THE OHIO STATE UNIVERSITY

Biomass Gasification for Chemicals Production Using Chemical Looping Techniques

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DOE Bioenergy Technologies Office (BETO)
2019 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 Goal

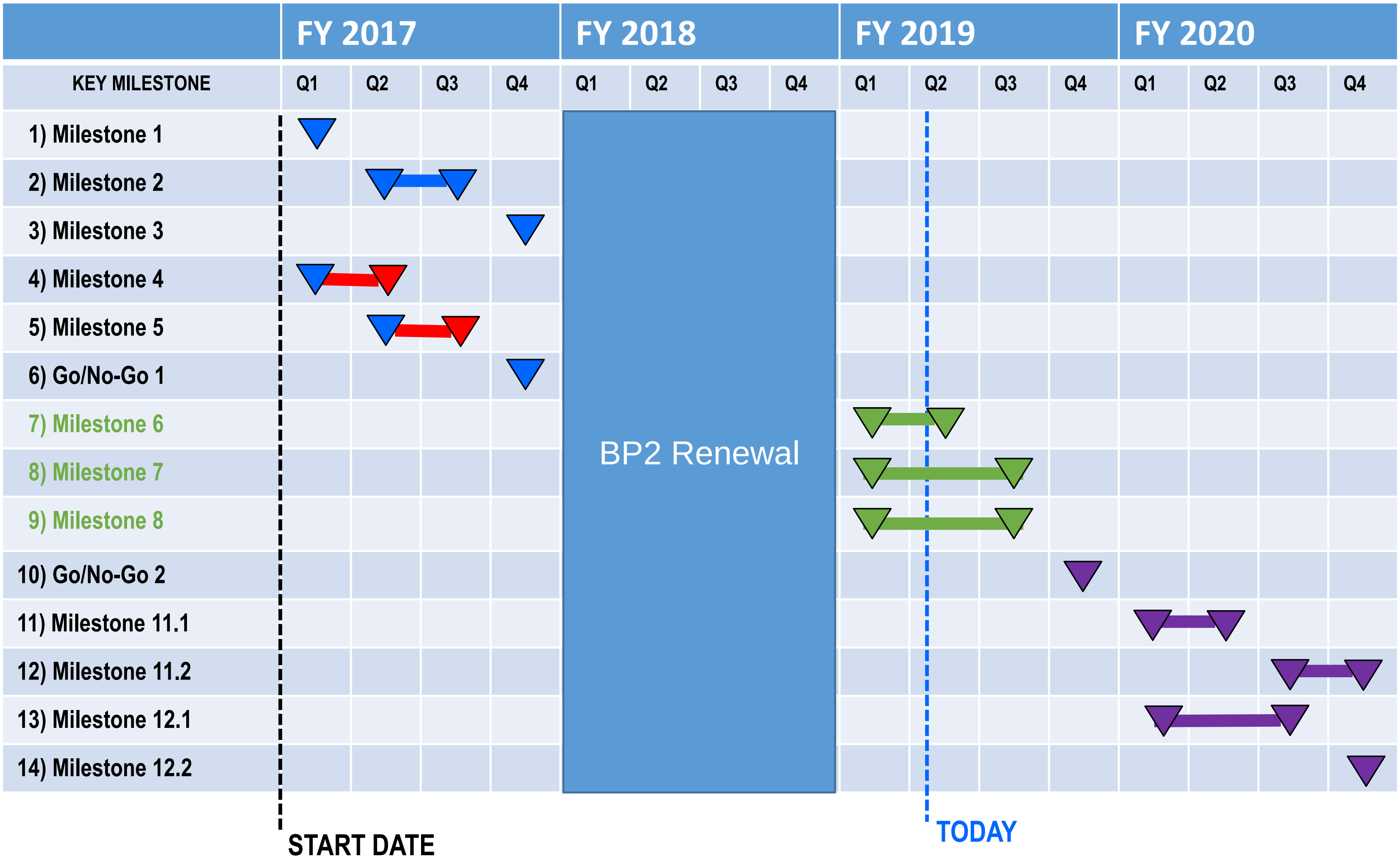
- The project will address the continuous operation of the BTS reactor system in a sub-pilot test unit and perform a comprehensive TEA of a BTS-Methanol plant
  - To demonstrate the capability of the biomass to syngas chemical looping (BTS) process for continuous 2:1 ratio (H_2:CO) syngas production 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:
  - Design and operation experience of an advanced thermal chemical biomass gasification technology
  - Comprehensive understanding on the techno-economic feasibility of the BTS technology
- Potential impact
  - Development of a biomass gasification technology with low cost and high efficiency

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

Key Milestones



Project Budget Table

	Original Project Cost (Estimated)		Project Spending and Balance		Final Project Costs
Budget Periods	**DOE Funding**	**Project Team Cost Shared Funding**	**Spending to Date**	**Remaining Balance**	**What funding is needed to complete the project.**
BP 1	$478,656	$201,673	$616,900		$616,900
BP 2	$543,958	$147,434	$143,786	$611,036	
BP 3	$477,386	$150,892		$628,279	

Quad Chart Overview

Timeline

- Start Date: 10/1/2016
- End Date: 9/30/2020
- Percentage Complete: 35%

Barriers

- BETO MYPP Barriers
  - Ct-F. Efficient High-Temperature Deconstruction to Intermediates
- Technical Targets:
  - Year 1: Detailed design of 10 kW_{th} reactor system complete and ready to fabricate
  - Year 2: Completion of reactor installation and commissioning
  - Year 3: Completion of techno-economic analysis and 10 kW_{th} unit testing

