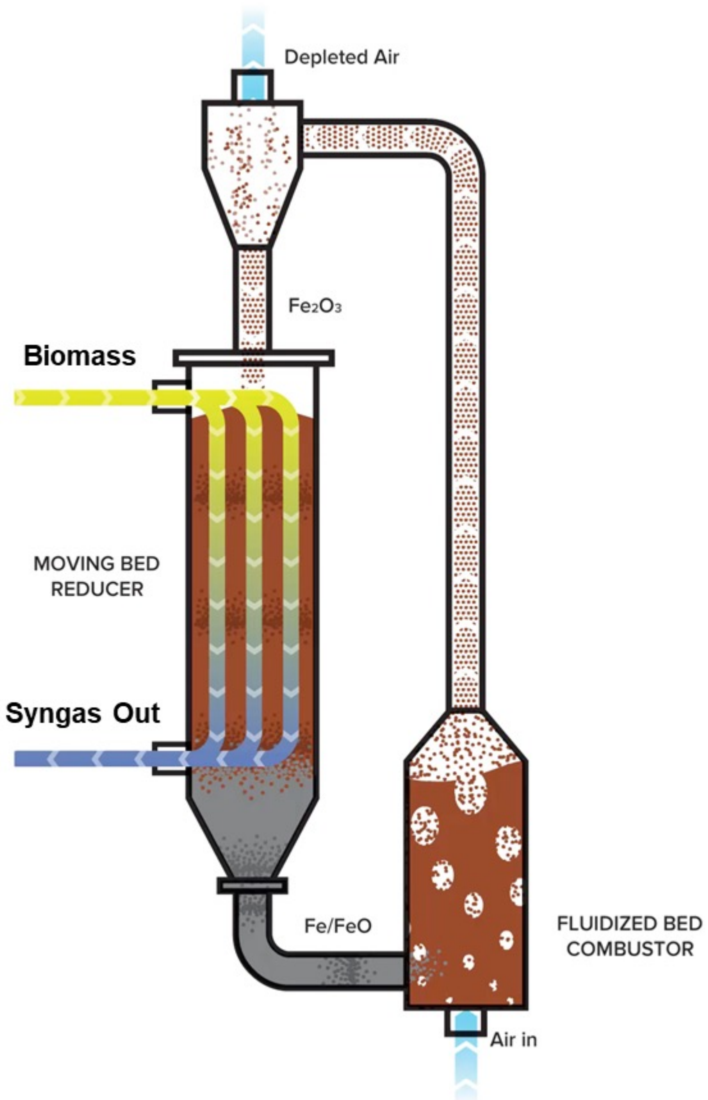
2021 Project Peer Review

Advanced Development and Optimization: Integration and Scale-Up

Acronyms

- BTS: Biomass-to-Syngas
- CFM: Cold Flow Model
- PHA: Process Hazard Analysis
- IRC: Industrial Review Committee
- TEA: Techno-Economic Analysis
- BP: Budget Period
- ITCMO: Iron-Titanium Composite Metal Oxide

Project Overview



Main reactions:

Reducer:	Biomass + H_2O + Fe_2O_3 → CO + H_2 + Fe/FeO
Combustor:	Fe/FeO + O_2 (Air) → Fe_2O_3 + Q
Net:	Biomass + H_2O + O_2 (Air) → CO + H_2 + Q

- Co-current moving bed reducer design
  - Tight control of gas-solid flow
  - High fuel conversion to syngas
- No tar reforming required
- H_2/CO molar ratio reach 2.12 while syngas purity is 70.4%
- Syngas generation and conditioning 44% cost reduction
- Total plant cost 22% reduction

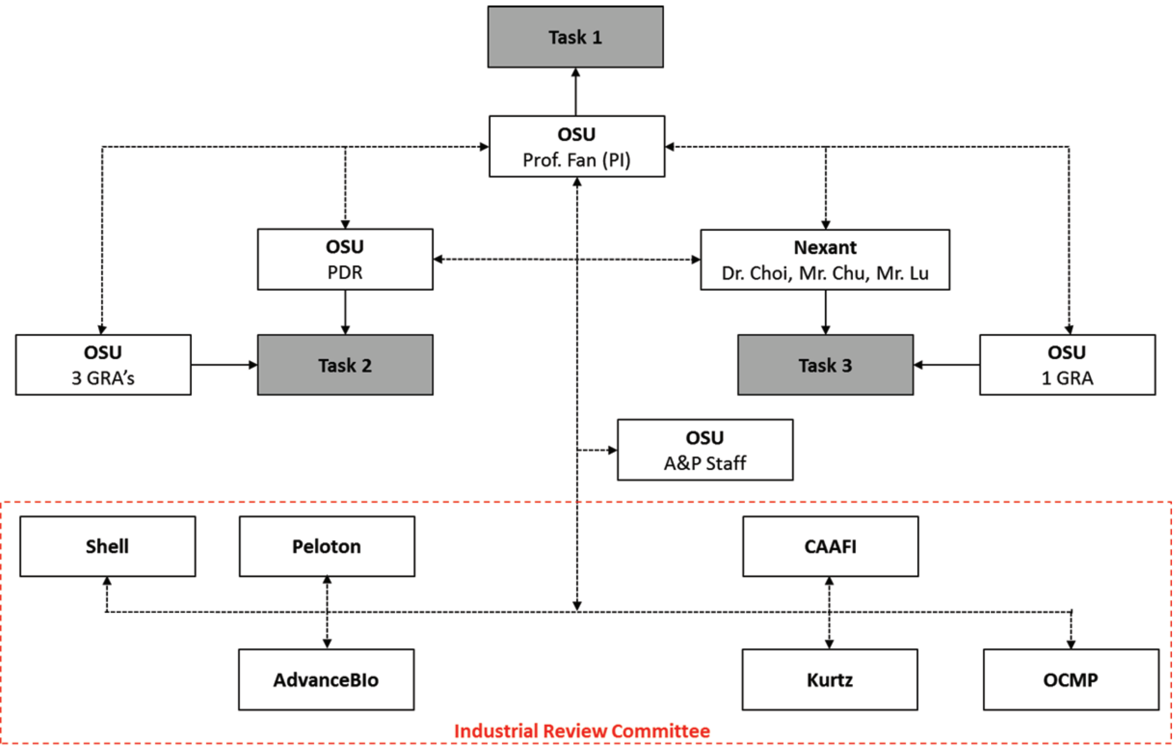
Project Goal

- The goal of the project is to develop an efficient thermochemical method for converting biomass to syngas.
- The project will address the continuous operation of the BTS reactor system in a sub-pilot test unit and perform a comprehensive TEA of a BTS-Methanol plant
  - To demonstrate the capability of the biomass to syngas chemical looping (BTS) process for continuous 2:1 ratio (H_2:CO) syngas production at the 10 kW_{th} biomass processing capacity using a scalable reactor design
  - Develop a process model and economic assessment of the BTS process integrated with a methanol synthesis plant to determine the required selling price in comparison with a reference plant case.
- Expected outcome:
  - Prove feasibility of chemical looping biomass to syngas process at sub-pilot scale, TRL-3 to TRL-5.
  - Complete estimation of required selling price of methanol using the chemical biomass to syngas process
- Potential impact
  - Development of a biomass gasification technology with low cost and high efficiency

