Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions

Project ID #PD111

PI: Wei Liu

Pacific Northwest National Laboratory

6/11/2015

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

Overview

Timeline

- Start – November 2014
- End – October 2017
- 15% Complete

Budget

- Total Project Budget – $2,755K
- Total Recipient Share – $555K
- Total Federal Share – $2,200K
- Total DOE funds spent* – $350K
  *as of 3/31/15

Barriers

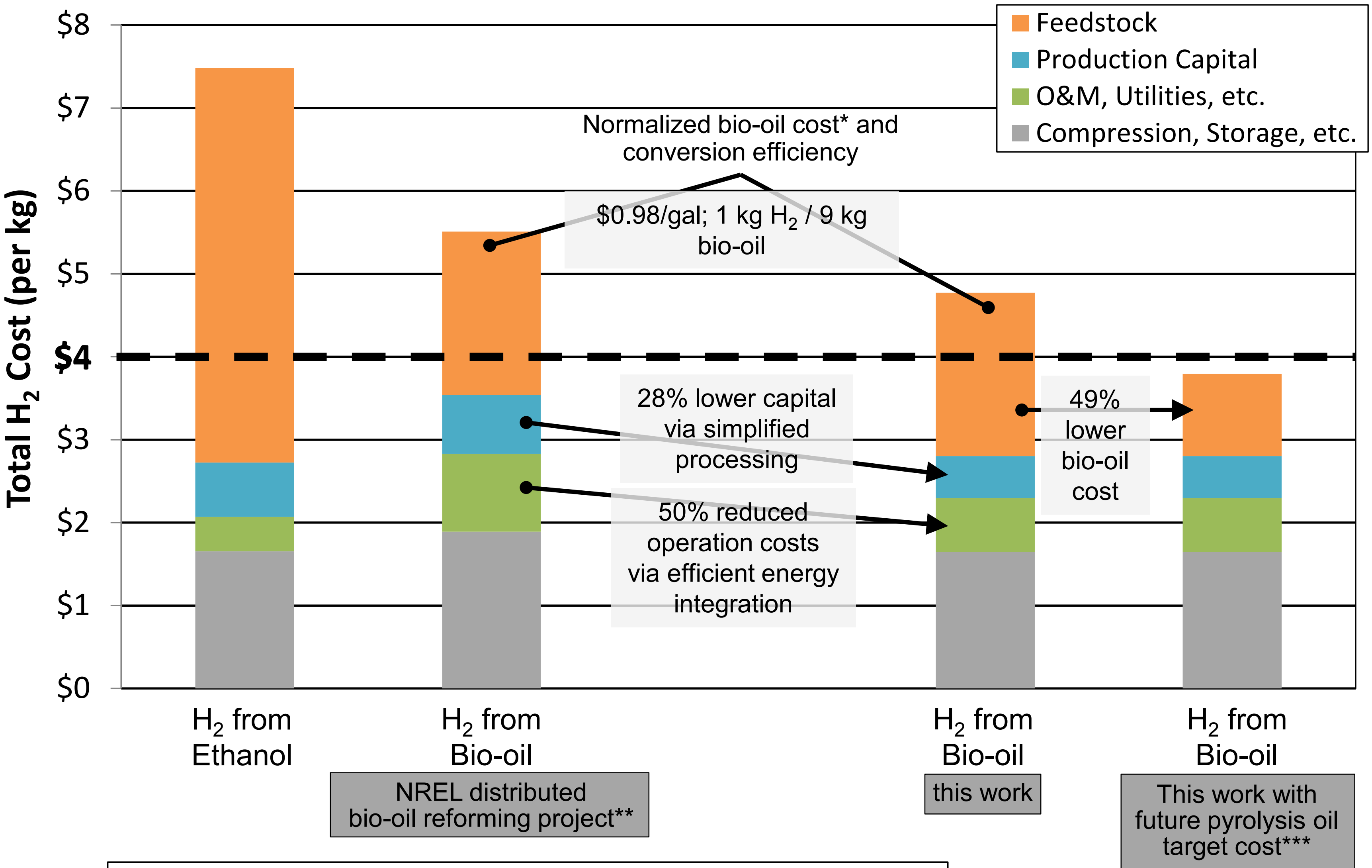
- Barriers addressed:
  - Plant capital cost and efficiency (unit scale of economy)
  - Operations and Maintenance (O&M)
- Target:
  - Cost of distributed H_2 from bio-mass to <$4/Kg H_2

Partners

- Cormetech
  - Monolith support
  - Catalyst/sorbent commercialization
- Washington State University
  - Reforming catalysis and kinetics
- Dason Technology
  - Integrated test apparatus
  - Process development

Relevance - H2A analysis (HPTT feedback)

Impacts of production technology innovations on H_2 cost



* PNNL-23053, NREL/TP-5100-61178
** S Czernik et al, 2010 AMR, Washington, D.C., NREL/PR-560-48066
*** NREL/TP-510-37779

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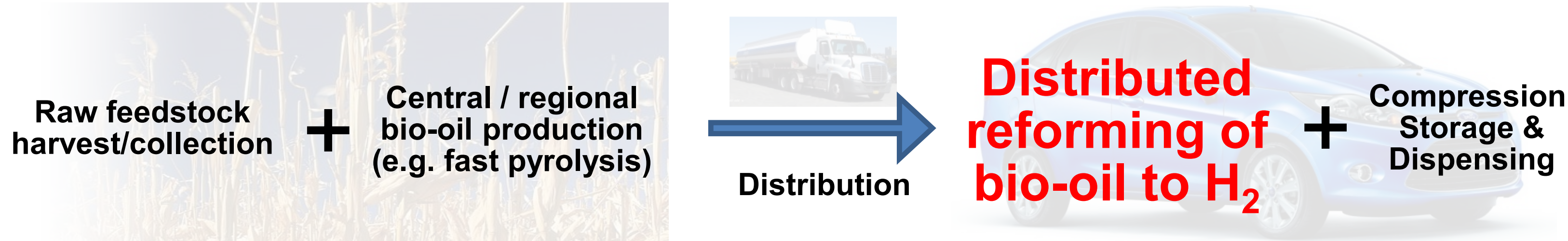
Relevance

Facilitating DOE's H_2 Cost Goal = $4/gge



Bio-oil reforming technology advancements being pursued in this work

1. **Reduced Capital Costs of Plant**
   - Minimizing unit operations (e.g., no furnace requirements)
   - Smaller PSA, smaller (or possible elimination of) WGS, no air separation
   - Process simplification minimizes BOP components

2. **Increased Energy Conversion Efficiency**
   - In situ CO_2 capture, push thermodynamics of reforming to higher conversion
   - In situ heat exchange between reaction & regeneration to minimizes heat loss
   - 80% energy conversion efficiency achievable (versus 71.4% for methane reforming, 2011 status)

3. **Increased Durability**
   - Reduced O&M (operations & maintenance) requirements
   - Directly addresses coking & catalyst deactivation
   - Modular, compact reactors to make unit turn-around easier