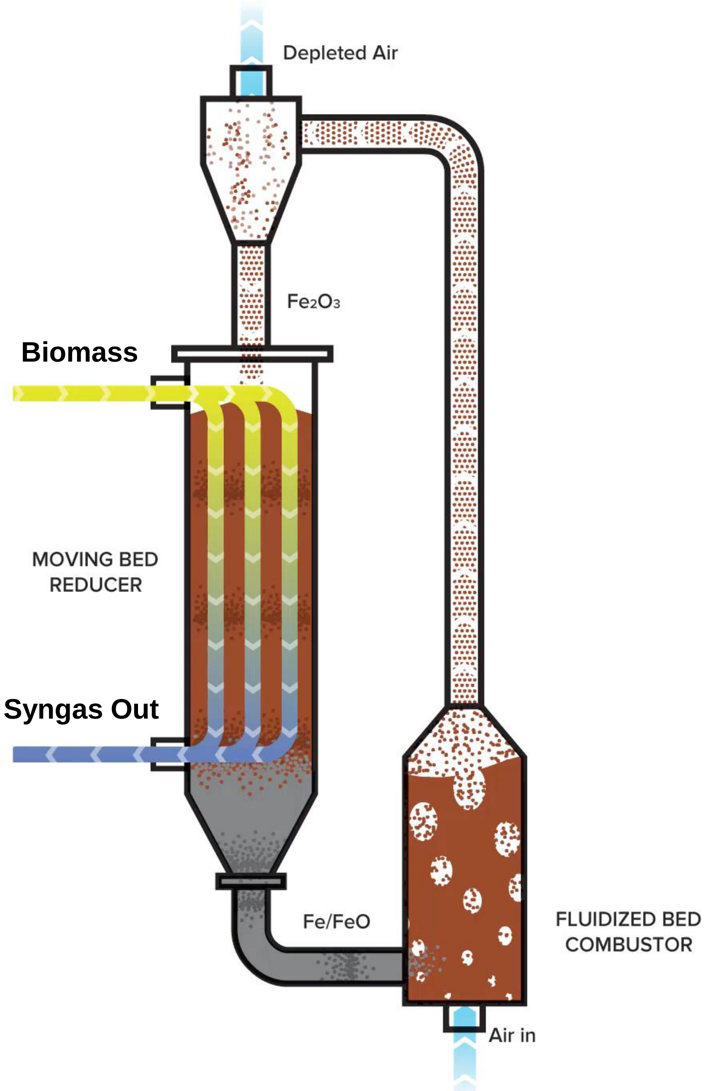
Budget

	BP1 Costs	BP2 Costs	BP3 Costs
DOE Funded	$478,656	$543,958	$477,386
OSU	$133,006	$78,768	$82,225
IRC Partners	$ 53,667	$ 53,667	$ 53,667

Partners

- Nexant, Inc (11%)
- Industrial Review Committee members
  - Commercial Aviation Alternative Fuel (CAAFI) (1.3%)
  - AdvanceBio (2.3%)
  - ZeaChem (2.3%)
  - Kurtz Brothers (2.3%)
  - Peloton (2.3%)

1 - Project Overview

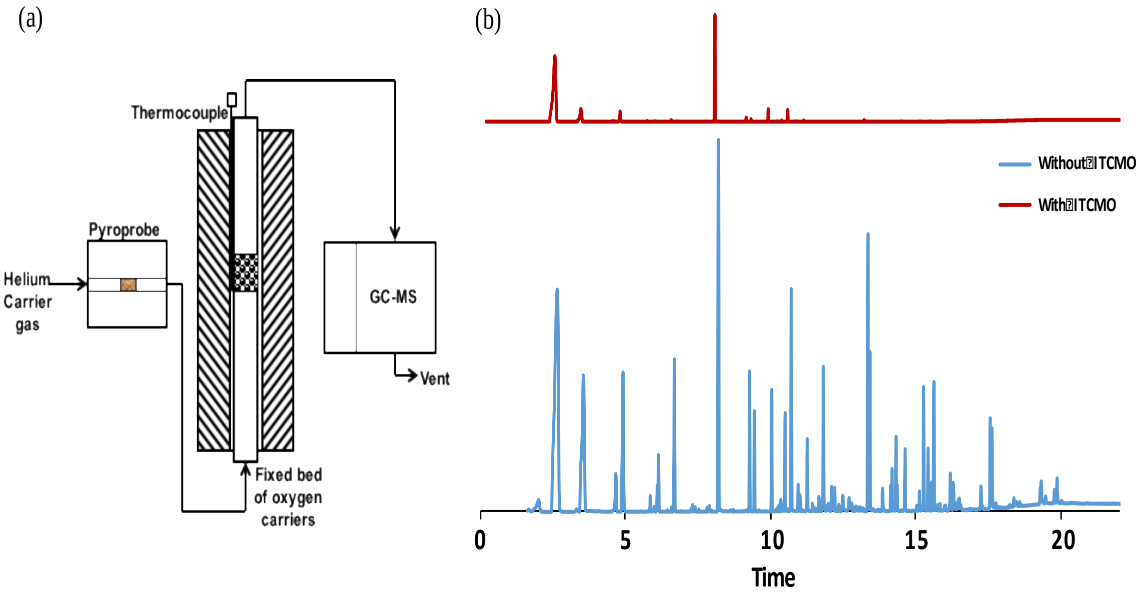


Main reactions:

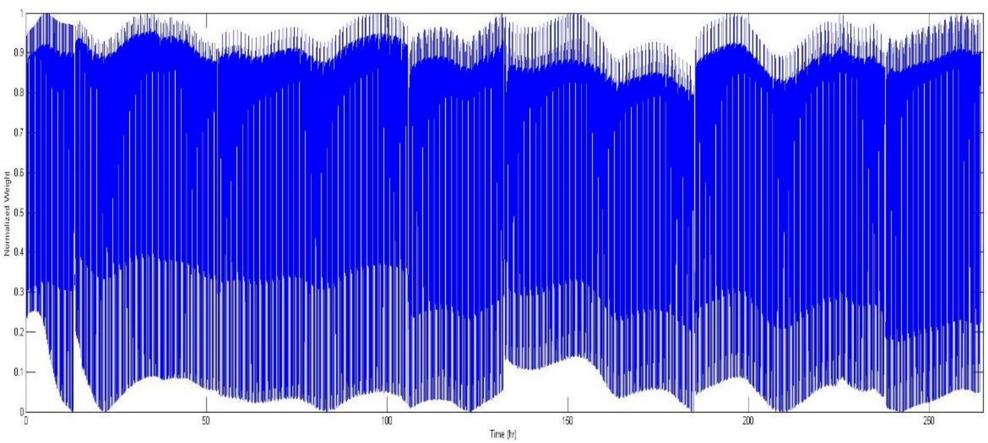
Reducer:	Biomass + H_2O + Fe_2O_3 → CO + H_2 + Fe/FeO
Combustor:	Fe/FeO + O_2 (Air) → Fe_2O_3 + Q
Net:	Biomass + H_2O + O_2 (Air) → CO + H_2 + Q

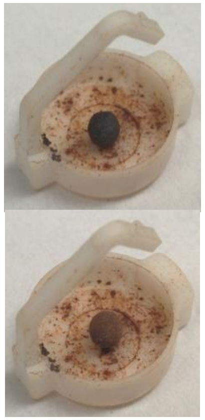
- Co-current moving bed reducer design
  - Tight control of gas-solid flow
  - High fuel conversion to syngas
- No tar reforming required
- H_2/CO molar ratio reach 2.12 while syngas purity is 70.4%
- Syngas generation and conditioning 44% cost reduction
- Total plant cost 22% reduction