Project Overview

- FOA
  - Fiscal Year 2015 BIOMASS RESEARCH AND DEVELOPMENT INITIATIVE (BRDI), USDA-NIFA-9008-004957
  - *<summarize BETO's objective of this FOA>*
  - *Optional: Use matrices approach*
- Project Tasks
  - Completed (BP1):
    - 10 kW_{th} Sub-Pilot Test Unit Detailed Design
    - Development of Design Basis, and Initial Performance and Economic Model
  - Completed (BP2):
    - Reactor System Fabrication, Assembly, and Commissioning
    - IRC Meeting and Technology to Market Assessment
  - In Progress (BP3):
    - Sub-Pilot System Operation
    - Finalization of TEA and Sensitivity Analysis

1 – Management



End-User Advisory Stakeholders:

- Peloton Technology
- Commercial Aviation Alternative Fuels Initiative (CAAFI)

Technology Advisors:

- Shell Global Solutions – Gasification Technology Experts
- AdvanceBio LLC – Biomass Feed System

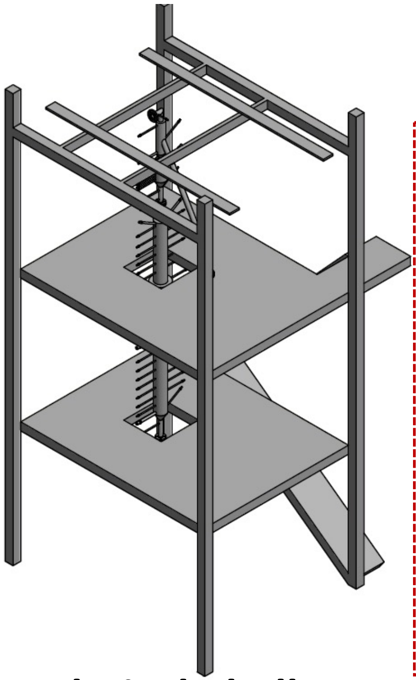
Biomass Supplies:

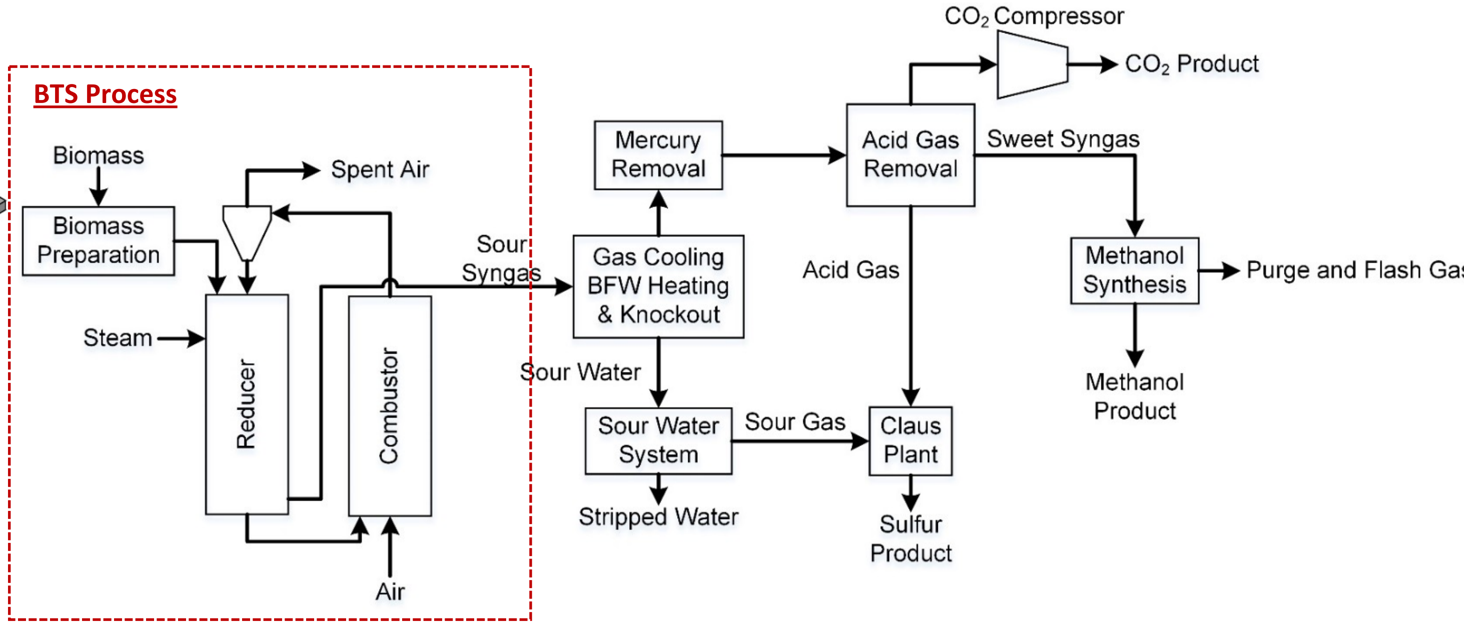
- Ohio Corn Marketing Program (OCMP)
- Kurtz Brothers

2 – Technical Approach

1. **Design, Construction, and Operation of the 10 kW_{th} BTS Sub-Pilot System**
2. **BTS Process Techno-Economic Analysis for Methanol Production Application**

Metrics: Carbon Conversion Efficiency, Syngas Composition, Production Cost of Methanol





Technical Challenges

- Integrated reactor system design: Cold flow studies performed in Year 1
- Sub-pilot reactor costs: existing sub-pilot facility available resources and equipment will minimize process costs
- Methanol plant integration with BTS process: Nexant support will ensure task completion

Nexant

Extensive experience with DOE techno-economic analysis

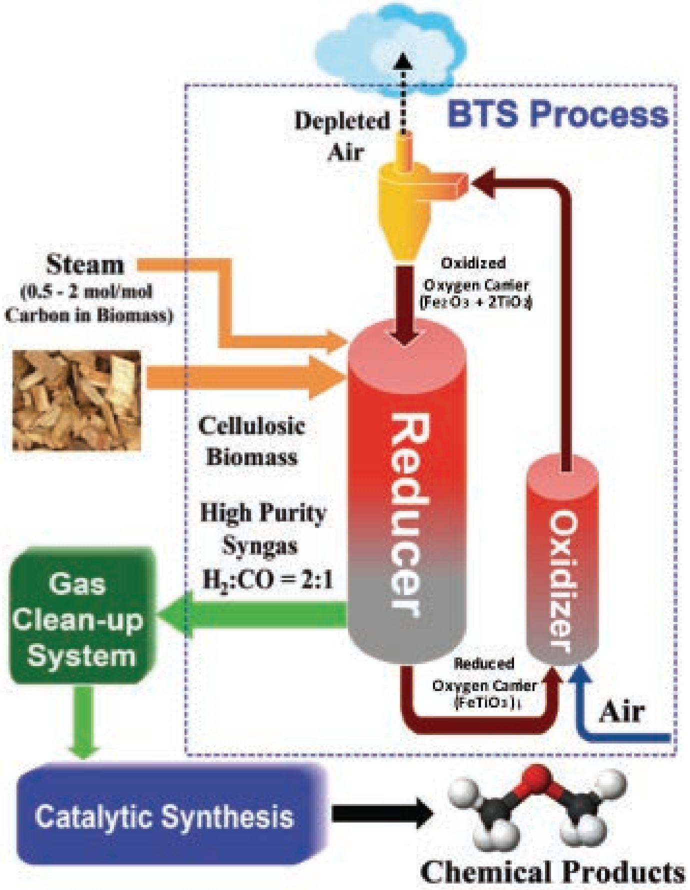
NATIONAL ENERGY TECHNOLOGY LABORATORY

- **Partnered with numerous technology developers** for various DOE-funded projects and performed overall systems integration and techno-economic analysis (TEAs) of their technologies
- Investigated **gasification, syngas desulfurization, post-combustion CO_2 capture (PCC), oxy-combustion, advanced water-gas shift, membrane reactor technologies, coal-to methanol production(CTM), and Fischer-Tropsch (FT) liquids production**, among others
- Provide **"big-picture" analysis** from an **overall systems standpoint** in evaluating pros and cons of the technology