Approach – our process innovations

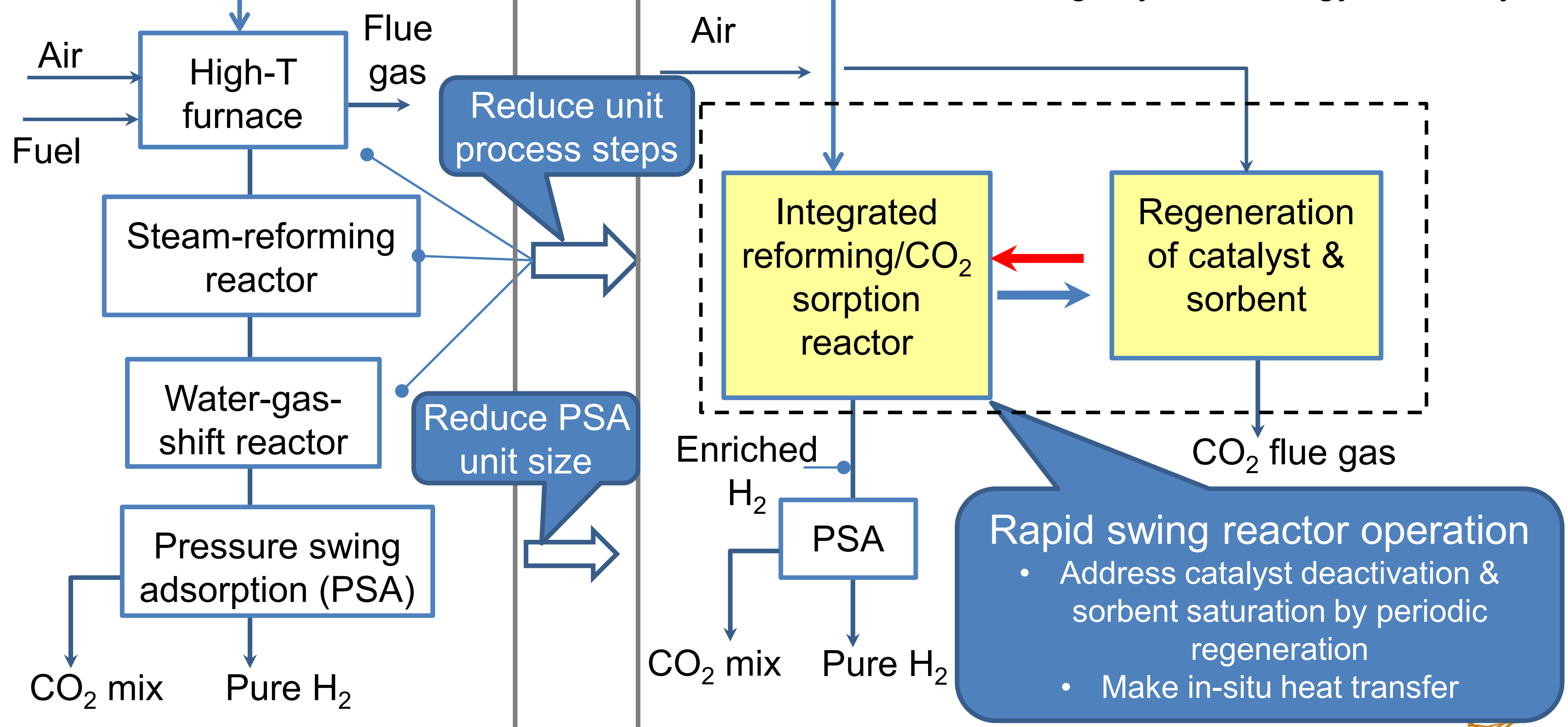
Reduce unit process steps and intensify heat/mass transfer

Typical commercial processes for centralized H_2 production

Present process

Project focuses:

- Compact, high throughput. low-cost reactor
- Effective and stable catalyst and sorbent materials
- High system energy efficiency



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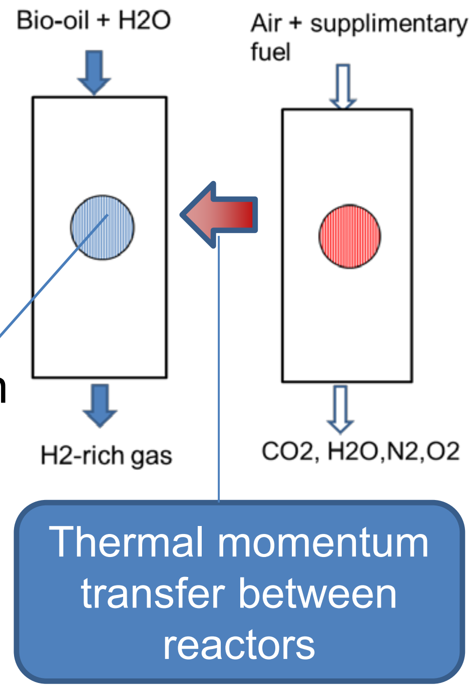
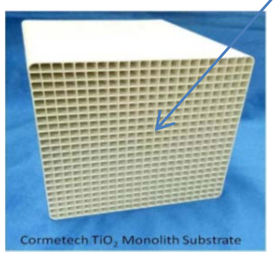
Approach – monolith reactor innovation for rapid (1-10 min) swing operation

Reforming conditions:

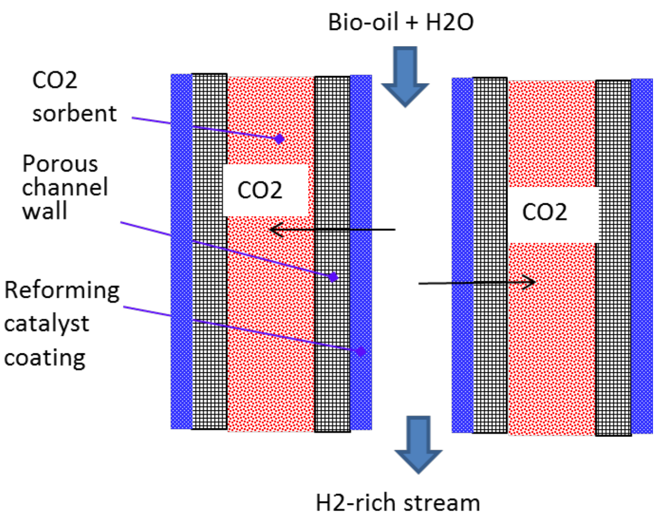
- T < 600ºC, P < 24 bar
- Endothermic steam-reforming reaction
- Coking & de-oxygenation reaction
- Exothermic carbonation reaction





Regeneration conditions:

- T < 750ºC, P ~ 1 bar
- Exothermic coke combustion
- Endothermic carbonate decomposition