1 - Project Overview: ITCMO Performance



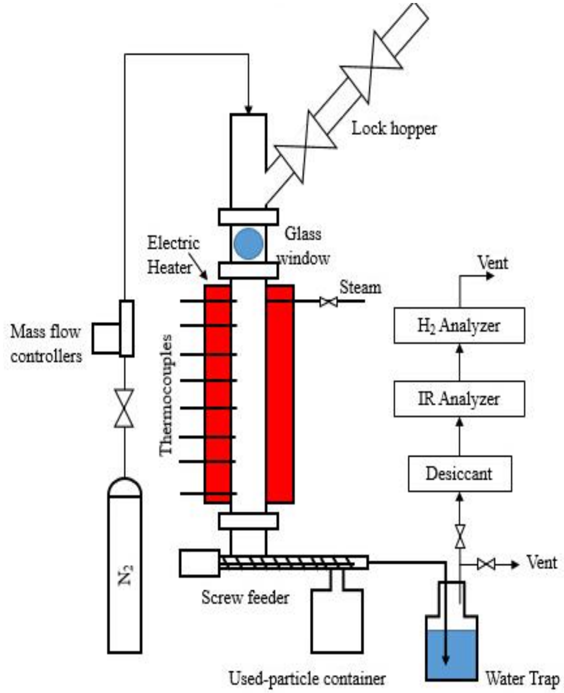
ITCMO oxygen carrier able to crack tar constituents in biomass

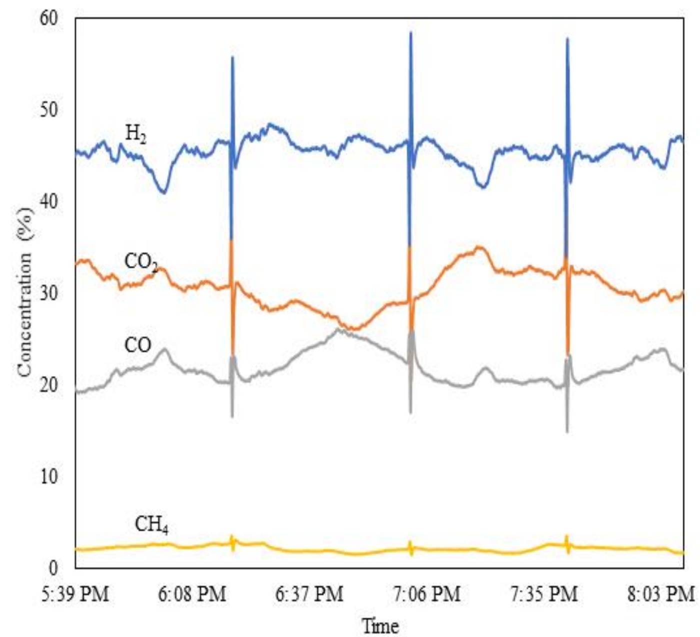




>1,000 redox cycles completed without loss in reactivity, recyclability, or strength

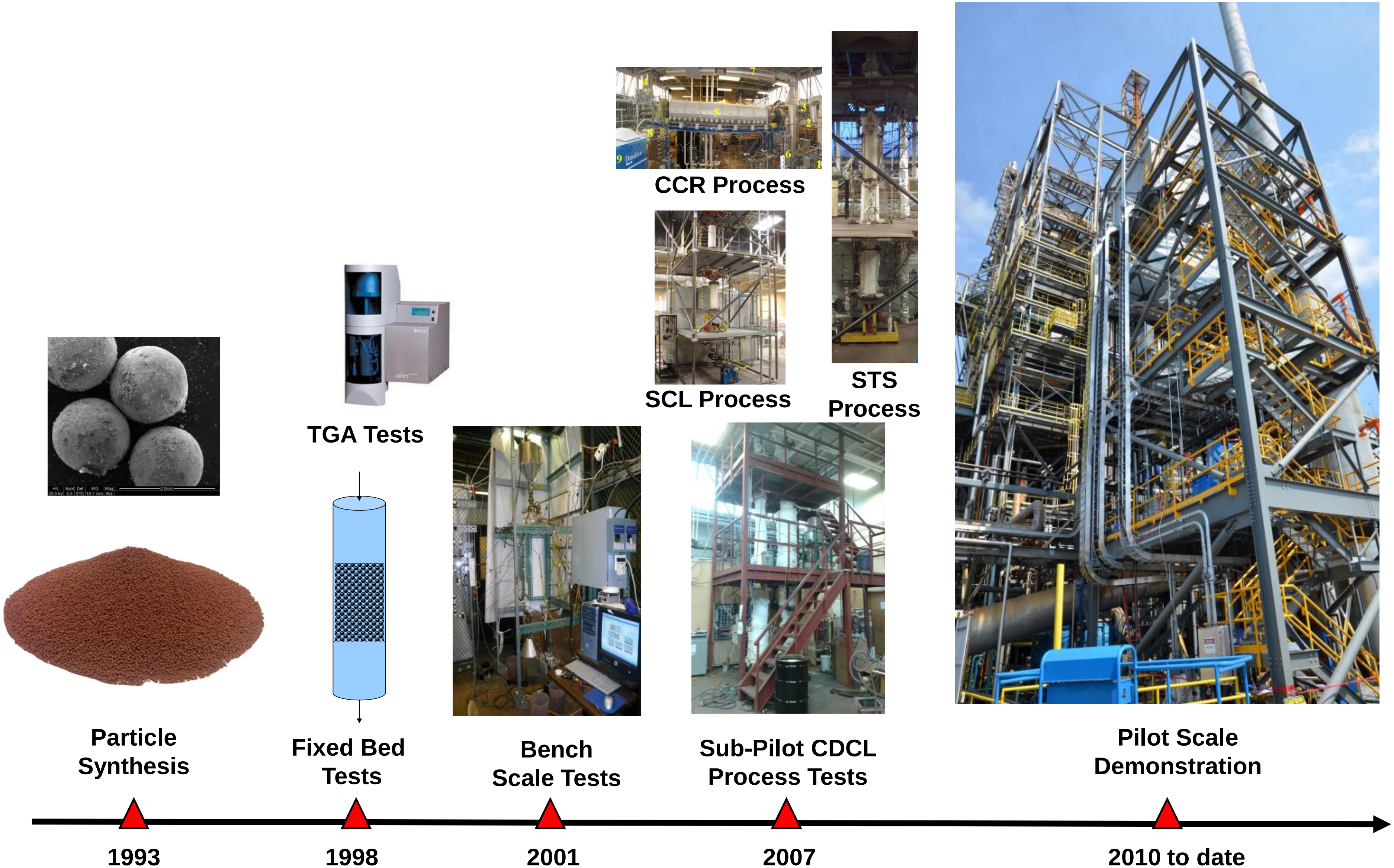
1 - Project Overview: 1.5 kW_{th} Bench Unit Operation