Key Milestones

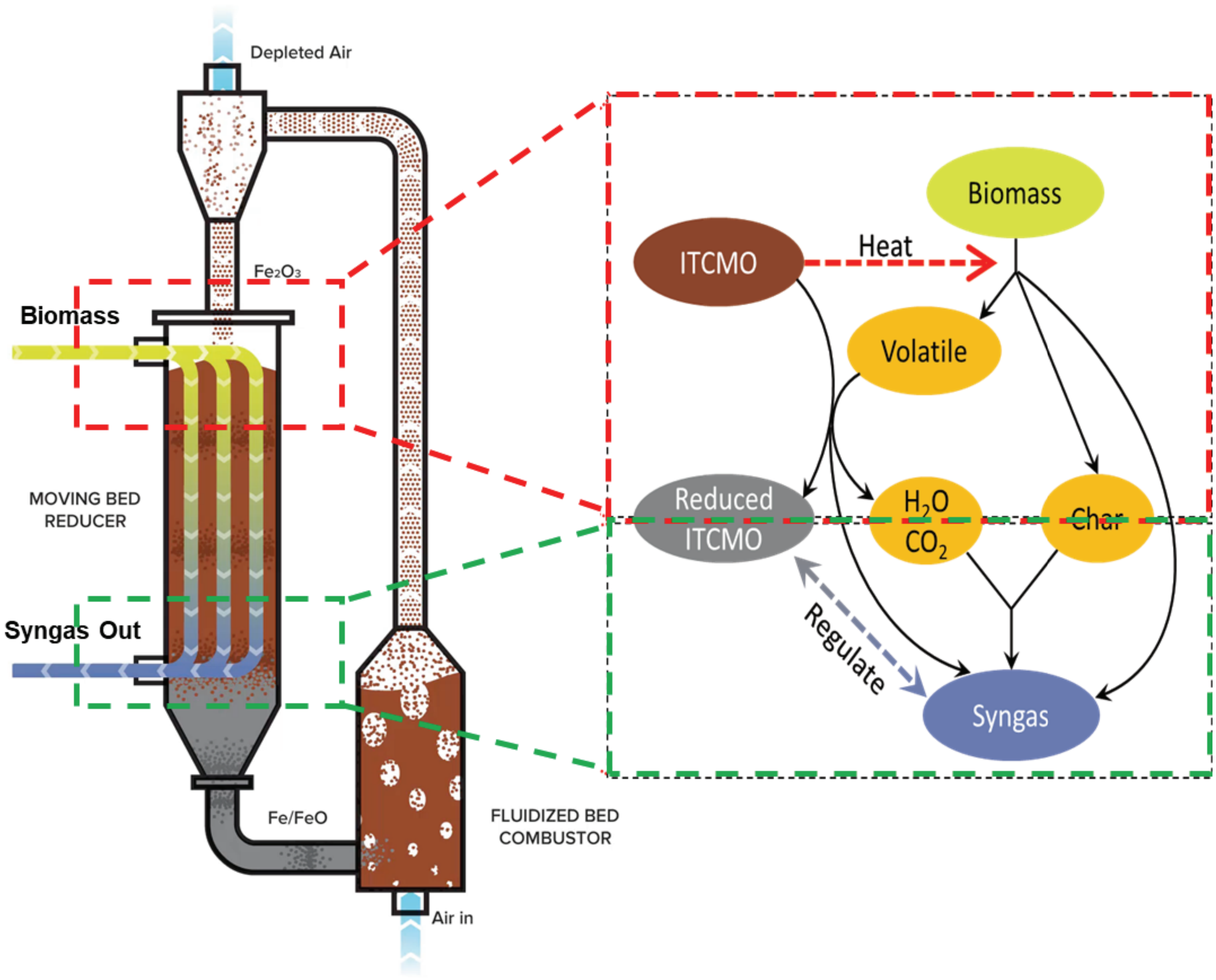
KEY MILESTONE NUMBER	KEY MILESTONE CONTENT
1) Milestone 1	Internal Dimensions of the reactor and interconnecting components complete and sized
2) Milestone 2	CFM construction complete and ready for operation
3) Milestone 3	PHA review of BTS process passed and all necessary safeguards identified
4) Milestone 4	Design basis and reference case for biomass to methanol selected
5) Milestone 5	IRC Quarter 2 Meeting completed
6) Go/No-Go 1	Detailed 10 kW_{th} reactor design complete
7) Milestone 6	BTS reactor fabrication complete to initiate assembly
8) Milestone 7	Equipment procured and instrumentation and controls programming complete
9) Milestone 8	BTS sub-pilot test unit assembled and ready for commissioning
10) Go/No-Go 2	BTS sub-pilot test unit fully assembled, commissioned, and ready for parametric testing
11) Milestone 11.1	Syngas production for short term operation achieved
12) Milestone 11.2	Sub-pilot unit demonstration for >100 hour of continuous operation completed
13) Milestone 12.1	Updated TEA of BTS-Methanol plant completed
14) Milestone 12.2	Final TEA Report completed for BTS-Methanol Plant

3 – Impact



- Directly Supports BETO's Mission:
  - "Develop and transform our renewable biomass resources into commercially viable high performance biofuels"
- Address BETO Level Barriers and Challenges
  - Cost of Production
- Project driven by TEA – verify reactor sizing/capital cost based on continuous process performance results
  - Methanol chosen as the product because baseline report provides detailed analysis for comparison
- BTS process considered process intensification approach to biomass gasification:
  - Eliminates tar reformer and air separation unit
  - Flexible H_2/CO ratio production
  - High carbon efficiency to syngas
  - Enabling the ability to use biomass gasification as a means for chemical synthesis

3 – Impact



Depleted Air
Fe_2O_3
Biomass
MOVING BED
REDUCER
Syngas Out
Fe/FeO
FLUIDIZED BED
COMBUSTOR
Air in
Biomass
ITCMO
Heat
Volatile
Reduced
ITCMO
H_2O
CO_2
Char
Regulate
Syngas