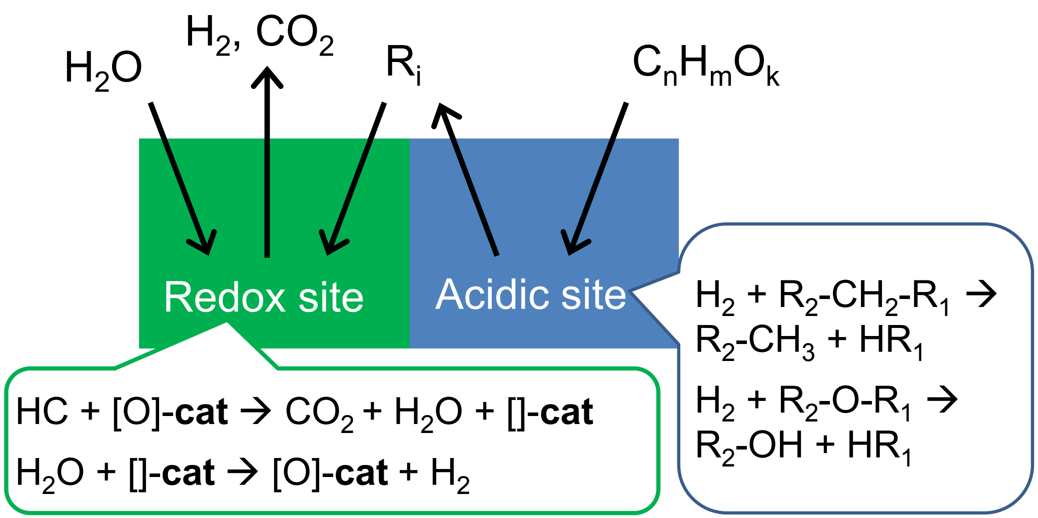
Design features:

- Place catalyst/sorbent at the same spot to achieve rapid mass and heat transfer
- Have straight flow channels to minimize dead space and pressure drop
- Fix the sorbent and catalyst to avoid attrition and hydrodynamic erosion

Approach - materials innovation for integrated steam-reforming and CO_2 carbonation

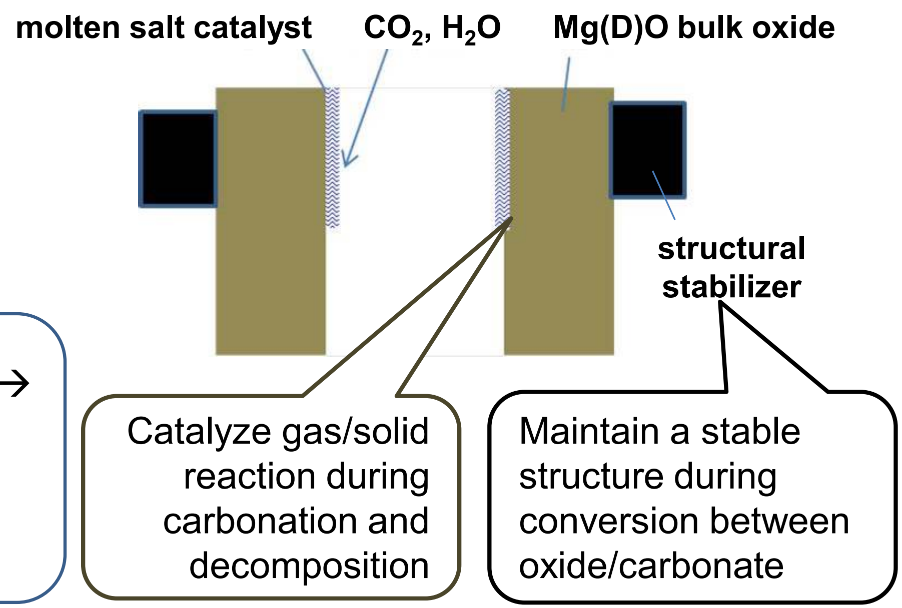
Composite catalyst of synergistic functions

- Provide redox and acidic sites for concerted cracking and reforming and reactions
- Be activated by air calcination



CO_2 sorbent with tailored properties

- Work under the reforming conditions
- Provide adequate working capacity, rapid kinetics, and stability



- Reforming catalysts are designed based on team's previous experiences and synergistic catalyst design model

Liu. Chem. Eng. Sci. 62(2007)3502-3512.

- CO_2 sorbents are formulated based on previous CO_2 capture studies at PNNL

Zhang et al. *Int. J. Greenhouse Gas Control* 12 (2013)351-358.

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Approach - milestones addressing three critical challenges

Milestone 1 (FY15) – **material innovations**: development of optimum reforming catalysts and in-situ CO_2 sorbents under proposed operation conditions *(single-tube reactor tests at gram levels)*

- H_2 productivity (0.6 [kg-H_2/h]/kg of catalyst
- CO_2 capture productivity >0.2 [kg-CO_2/h]/kg of sorbent

Milestone 2 (FY16) – **monolithic reactor innovation**: demonstration of in-situ CO_2 capture for pure H_2 production and catalyst/sorbent stability *(single-tube & integrated reactor tests in tens of g level)*

- >100 cycles of reforming/regeneration tests with production of >90% pure H_2 at GHSV >10,000 v/v/h
- Update techno-economic analysis

Milestone 3 (FY17) – **process innovation**: Demonstration of an integrated reactor system with technical readiness level ≥ 4 (*tests in hundreds of g level)*

- H_2 production capacity =2 kg/day, >90% H_2 in reactor, >99% H_2 after PSA
- ≥10 wt% H_2 yield
- A mobile testing skid for continuous swing reactor operation

Collaboration and technology transfer

Dr. Chris Bertole
Cormetech
- Development of monolith support of tailored properties

Future

Scale-up, manufacture, and commercialization of monolith support &catalyst

Prof. Yong Wang
Washington State Univ.
- Fundamental understandings and discovery of new reforming catalysis
- Catalyst characterization and kinetics studies

PNNL
- New technology innovations (material, reactor, process)
- Critical process or product concept studies