Condition	1		2		3		4	
Feedstock	Methane		Methane		Woody Biomass		Woody Biomass	
Temperature	960 °C		975 °C		1000 °C		1000 °C	
$[O]:C_{Feed}$	2.5		2.2		2.0		1.7	
$H_2O:C_{Feed}$	0		0		1.59		1.55	
Concentration (dry base)	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
H_2 (%)	62.69	63.81	63.53	63.84	46.28	46.88	46.99	46.56
CO (%)	33.89	33.41	33.62	33.42	20.74	26.52	28.29	26.67
CO_2 (%)	3.42	2.78	2.85	2.74	32.98	26.60	24.72	26.77
H_2:CO	1.85	1.91	1.89	1.91	2.23	1.77	1.66	1.75

Evolution of OSU Chemical Looping Technology



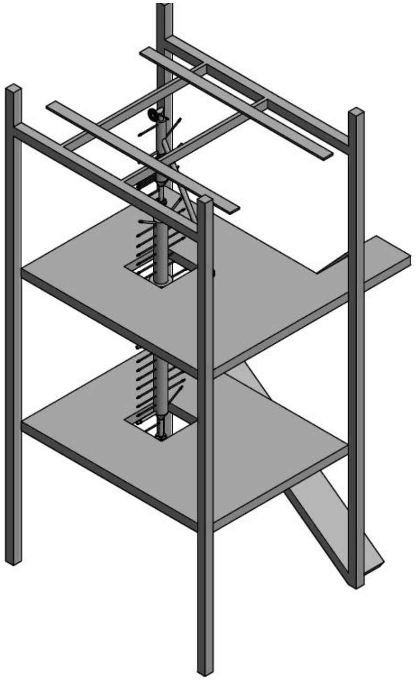
Fan, L.-S., Zeng, L., Luo, S. *AIChE Journal*. 2015.

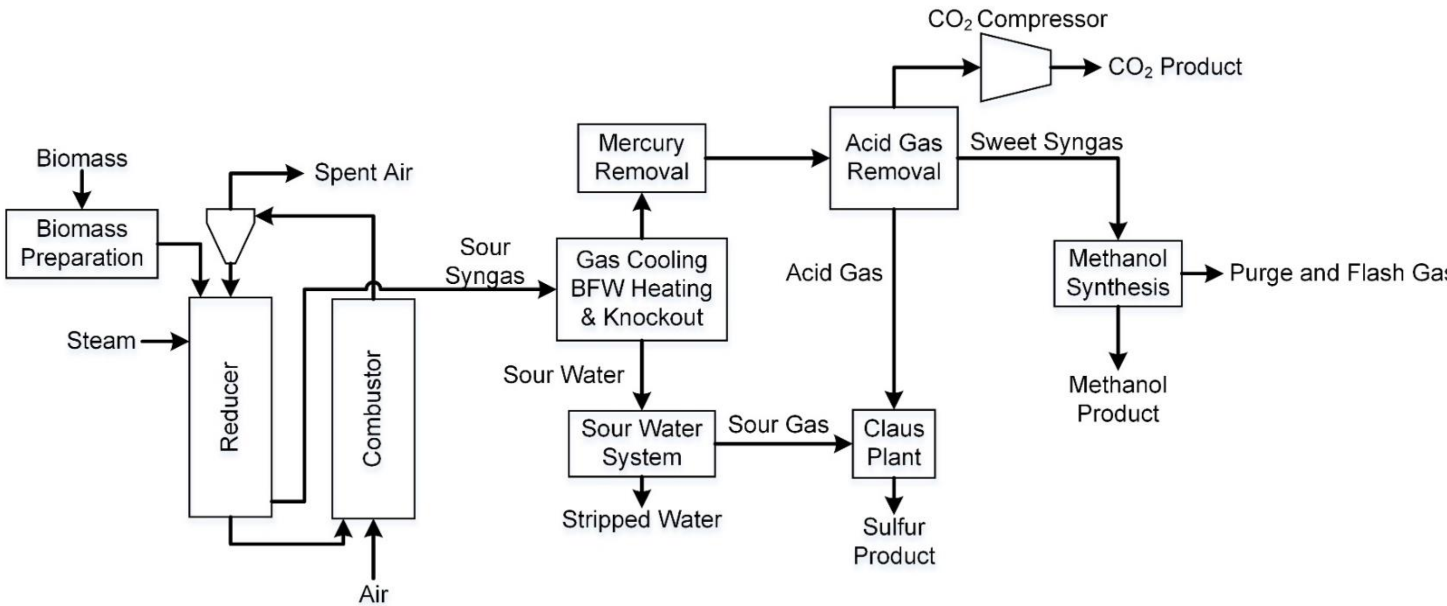
1 - Project Overview

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

2 – Technical Approach (Technical)