3 – Impact– 1.5 kWth Bench Unit Testing

Experimental Results Comparison to Process Model

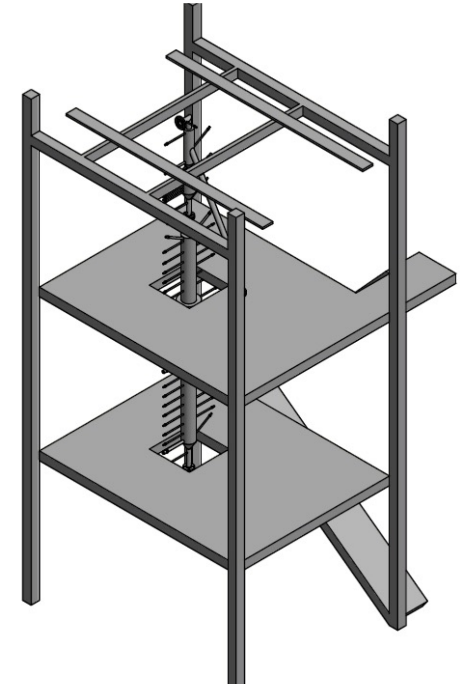
Interval	A		B	
$[O]:C_{Feed}$	2.0		1.7	
$H_2O:C_{Feed}$	1.57		1.41	
Concentration (dry base)	Exp.	Sim. X_C=75%	Exp.	Sim. X_C=90%
H_2 (%)	45	46.3	45	49.1
CO (%)	20	20.6	25	26.4
CO_2 (%)	32	33.1	25	24.6
Syngas Purity (%)	65	66.9	70	75.4
H_2:CO	2.3	2.2	1.8	1.9

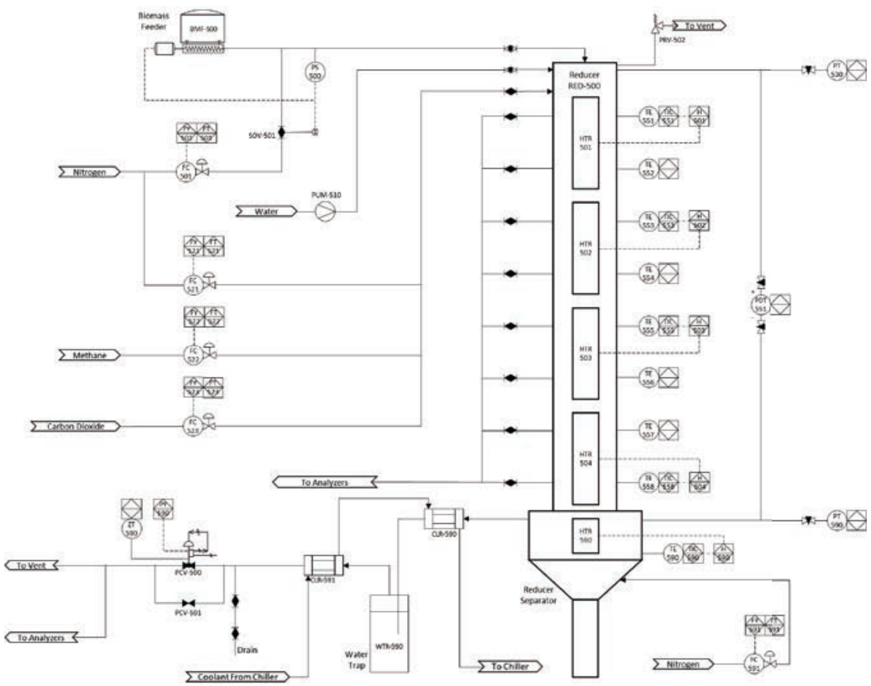
4 – Technical Accomplishments: Cold Model Tests

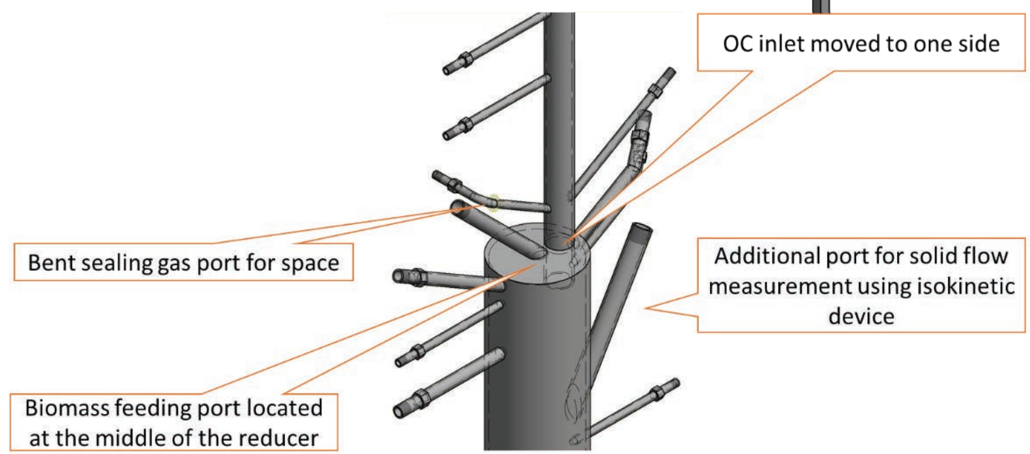
- 10 kW_{th} Sub-Pilot BTS Reactor
  - Cold Flow Model Studies Completed
    - Internal and interconnecting component sizing (HMB)
    - Test condition studies based on varying operating capacities
    - Feeding through heated pipe
  - What was learned:
    - Validated hydrodynamic calculation
    - Obtained operation experience under various operating conditions
      - Maintain solid circulation
      - Maintain gas seal
    - Tested biomass feeding
      - Gravimetric feeding is feasible at this scale
      - No sticking/agglomeration at temperature
      - Lack of lateral mixing

4 – Technical Accomplishments: Sub-Pilot Design

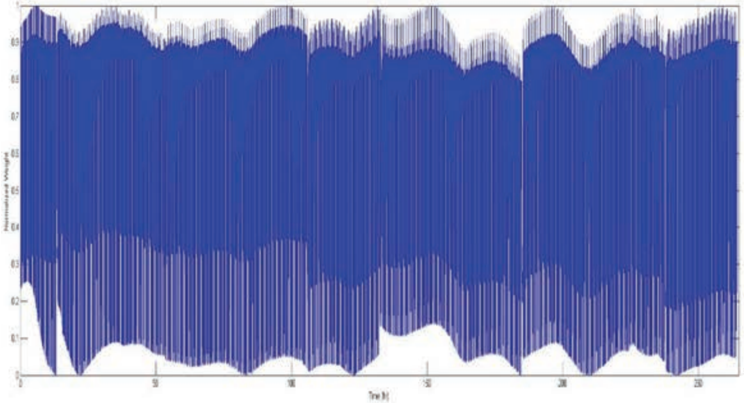
- 10 kW_{th} Sub-Pilot BTS Reactor
  - Sub-pilot Reactor Modification Completed
    - P&ID specifications
    - Controls specifications
    - Process Safety Review
    - Fabrication, Installation, and Commissioning