Dr. Bang Xu
Dason Technology
- Reactor system tests and process development

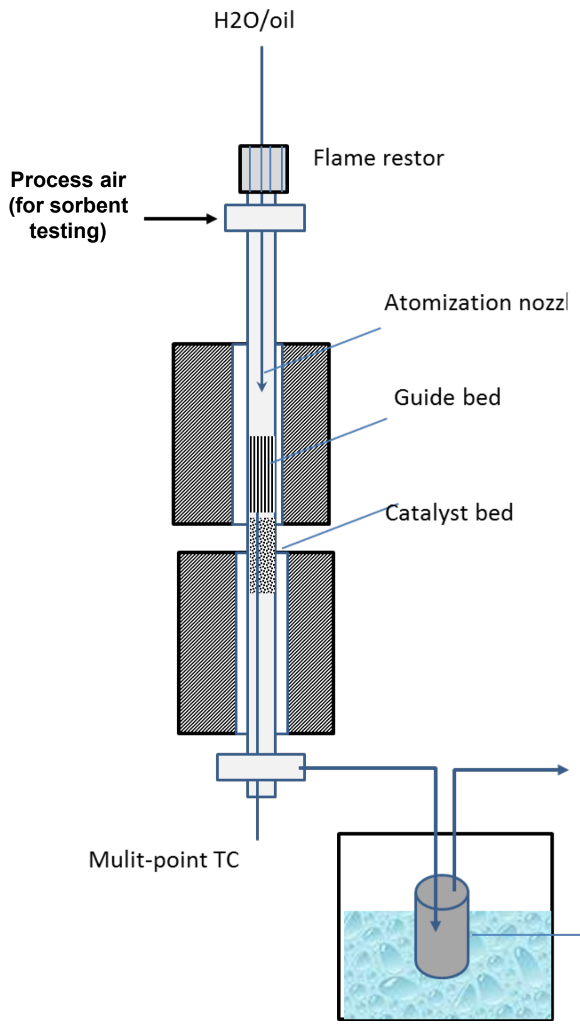
Future

Process design, engineering and field tests for process commercialization

Accomplishment & Progress

Versatile laboratory-bench system built for reaction/sorption tests

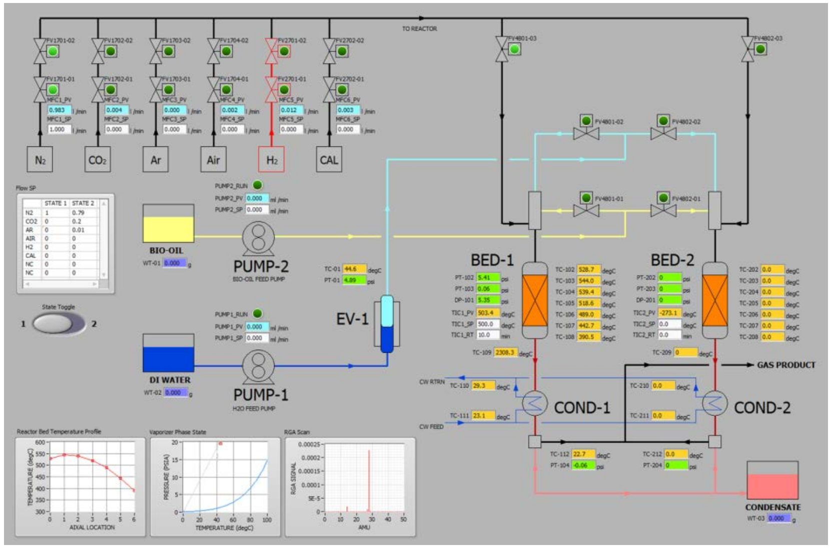
Single-tube reactor



- Different sizes of reactor tubes
- Particle-packed and monolith-inserted beds
- Rapid temperature or pressure swing
- Multi-cycle operation
- Tests of new materials and new process concepts

Schematic of test apparatus

Control system



Accomplishment & Progress

CO_2 sorbents prepared in-house and screened by TGA tests

Material + promoters	**Working capacity measured with multiple cycles of CO_2 sorption/air purge, wt%** [sorption↔regeneration temperature]		
	360°C↔450°C	400°C↔500°C	500°C↔750°C
MgO	60% 1st cycle <1% cycles 2+	Temperature too high for sorption	
MgO +Na_2CO_3	15% stable	15% stable	T too high for sorption
CaO	Temperature too low for regeneration		
Decomposed dolomite	5-8% stable	20% 1st cycle <1% cycles 2+	25%

Promising sorbent materials and respective operating temperatures are identified in GREEN

- Promoted MgO-Na_2CO_3 and dolomite sorbents prepared for packed bed testing
- Packed bed tests are ongoing
- Design and preparation of new sorbents is ongoing

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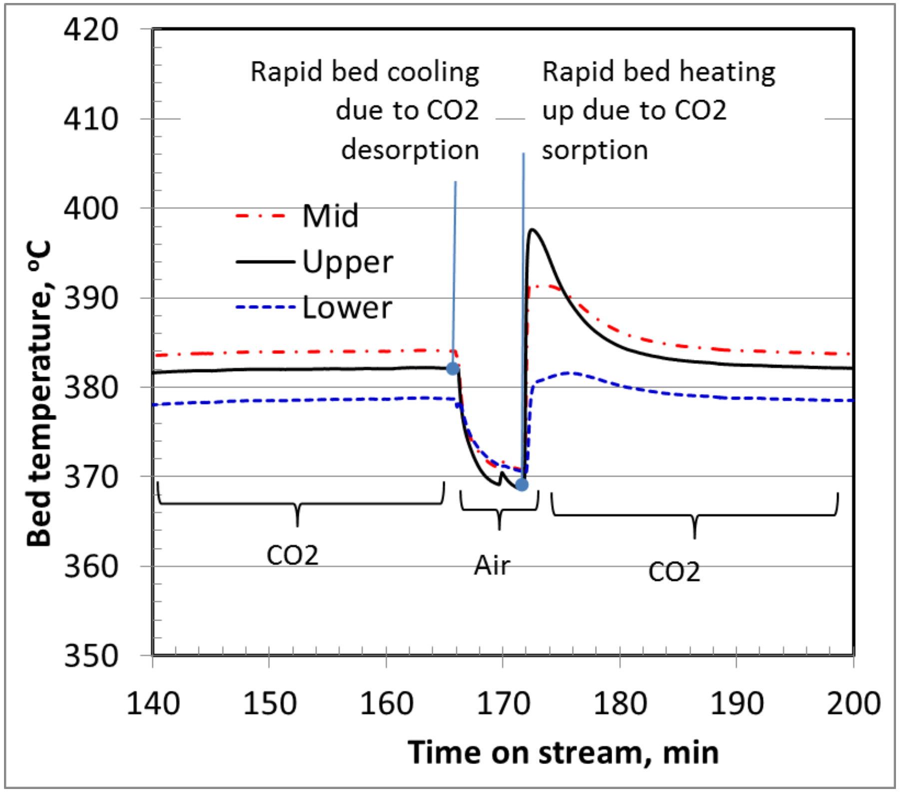
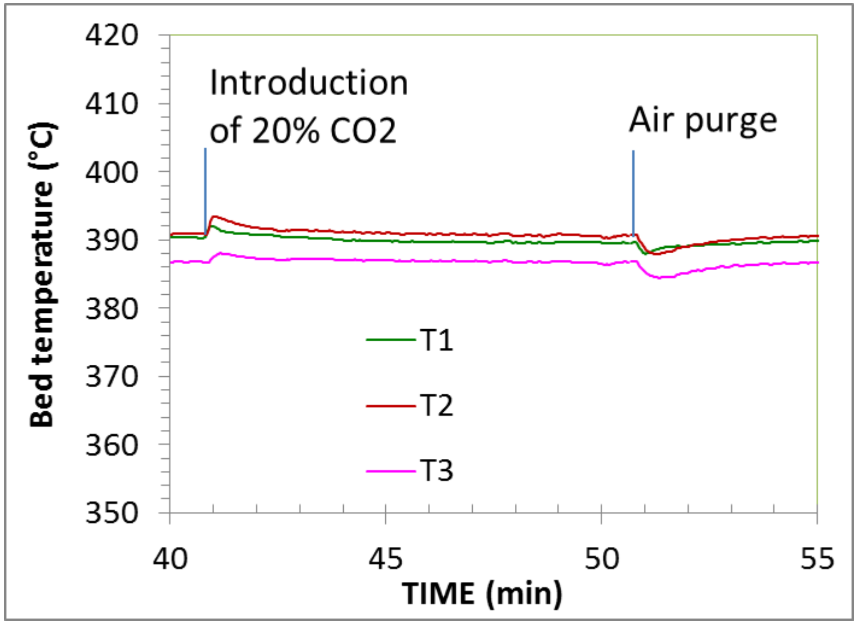
Accomplishment & Progress