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

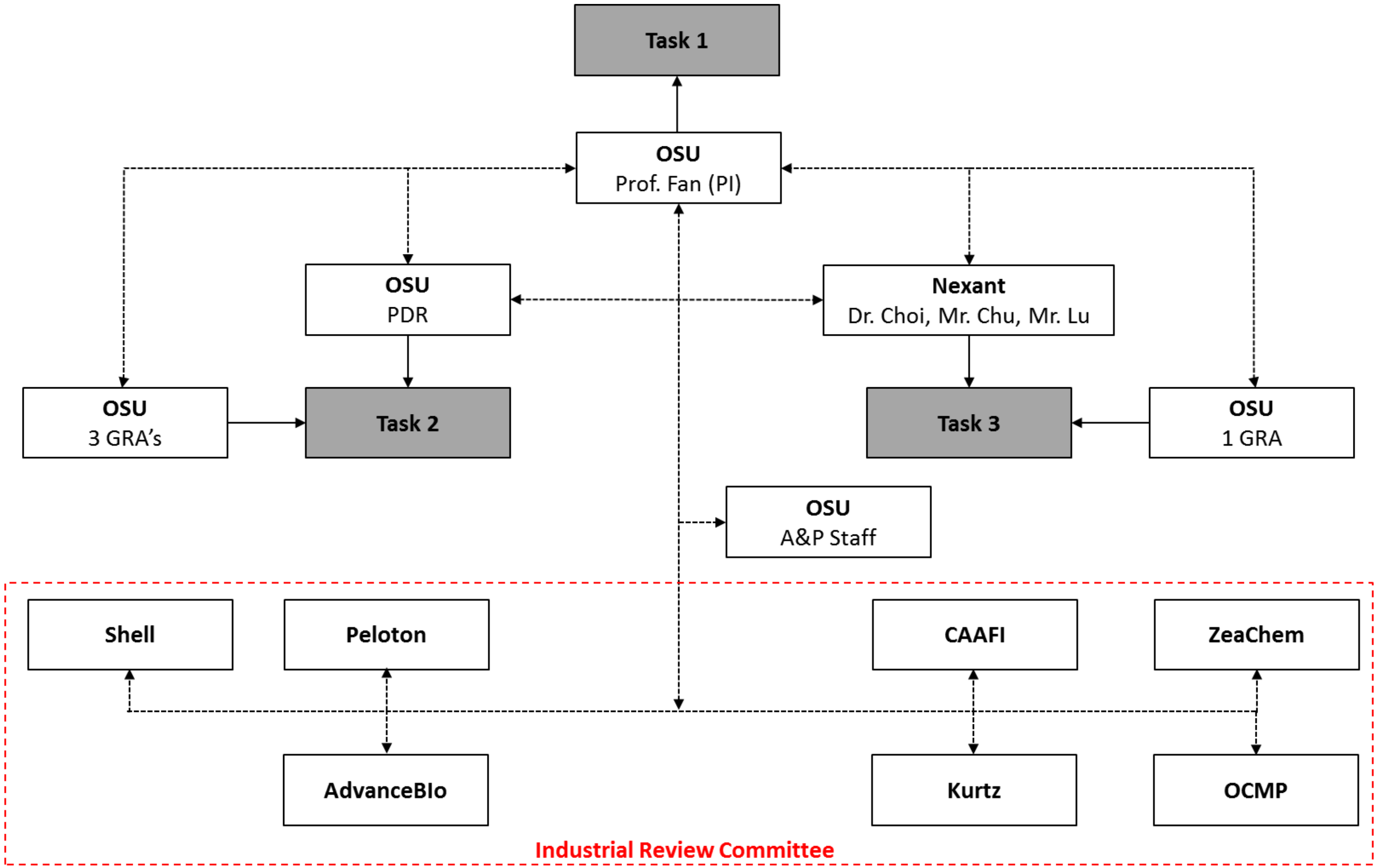




Technical Challenges

- 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

2 – Technical Approach (Management)

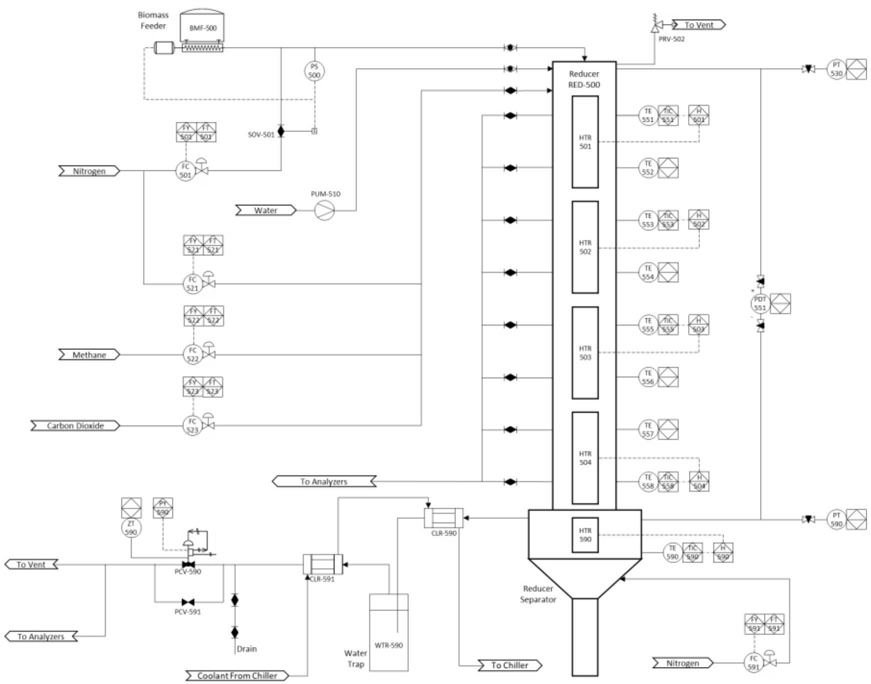


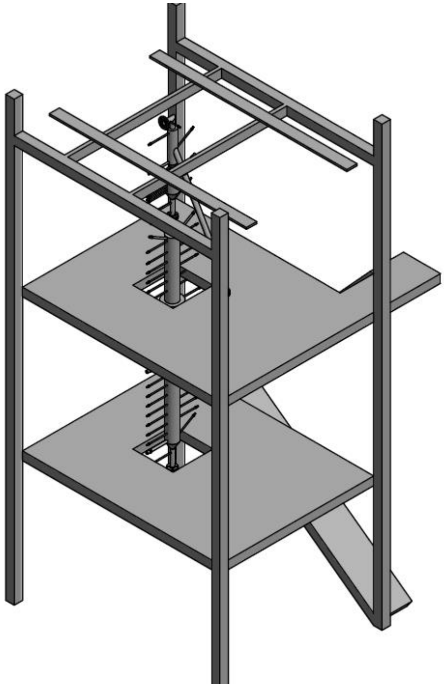
3 – Technical Accomplishments

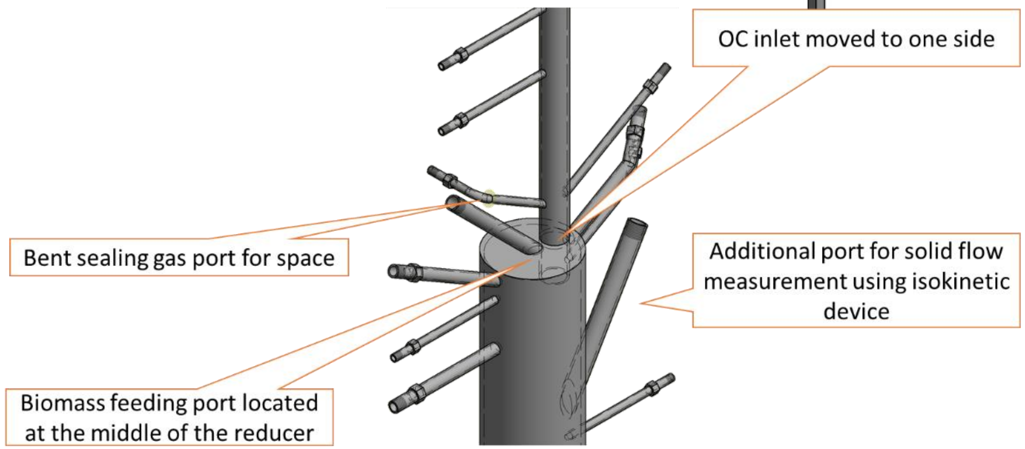
- 10 kW_{th} Sub-Pilot BTS Reactor
  - Cold Flow Model Studies Completed
    - Internal and interconnecting component sizing (HMB)
    - Test condition studies based on varying operating capacities
    - Feeding through heated pipe
  - What was learned:
    - Validated hydrodynamic calculation
    - 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