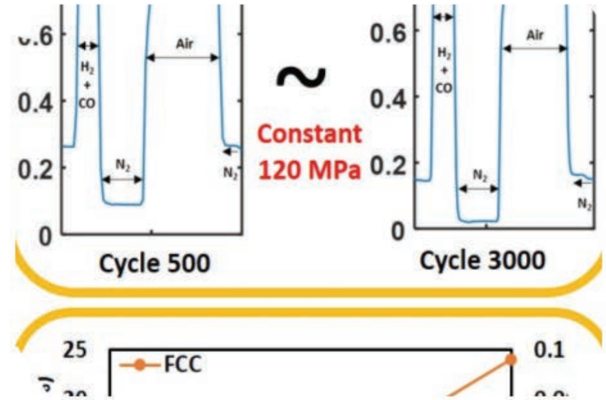


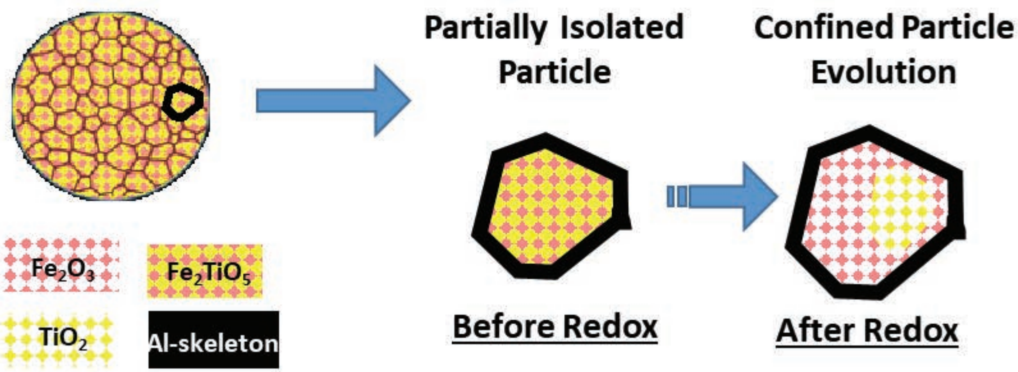
4 – Technical Accomplishments: Oxygen Carrier Particle

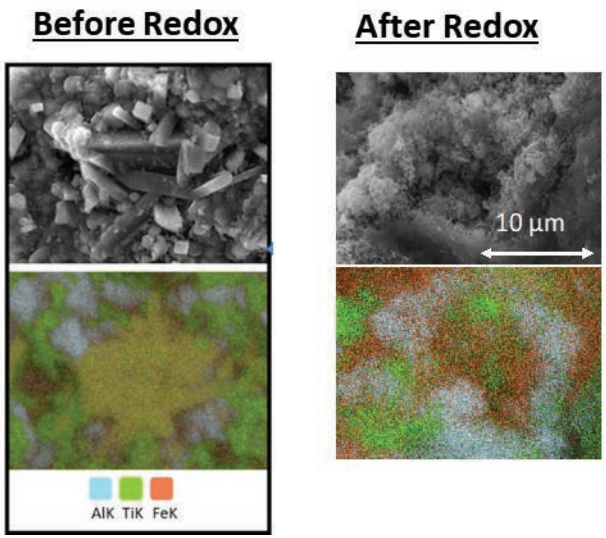


After 0 redox cycles

After 3,000 redox cycles



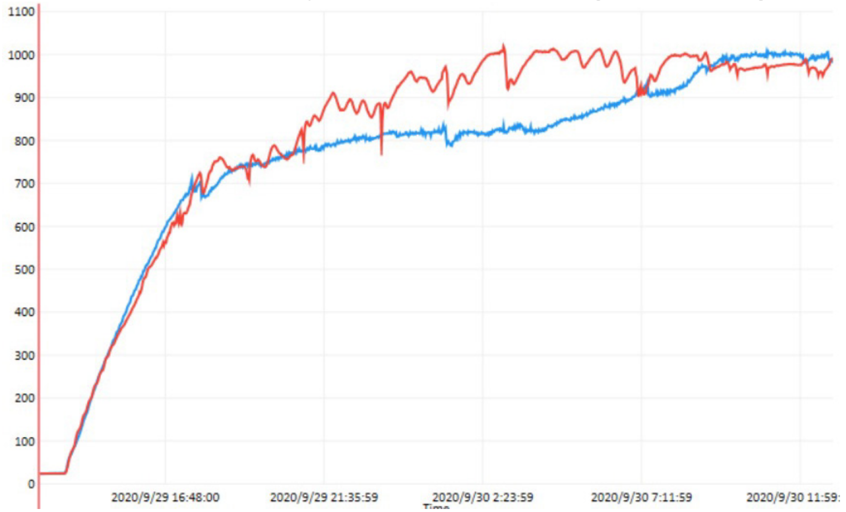




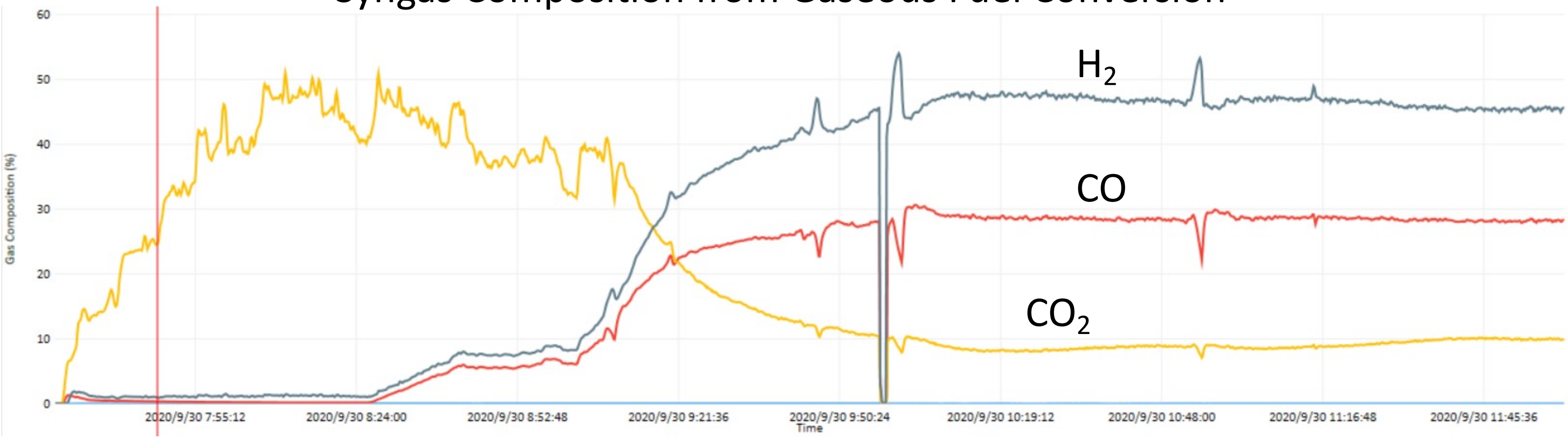
4 – Technical Accomplishments: Sub-Pilot Testing

- 10 kW_{th} Sub-Pilot BTS Reactor Operation
  - Heating to operation temperature
  - Conversion test on gaseous fuel
    - Full CH_4 conversion achieved
    - Syngas purity >80% (dry base)