Temperature variation due heat of *CO_2 sorption in a particle-packed bed*



Degree of temperature rise-up decreased by reducing p_{CO2} from1.0 to 0.2 bar



- ➢ Pronounced temperature variations shown in such a small particle-packed bed (1/2" OD tube)!
- ➢ Efficient heat transfer is important
- ➢ The results affirm present approaches:
  - ✓ In situ coupling of endothermic reforming reaction with exothermic CO_2 capture
  - ✓ In situ coupling of exothermic coke combustion with endothermic CO_2 desorption

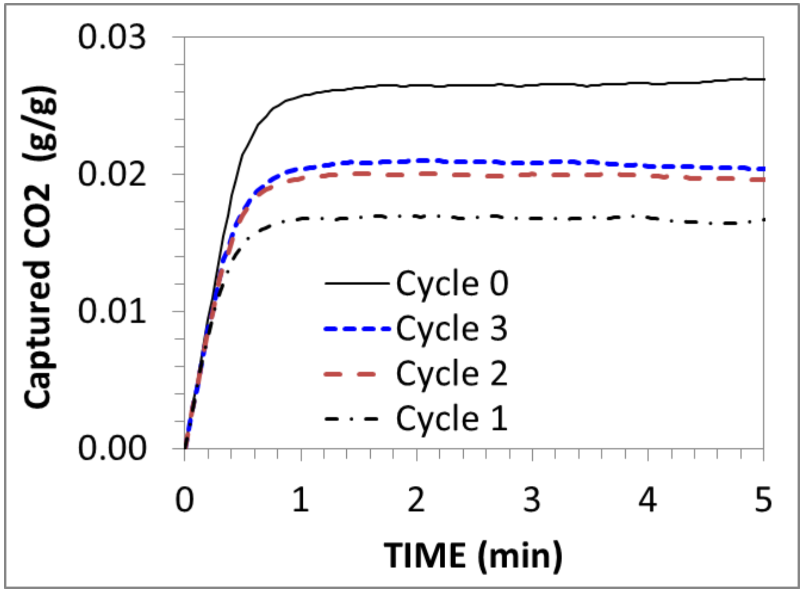
Accomplishment & Progress

Presence of steam promotes working capacity of a MgO-based sorbent

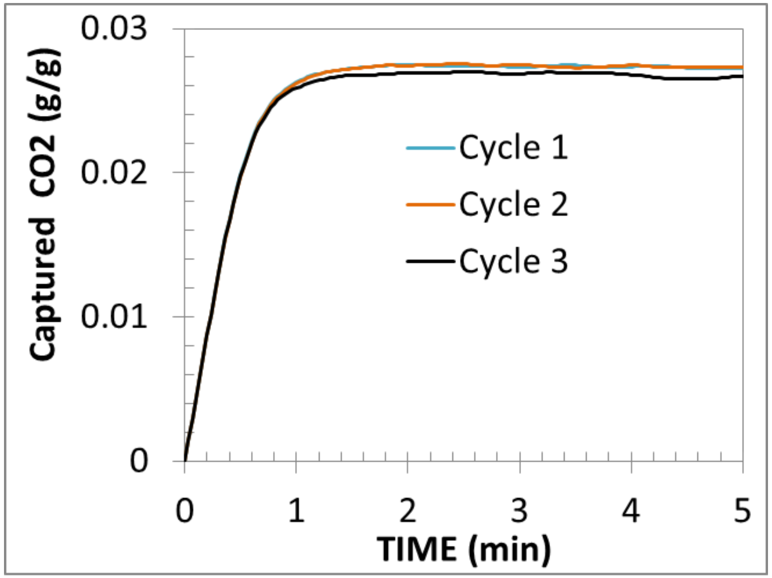
Adsorption conditions: 390°C, 1 bar, 20% CO_2, GHSV =4,200 1/h

Regeneration conditions: 450°C, 1 bar, air

Break-through curves with dry gas



Break-through curves with 30% H_2O

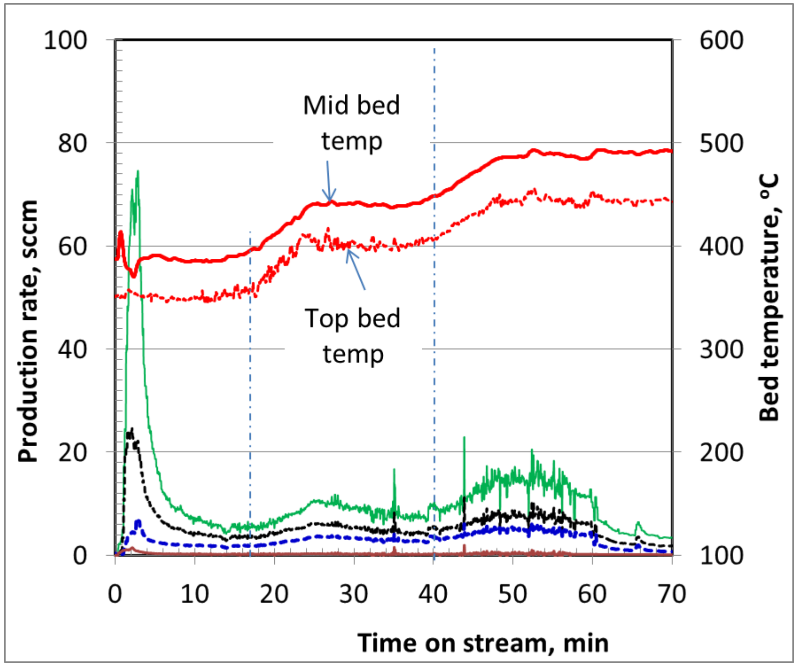


- Rapid sorption/desorption kinetics is shown
- Sorbent can be regenerated by either PSA or TSA
- Presence of steam slightly stabilizes the sorbent performance, promising for usage under steam-reforming conditions