3 – Technical Accomplishments

- 10 kW_{th} Sub-Pilot BTS Reactor
  - Sub-pilot Reactor Detailed Design Completed
    - P&ID specifications
    - Controls specifications
    - Process Safety Review
    - Detailed reactor design and costing







3 – Technical Accomplishments

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  - Sub-pilot Reactor Detailed Design Completed
    - P&ID specifications
    - Controls specifications
    - Process Safety Review
    - Detailed reactor design and costing

NODE: B Title: Reducer
Design Intent of Node: Convert biomass (20g/min) into syngas. Hazards: heat, flow, combustible gas

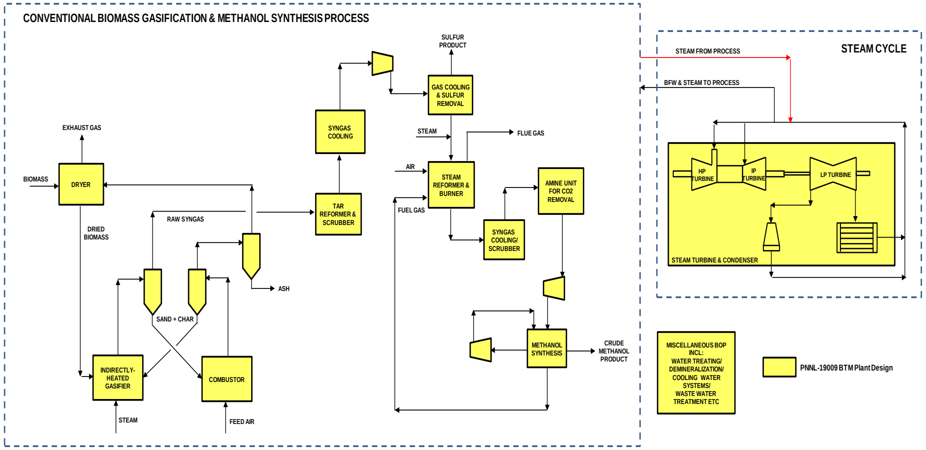
Guideword/ Deviation	Cause	Freq	Consquences	Severity	Safeguards/Protection Factors	Protec Factor	Scenario Freq	Scenario Risk	Action Priority	Rec # Comments
None of								---		
Biomass flow	BMF-500 Failure	0	No reaction	0		0	0	0	C	Order spare screws for biomass feeder. Monitor biomass feeder operation by weighing scale
	Depleted biomass supply	0	No reaction	0		0	0	0	C	
	Plugged line or injection port	1	No reaction; Biomass feeding damage; Pressure buildup in biomass feeder	1	Operator recognition	1	0	1	B	Install hard wired pressure switch to shut down biomass feeder when the pressure is high.
steam flow	PUM-501 Failure	-1	Low H2 concentration	0		0	-1	---		
biomass feeder N2 flow	FC-501 Failure	-1	Syngas leak into biomass feeder.	2		0	-1	1	B	In PLC: Show alarm if FC-501 flow is low
	N2 tank runout	0	same as above	2		0	0	2	A	Operation: check gas tank inventory every 2 hours; Install gas alarm near the biomass feeder; Leak test the biomass feeder before run
gas flow	FC-521 or FC-522 or FC-523 Failure; gas tank runout	-1	Incorrect reaction condition; inaccurate gas analysis	0		0	-1	---		
		-1	Low reactor pressure drop, causing air flow into reducer	3		0	-1	2	A	In PLC: trip system when zone seal flow direction reversed and switch gas flowing into combustor to N2 Operation: check gas tank inventory every 2 hours
solid flow	Plug in system / no solids circulation	2	Accumulation of biomass at the top of the reducer; sintering of oxygen carrier particles	0	Operator recognition	1	1	1	B	Add isokinetic solid circulation measurement device to the reducer
outlet gas flow	Gas outlet plug	0	Pressure buildup in system; Syngas leakage into combustor; potential skin burn	3	PPE and insulation/heater	1	-1	2	A	In PLC: trip system when zone seal flow direction reversed and switch gas flowing into combustor to N2 Add pressure releive valve at the top of the reducer
reactor temperature	Heater Failure	0	Loss of reaction; inability to operate	0		0	0	0		Stop biomass feed when reactor temperature is too low; Install heater protection TCs
pressure drop	PDIT-550 Failure	1	no indication of pressure drop accross reducer; difficulty in operation	0		0	1	1	B	Add purge gas to pressure ports
More of								---		
Biomass flow	Biomass Feeder Malfunction	-1	biomass feeding line plug; high reactor pressure; syngas leakage into combustor; potential skin burn	3	PPE and insulation/heater	1	-2	1	B	In PLC: trip system when zone seal flow direction reversed and switch off biomass feeder.
biomass feeder pressure	biomass feeding line plug	1	biomass feeder damage; pressure buildup in biomass	1	Operator recognition	1	0	1	B	Install hard wired pressure switch to shut down biomass feeder when the pressure is high.
steam flow	PUM-501 malfunction	-1	Pressure buildup in system; Syngas leakage into combustor; potential skin burn	3	PPE and insulation/heater	1	-2	1	B	In PLC: trip system when zone seal flow direction reversed and switch off water pump.
gas flow	MFCs malfunction	-1	Pressure buildup in system; Syngas leakage into combustor; potential skin burn	3	PPE and insulation/heater	1	-2	1	C	In PLC: trip system when zone seal flow direction reversed and switch off water pump.
reactor pressure	Outlet or system plug		Same as "None of: gas outlet flow"					---		
pressure drop	Excessive gas flow caused by excess gas or biomass		Same as "More or: biomass flow/steam flow/gas flow"					---		
As well as								---		
Liquid water flow into reducer	PUM-501 malfunction	-1	system pressure fluctuation	0	The reactor is heated. Liquid water will be evaporized when entering the reactor.	1	-2	---		Previous experience shows that liquid water is not going to cause significant fluctuation
moisture into analyzer	CLR-590 failure	-1	damage IR analyzers	0	Gas conditioning system	1	-2	---		
Other than								---		
air flow into reducer	Incorrect pressure balance	-1	biomass burning in reducer; local hot spot; reactor damage; potential skin burn	3	PPE and insulation/heater	1	-2	1	B	In PLC: trip system when zone seal flow direction reversed. switch gas flowing into combustor to N2
Part of								---		
Reducer integrity	High temperature or stress	-1	Syngas or high temperature solid leakage; potential skin burn or toxicity; potential fire	3	PPE and insulation/heater	1	-2	1	B	Install gas alarms around the reactor