Reactor Temperature during Heating



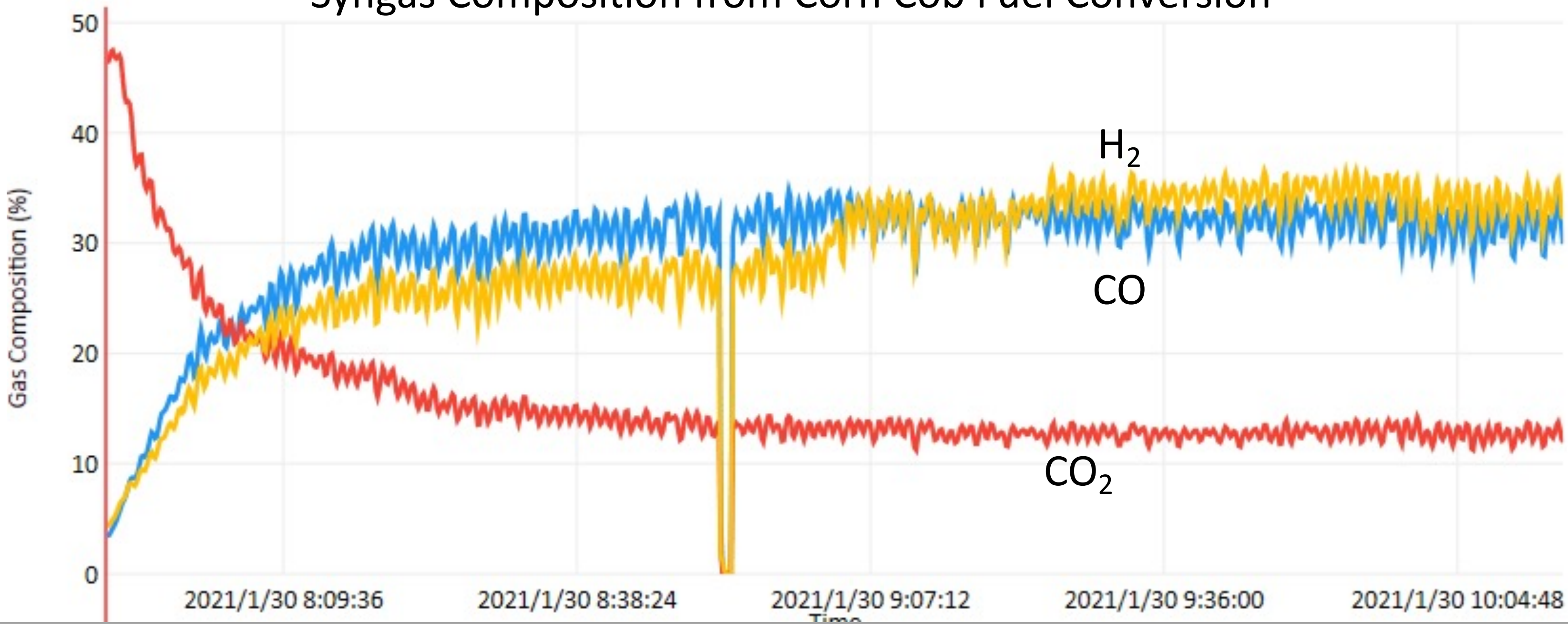
Syngas Composition from Gaseous Fuel Conversion



4 – Technical Accomplishments: Sub-Pilot Testing

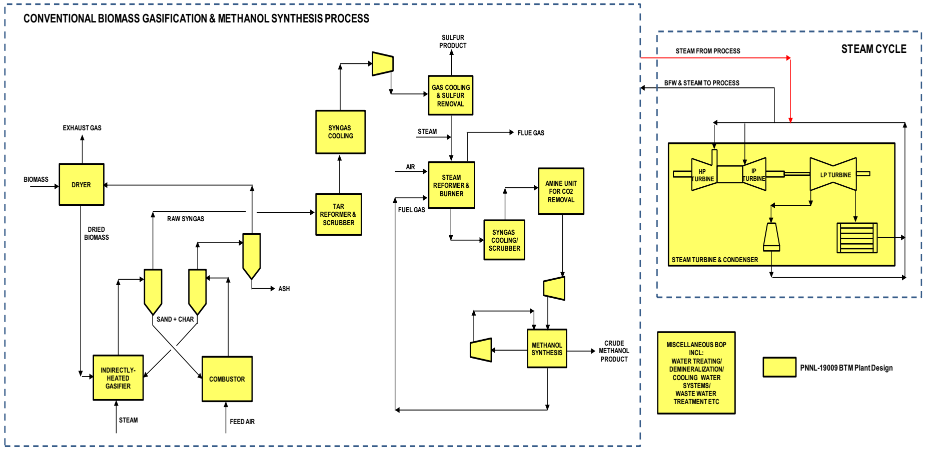
- 10 kW_{th} Sub-Pilot BTS Reactor Operation
  - Conversion test on corn cob
  - Syngas Purity >80%
  - Further testing ongoing
    - Adjust H_2:CO Ratio
    - Various biomass feedstock

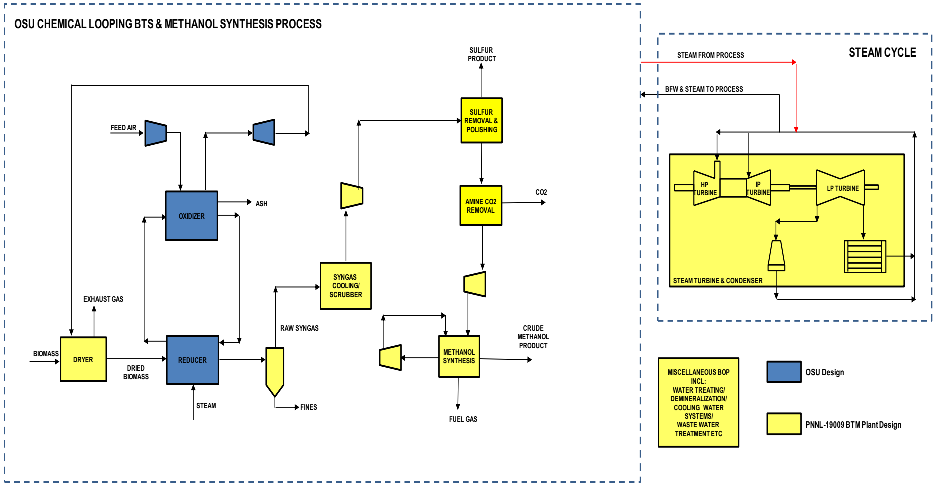
Syngas Composition from Corn Cob Fuel Conversion



4 – Technical Accomplishment: Process Analysis

- TEA economic studies
  - Design basis report development with selected reference cases completed
  - Process modeling of BTS-Methanol plant and reference case completed
  - Heat integration optimization in progress
  - Initial economic assessment in progress





Clean up to make more visible

4 – Technical Accomplishments: Process Analysis

- Reference Case – PNNL-19009 "Techno-economic Analysis for the Thermochemical Conversion of Biomass to Liquid Fuels", June 2011
- Chemical looping reactors simulated by RGIBBS model
  - Based on 1.5 kW_{th} Bench Unit Operation
  - Performance and sizing will be updated with 15 kW_{th} sub-pilot operation

Case Name for Current Study	Reference Case	OSU Case
Feed Handling and Preparation		
Steam-Heated Rotary Dryer	✓	✓
Biomass Gasification Technology		
Indirectly-Heated Gasifier	✓	
OSU BTS Chemical Looping		✓
Tar Reforming		
Bubbling Fluidized-Bed Reactor	✓	NR
Syngas Cleanup		
LO-CAT & Zinc Oxide Sulfur Removal	✓	✓
Steam Reforming	✓	NR
Water Gas Shift		✓
Amine Unit for CO_2 Removal	✓	✓
Rectisol for CO_2 and Sulfur Removal		Not Used
Methanol Production	✓	✓
Power Generation via Steam Turbine	✓	✓