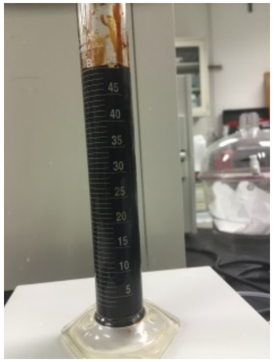
Accomplishment & Progress

Preliminary low-temperature catalytic bio-reforming

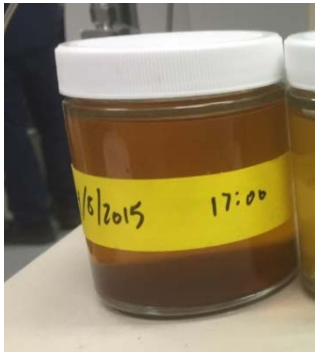
Bio-oil feed: NREL 500 Oak - Pyroil NREL TCPDU
Received: 10/29/10
Composition: 44.94 % C, 7.29 % H, 47.66 % O, 0.01% S, <0.05 % ash
Reaction conditions: GHSV =100,000 1/h, atmospheric pressure



Bio-oil $CH_{1.95}O_{0.80}$



Condensed reactor effluent



Spent bed packing materials

- A metal oxide nano-composite catalyst showed significant reforming activity at 400°C
- Deactivation by coking occurred rapidly and activity could not be restored by raising temperature
- Catalytic performances are drastically affected by bio-oil flow distribution

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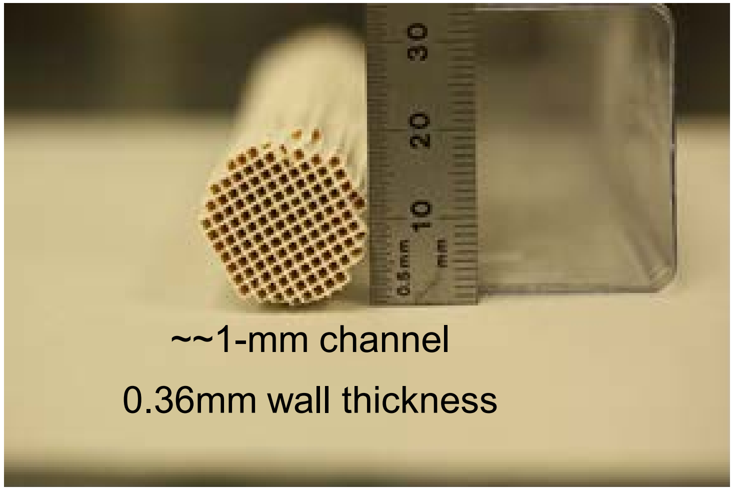
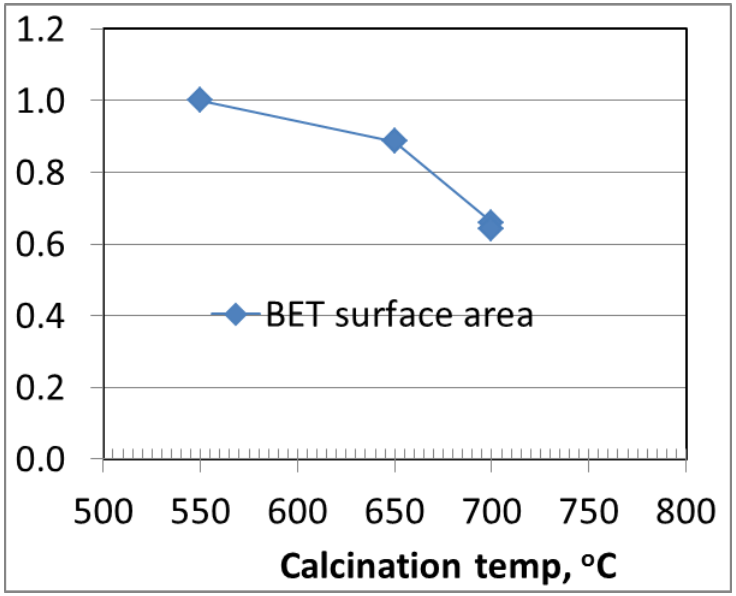
Accomplishment & Progress

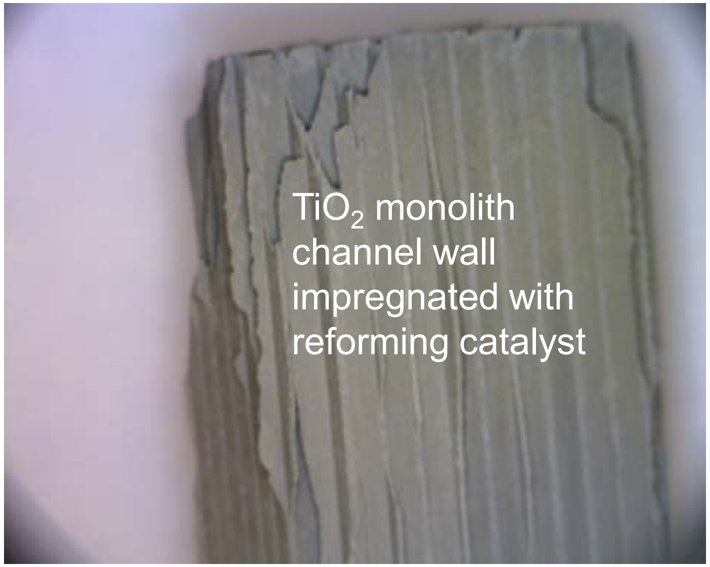
TiO_2 monolith support prepared and catalyzed for reforming reaction

Core-drilled 20mm x 120mm monolith (~300cpsi) for 1-inch reactor

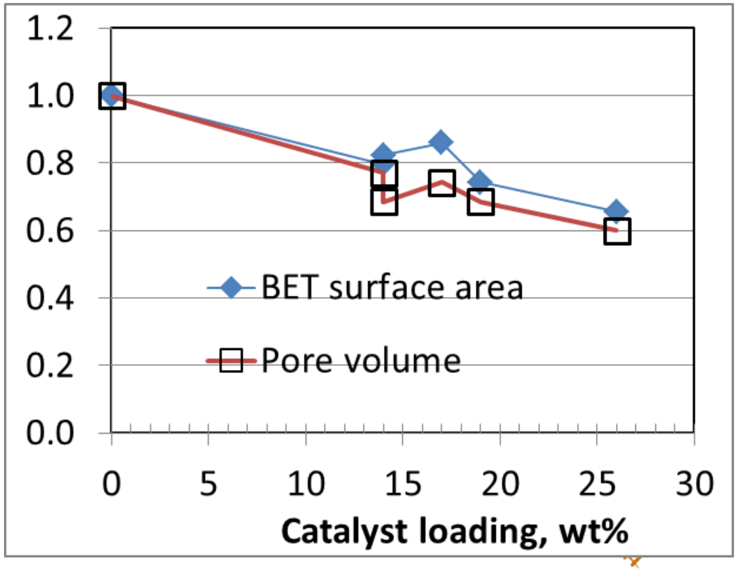


- Monolith integrity and porous structures are maintained at high calcination temperature