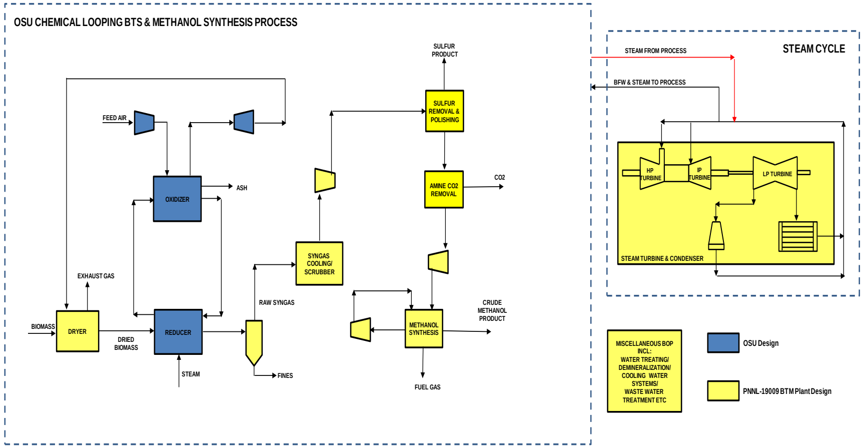
Findings & Recommendations

Recommendation Number (Rec #)	From Study Node	Risk Priority	Review Team Finding / Recommendation	Finish Date
1	A	B	Switch off biomass feeder when air flow rate is lower than Umf	
2	A	B	Use N2 to flush combustor when air flow rate is lower than Umf	
3	A, B, C	A	In PLC: when zone seal flow direction reversed, trip system, switch gas flowing into combustor to N2	
4	A	C	In HMI: mornitor gas velocity in gas-solid separator	
5	A	C	Install heater protection TCs to monitor heater temperature	
6	A	A	Mornitor pressure drop across gas outlet pipe	
7	A	A	Add additional gas outlet line for combustor	
8	A		In HMI: Show Umf and Ut at operating condition to guide air flow rate setting	
9	A	C	Increase the length of the primary particle separator. Add metal plate to enhance solid separation	
10	A	C	Automatically calculate the required riser air flow based on the temperature in the primary particle separator	
11	A	C	In PLC: stop HTR-210 if gas flow rate is low or gas temperature is high	
12	A	C	Stop heaters if the TCs around the heater is reading greater than 1050 C	
13	A	C	Shut off HTR-201/202 if combustor temperature is greater than 1000C	
14	B	C	Order spare screws for biomass feeder.	
15	B	C	Monitor biomass feeder operation by weighing scale	
16	B	C	Install hard wired pressure switch to shut down biomass feeder when the pressure is high.	
17	B		In PLC: switch off biomass feeder if FC-501 flow is low	
18	B	B	Install hard wired pressure switch to shut down biomass feeder when the pressure is high.	
19	B	B	Install gas alarm near the biomass feeder	
20	B, C	A	Operation: check gas tank inventory every 2 hours	
21	B, C	B	Add pulsing ports to the stand pipes in the system	
22	B	A	Add pressure releive valve at the top of the reducer	
23	B, C	B	Add purge gas to pressure ports	
24	B		Stop biomass feed when reactor temperature is too low	
25	B	B	Install gas alarms around the reactor	

3 – Technical Accomplishments

- 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





3 – Technical Accomplishments

- 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	✓	✓

3 – Technical Accomplishments

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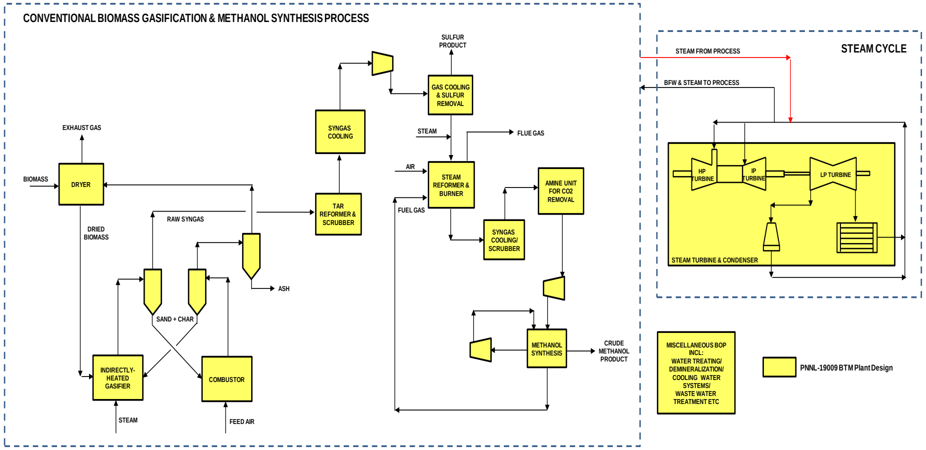
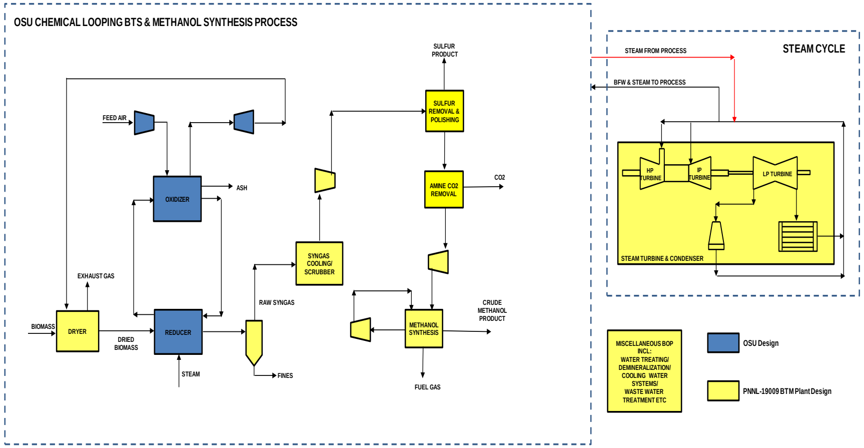
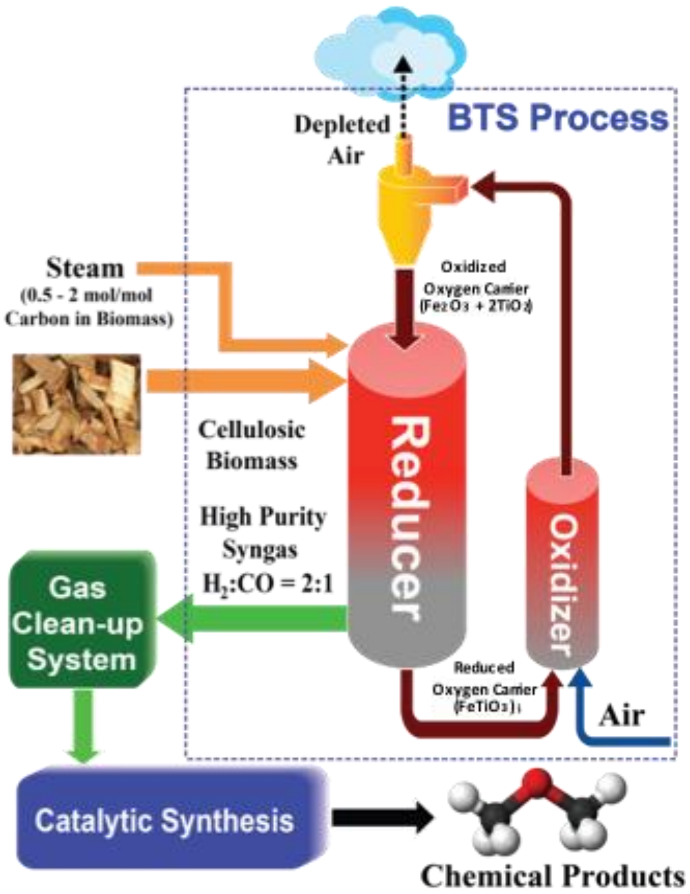