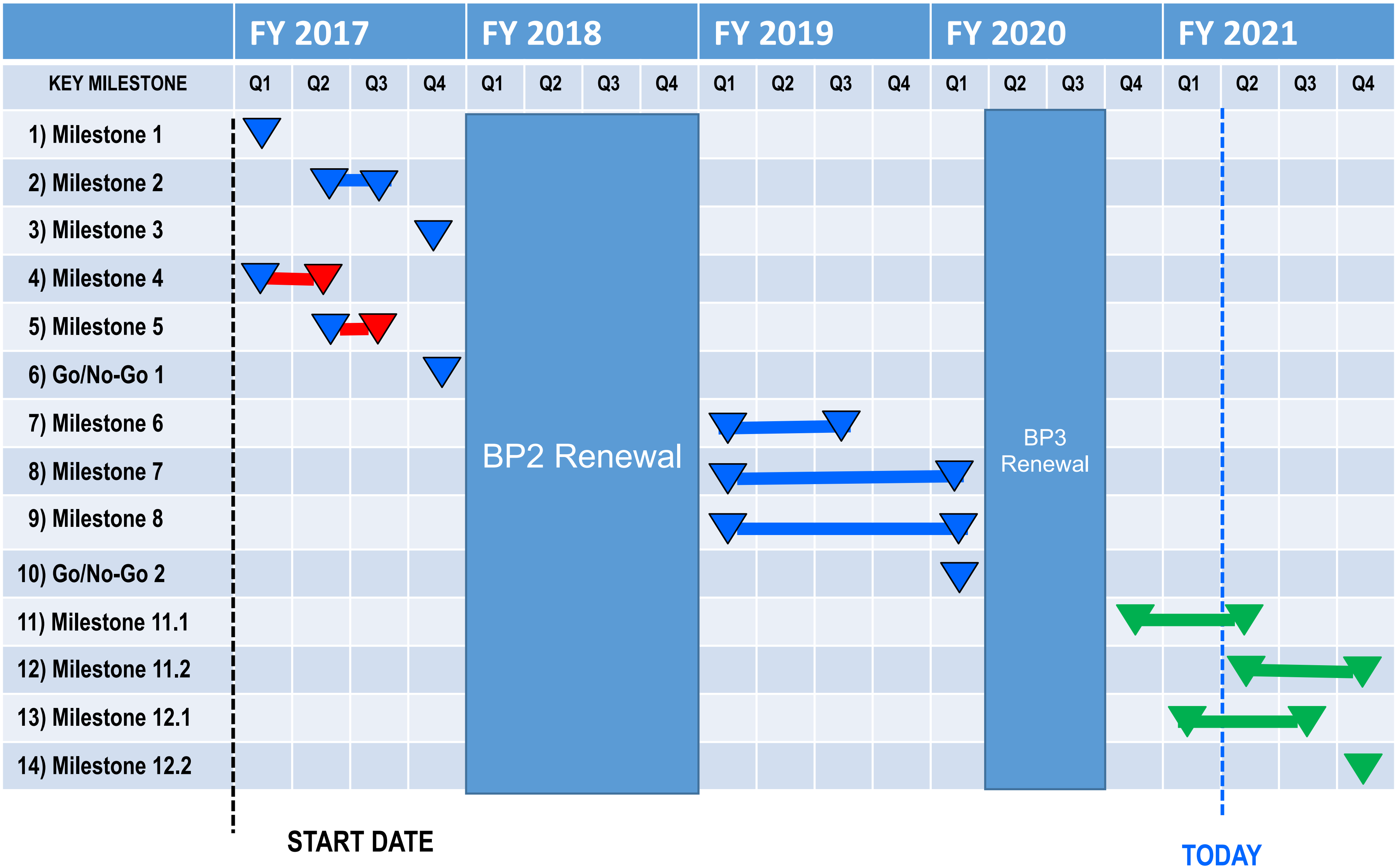
4 – Technical Accomplishments: Process Analysis

- BTS v.s. reference case: gasifier syngas flow is ~1.5x higher
  - Higher carbon efficiency
  - Higher compression power and CO_2 removal demand

- Mitigation Strategy
  - Convey unconverted char to combustor
    - Reduces CO_2 in syngas
    - Reduces steam demand

	Gasifier Syngas	
Case Description	OSU Chemical Looping BTM	Nexant IHGBTM Model
Gas Compositions (lbmols/hr)		
H2	6,925	1,427
CO	3,274	2,607
H2+CO	10,199	4,034
H2/CO	2.11	0.55
H2O	9,042	5,562
CH4	1.12	992
CO2	4,464	828
% CH4 (dry)	0.01%	16%
% CO2 (dry)	30%	13%
Tar, lbmols/hr	-	349
% Other Inerts (dry)	0.3%	-
	-	-
Stream Conditions	-	-
Total lbmols/hr	23,748	11,848
Total lbmols/hr (Dry)	14,706	6,285
Total lbs/hr	466,235	241,582
Mol Wt	20	20
Temp. degF	1,480	1,598
Psia	23	23
Total SCFM	150,207	74,936
Total ACFM	358,156	189,505

Key Milestones



Summary

- The BTS process is capable of substantial cost savings due to its process intensification attributes (i.e. gasifier, tar reformer, and ASU combined operation) and high carbon conversion efficiency. Proof of concept studies verified the sustained reactivity and strength of the ITCMO oxygen carrier and the moving bed reactor performance for high purity syngas production
- The project will address the continuous operation of the BTS reactor system in a sub-pilot test unit and perform a comprehensive TEA of a BTS-Methanol plant
- Budget period 1&2 activities focused on sub-pilot design and construction while budget period 3 is for extended unit operations
- IRC members will guide the direction of TEA and serve to market technology for continued scale-up
- BP3 in progress
    - Sub-pilot scale test unit operation in progress
    - Biomass conversion was achieved to produce syngas purity >80%
    - TEA sensitivity analysis ongoing
- BTS process meets BETO's objectives for advancing the use of biomass for biofuels production

Future Work of CL Technology

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Future Work of CL Technology Platform

H_2 production, Chemical Looping Full Oxidation

3.3

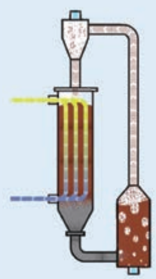
0.3

0

H_2/CO molar ratio in gas product

Chemical Looping for Syngas Production

Chemical Looping Partial Oxidation



Reducer

$(1+x+y)CH_4+xH_2O+yCO_2+Fe_2O_3 \rightarrow (1+x+2y)CO+(2+3x+2y)H_2+2FeO$

Combustor

$2FeO+1/2O_2 \rightarrow Fe_2O_3$

Overall Reaction

$(1+x+y)CH_4+xH_2O+yCO_2+1/2O_2 \rightarrow (1+x+2y)CO+(2+3x+2y)H_2$

CO production, Chemical Looping Full Oxidation

Quad Chart Overview

Timeline
- Start Date: 10/1/2016
- End Date: 9/30/2021

	FY20	Active Project
DOE Funding	$253,026	$1,500,000

Project Partners
- Nexant, Inc
- Industrial Review Committee members
  - Shell Global Solutions
  - Commercial Aviation Alternative Fuel (CAAFI) (1.3%)
  - AdvanceBio (2.3%)
  - Kurtz Brothers (2.3%)
  - Peloton (2.3%)