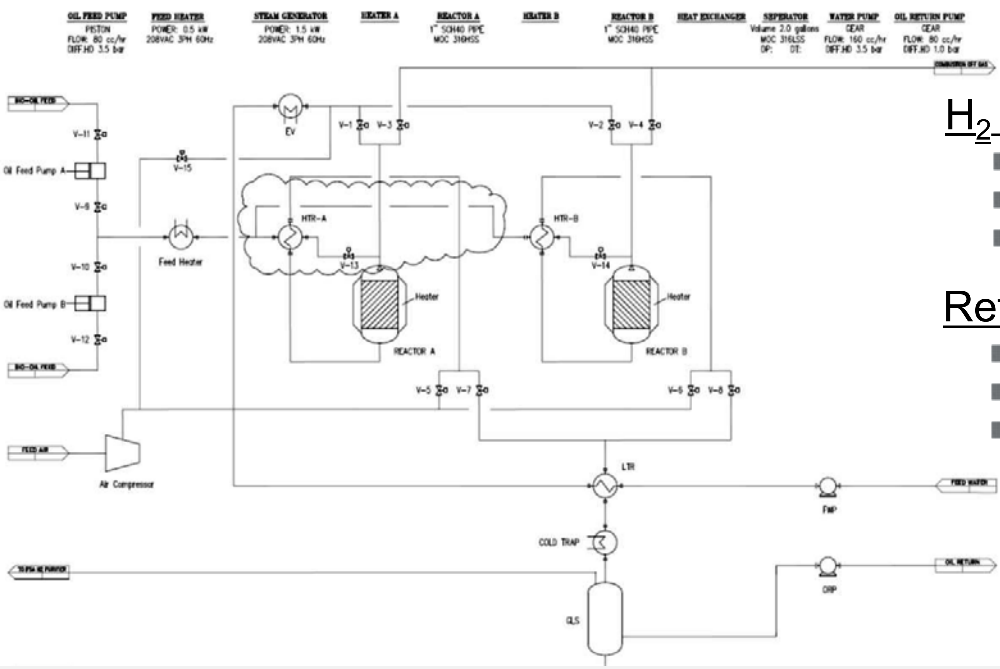
- Significant amounts of the catalyst can be loaded with uniform textures



Accomplishment & Progress

Integrated testing system designed and being built

Process flow diagram finalized for integrated testing unit



- Capability to recycle un-converted bio-oil

Scale of Development

H_2 production, kg/day
- Year 1 – 0.51
- Year 3 – 2.54
- Commercial – 1525

Reactor dimension
- Year 1 – 1 in.
- Year 3 – 2 in.
- Commercial – ~40 in.

Reforming catalyst
- Year 1 – 20 grams
- Year 3 – 40 grams
- Commercial – 60 kg

CO_2 sorbent
- Year 1 – 162 grams
- Year 3 – 808 grams
- Commercial – 485 kg

Design specifications:

500°C [reforming] ↔ 600°C [regeneration]

- 10wt% CO_2 sorbent working capacity
- 10 [g/hr]/g-catalyst bio-oil SV
- 2:1 H_2O:bio-oil
- 80% single pass conversion
- 80%/20% carbon yield to reforming/coke
- 90% CO_2 capture

Progress:

- Designs of key equipment are completed
- Vendor quotes are acquired and procurement is ongoing

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Remaining barriers and challenges, and proposed future work

Milestone	Challenges	Proposed approach
Low-T, regenerative reforming catalyst	Bio-oil flow distribution	FY15: New designs of distributor and reactor bed package
	Regeneration and stability, and activity enhancement	FY15: More catalyst designs and preparation, more reforming/regeneration tests
In-situ CO_2 sorbent	Matching of CO_2 sorption/regeneration conditions with steam-reforming	FY15: Tailoring CO_2 sorbent properties and more sorption process parametric tests
Monolith reactor integration	Material integration of reforming catalyst and CO_2 sorbent into TiO_2 monolith structures	FY16: Tailoring and understanding of monolith properties as a sorbent and catalyst support
	Synchronization of reforming reaction and CO_2 capture processes in the monolith structure	FY16: Operation of the integrated reactor testing system and parametric process tests

Summary

Material preparation & characterization	First group of TiO_2 monoliths prepared	Cormetech
	A few groups of new reforming catalysts prepared and tested, including monolith-supported ones	WSU &PNNL
	Review of recent literature on CO_2 sorbent and bio-oil reforming completed	PNNL
	Two promising CO_2 sorbents identified by TGA tests for respective low-T and high-T sorption	PNNL
Adsorption & reaction tests	Single-tube reactor testing capabilities built	PNNL
	Rapid kinetics and initial stability of the low-T CO_2 sorbent in presence of H_2O confirmed by packed bed tests	PNNL
	Two promising low-T reforming catalysts identified by respective model compound and actual bio-oil reforming tests	WSU & PNNL
Process research and development	A provisional patent application was filed "An integrated reactor unit for H_2 production"	PNNL
	Design of integrated test unit finalized and procurement of major components in progress	Dason Technology

Technical Back-Up slides (optional)

Approach — Swing operation of integrated reactor

Endothermic steam-reforming (SR) reaction:

$C_nH_mO_k + (2n\text{-}k)H_2O \longrightarrow (0.5m+2n\text{-}k)H_2 + nCO_2$

Coking & de-oxygenation reaction:

$C_nH_mO_k + Cat \longrightarrow C_nH_{n\text{-}2k}(coke)\text{-}cat + kH_2O$

Exothermic carbonation reaction:

$CO_2 + MO \longrightarrow MCO_3$

Exothermic coke combustion for catalyst regeneration:

$C_nH_{n\text{-}2k}(coke)\text{-}cat + 0.5(2.5n\text{-}k)O_2 \longrightarrow 0.5(n\text{-}2k)H_2O + nCO_2 + \Delta H(<0)$

Endothermic carbonate decomposition:

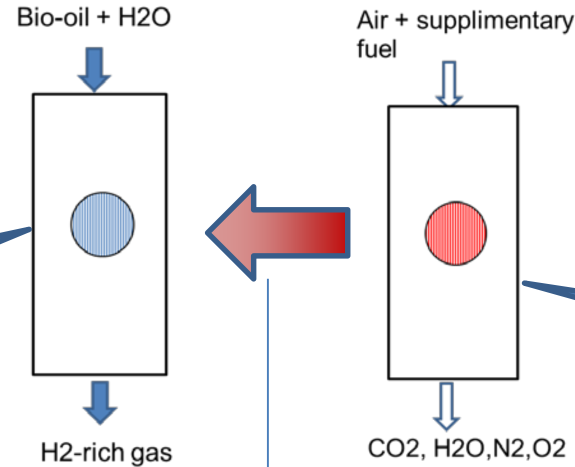
$MCO_3 \longrightarrow CO_2 + MO + \Delta H(>0)$

Reforming conditions:

- $T < 500^oC$
- P < 300psi (24 bar)