- BTS v.s. reference case: gasifier syngas flow is ~1.5x higher
  - Higher carbon efficiency
  - Higher compression power and CO_2 removal demand

4 – Relevance

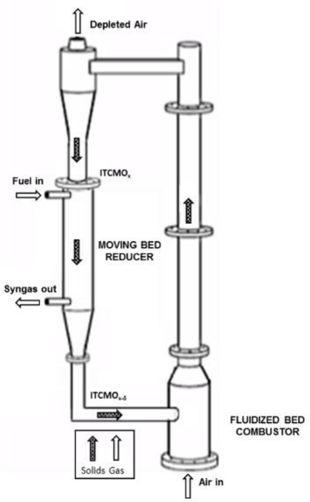


- Directly Supports BETO's Mission:
  - "Develop and transform our renewable biomass resources into commercially viable high performance biofuels"
- Address BETO Level Barriers and Challenges
  - Ot-B. Cost of Production
- Project driven by TEA – verify reactor sizing/capital cost based on continuous 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

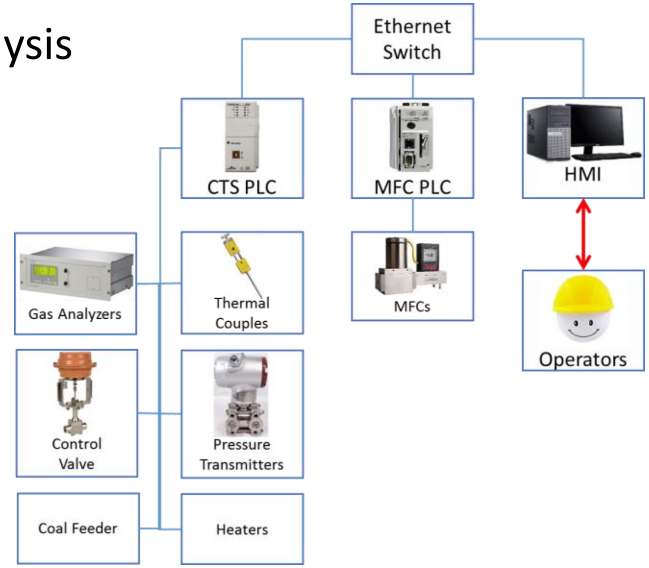
5 – Future Work: Budget Period 2

- 10 kW_{th} Sub-Pilot BTS Reactor
  - Test site preparation – equipment removal and structure preparation
  - Reactor fabrication and installation
  - Piping and electrical
  - Process commissioning – verify controlled solid circulation and heat up achievable
  - Control Programming
- TEA economic studies
  - Initial sensitivity analysis
- IRC Review Meetings

Site Preparation/ Student Training



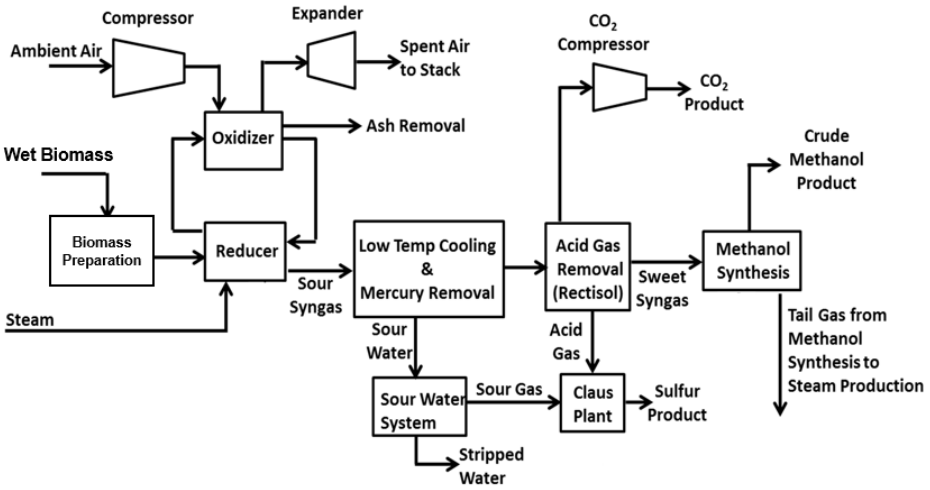
System Control



Structural Support Design/Installation

5 – Future Work: Budget Period 3

- 10 kW_{th} Sub-Pilot BTS Reactor
  - Sub-pilot parametric studies: biomass feed rate and type, operation temperature, steam/CO_2 feed input
  - Extended continuous operations – verify particle reactivity and attrition resist and non-mechanical reactor performance
  - Data reduction/analysis
- TEA economic studies
  - Update process model based on experimental results
  - Complete sensitivity analysis and report to IRC members
  - Deliver TEA final report
- IRC Review Meetings



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
- All tasks and milestones from budget period 1 has been completed.
  - 10 kW_{th} sub-pilot reactor system design completed
  - Process modeling of BTS-Methanol plant and reference case completed
- Budget period 2 is ongoing.
- BTS process meets BETO’s objectives for advancing the use of biomass for biofuels production

Additional Slides

Response to Previous Reviewers' Comments

- Biomass separation from oxygen carrier
  - Ash size is much smaller than oxygen carrier
  - Ash will exit the system with depleted air from the combustor and/or syngas from the reducer
  - Standard gas-solid separation device, such as baghouse, can be used

- Interaction between ash and oxygen carrier
  - At low concentration, interaction between mineral matter and oxygen carrier was not observed