Barriers addressed
BETO MYPP Barriers
  - Ct-F. Efficient High-Temperature Deconstruction to Intermediates

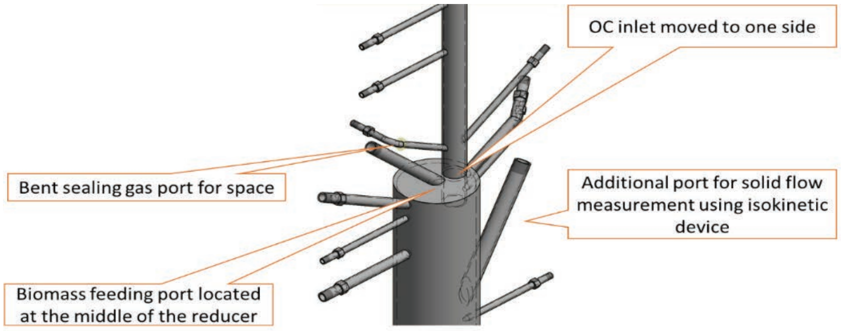
Project Goal
- The goal of the project is to develop an efficient thermochemical method for converting biomass to syngas.
- The project will address the continuous operation of the BTS reactor system in a sub-pilot test unit and perform a comprehensive TEA of a BTS-Methanol plant

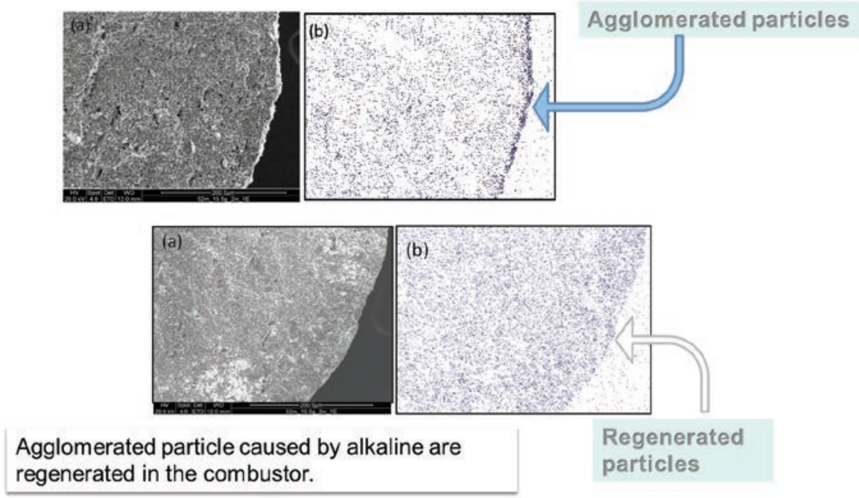
End of Project Milestone
- Syngas production with H_2:CO ratio >1.8 and >95% conversion
- Sustained sub-pilot unit operation for >100 hour of operation completed for two types of biomass fuels
- Updated TEA of BTS-Methanol plant completed incorporating results from sub-pilot operations

Funding Mechanism
Fiscal Year 2015 BIOMASS RESEARCH AND DEVELOPMENT INITIATIVE (BRDI), USDA-NIFA-9008-004957

2019 Response to Reviewer Comments

- Target of Methanol minimum selling price: less than $1.20/gal
- Biomass Delivery Design to Sub-pilot unit
  - Screw control flow rate combined with sealed inventory
  - Dry screw feed combined with rotary seal valve will be the initial commercial approach, like the coal delivery system developed for CDCL Technology
- Test Performance Outcomes
  - Residence time requirements for reactor sizing – thermodynamic vs kinetically limited design
  - TEA – set direction for advancement to maximize profit
- Mineral Matter in Biomass
  - Previous Alkaline studies showed no irreversible poisoning of OC material
  - Downstream syngas contamination and management under review with Nexant





2019 Response to Reviewer Comments

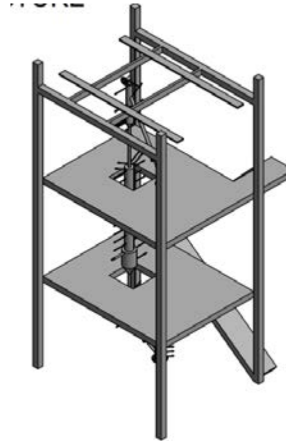
- Particle Strength and Attrition
  - Highly attrition resistant – lifespan expected to exceed 1 year of operation
  - Cyclic testing completed for over 10,000 cycles to date
- OC and Ash separation
  - Significant particle size and density difference allows for easy separation through control of gas velocity in reducer and combustor
    - Particle density: 3100 kg/m3
    - Particle Size: 1.5mm
  - The packed moving bed design allows OSU to utilize a larger OC size to make separation of ash easier

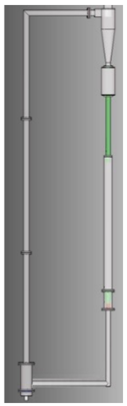
Sample results from Primary Particle Separation Testing

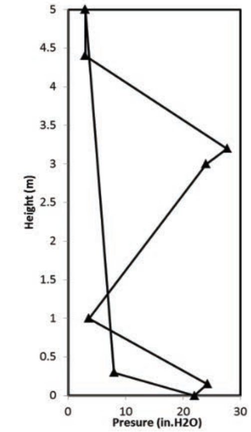
Operating Parameters							% Recovery			
Run No.	Time (s)	Air Q(scfm)	M (g/min)	Height (in)	Sec Q (scfm)	S holdup (%)	> 1.4 mm	1.4-1 mm	0.710-1 mm	<0.710 mm
1	300	60.2	~ 170	2	0	0.0124	97.93	74.28	17.46	12.14
2	300	60.2	170	2	0	0.0124	98.65	77.21	22.14	17.49
3	300	60.2	170	15	0	0.0124	99.92	99.09	27.29	16.42
4	300	60.2	170	8	0	0.0124	99.77	85.34	23.33	15.37
5	600	60.2	170	8	0	0.0124	99.69	84.02	16.68	9.30
6	600	60	364	8	0	0.0267	99.90	74.17	25.16	15.45
7	600	42.9	624	8	14.3	0.4424	99.85	61.24	15.48	5.54
8	300	42.9	1242	8	14.3	0.8806	99.78	65.32	15.71	5.93
9	300	42.9	1394	8	14.3	0.9883	99.86	54.59	17.17	7.20

2019 Response to Reviewer Comments

- System Novelty: Combination of multiple unit operations into one reactor system
  - Gasifier
  - Tar Reformer
  - WGS reactor
- Project Scope: Biomass Gasification – Methanol is used as the model product for cost comparison to SOTA reference design.
- Fluid flow challenges
  - Moving bed chemical looping operation resembles traditional CFB systems, except with an extended moving bed standpipe and 2 gas outlets. Primary challenge is properly design pressure balance to compensate for operational requirements
  - No mechanically moving parts in primary reactor section – increases system operation reliability







Gas Sealing and Solid Flow Control Devices

$P_1 \approx P_2$; $P_0 > P_1$; $P_0 > P_2$

If $L_1 = L_2$ $Q_1 = Q_2$