Regeneration conditions:

- $T < 600^oC$
- P ~ 1 bar



In situ coupling of endothermic steam reforming with exothermic carbonation

Thermal momentum transfer between reactors

In situ coupling of exothermic coke combustion with endothermic carbonate decomposition

Accomplishment & Progress

Originality of present CO_2 sorbent approach confirmed by literature review

CO2 sorbent materials reported in the literature:

CO_2 sorbents that may work under reforming conditions
• CaO-based: MgO-CaO, TiO_2-CaO, Li_2CO_3-CaO • MgO-based: K_2CO_3-MgO, Cs_2CO_3-doped MgO, KNO_3-MgO, alkaline and alkaline earth-promoted MgO • Other compounds: $Na_2Mg(CO_3)_2$, Li_8SiO_6 mixed with (K-, Na-carbonates), lithium silicate
CH_4 steam reforming with in-situ CO_2 capture
• CeZrOx-CaO + Ni/hydrotalcite • $Mg_{1-x}Al_x(OH)_2(CO_3)_x$ or Lithium zirconate +Rh/$Ce_aZr_{1-a}O_2$ • commercial K_2CO_3-promoted HTC from SASOL + Ni/alumina
Bio-oil steam reforming with in situ CO_2 capture
• Dolomite + Ni/La_2O_3−Al_2O_3

- CaO-based sorbents typically require regeneration above 700^{o}C, and the sorbent tends to deactivate with cycle.
- A stable CO_2 sorbent with fast kinetics has not been shown yet through sorption/regeneration cycles.

Accomplishment & Progress

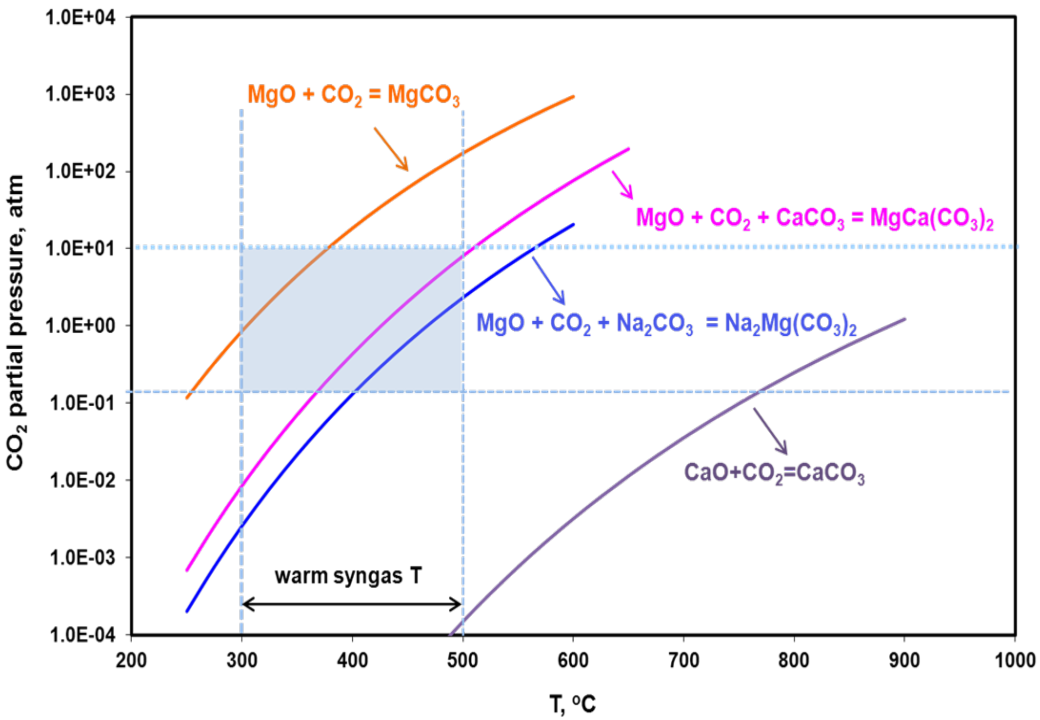
Bio-oil reforming catalyst background studies and preparation

Literature review conducted to understand pros/cons of different catalysts studied, and to address critical needs in this project work

Commercial catalyst	Z417, C11-NK and NREL#20
Ni on different support	Ni/alumina, Ni/La-alumina, Ni/$CaAl_2O_4$, Ni/CeO_2–ZrO_2; Ni/HZSM-5(Si/Al=25), Ni/CNFs catalyst
Ni (+ additive)	Ni (+ additive)/ Al_2O_3, NiCu/MgCe/Al mixed oxides
Previous metal	Ru/MgO/Al_2O_3, 1%Pt/Al_2O_3, Rh or Ir/$CaAl_2O_4$
Mixed metal oxide	Ni–Al modified with Mg and Ca 2CaO -7Al_2O_3 doped with Mg, K or Ce

- Most catalysts are studied at reaction temperatures > 500^{o}C.
- Catalyst deactivation is common problem. Coke formation is the major cause, more pronounced in the Ni-based catalysts.
- No regeneration and stability of the catalysts have been reported.

Technical Accomplishments – Task 1 thermodynamic analysis of CO_2 sorbent design



- MgO is in the lower working temperature range for present application
- CaO is in the higher end
- Compounds are likely needed to shift the CO_2/MgO equilibrium toward higher temperature

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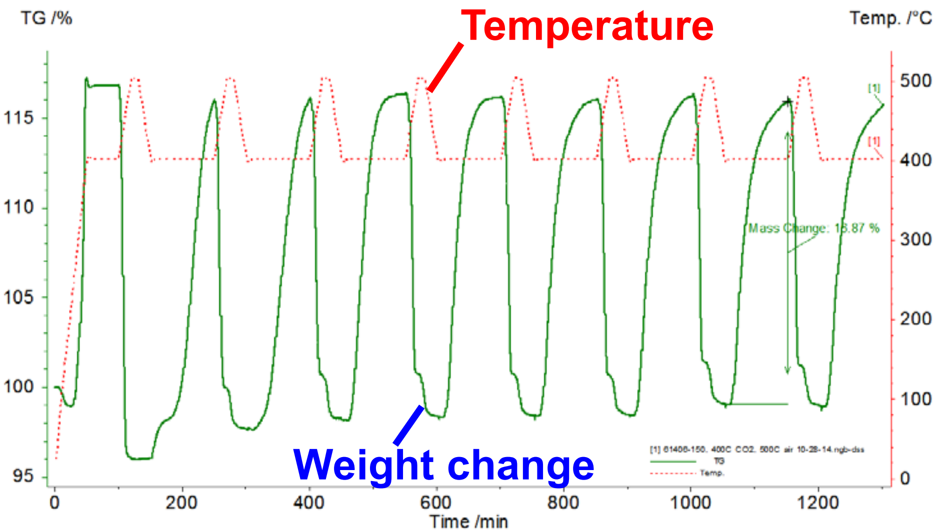
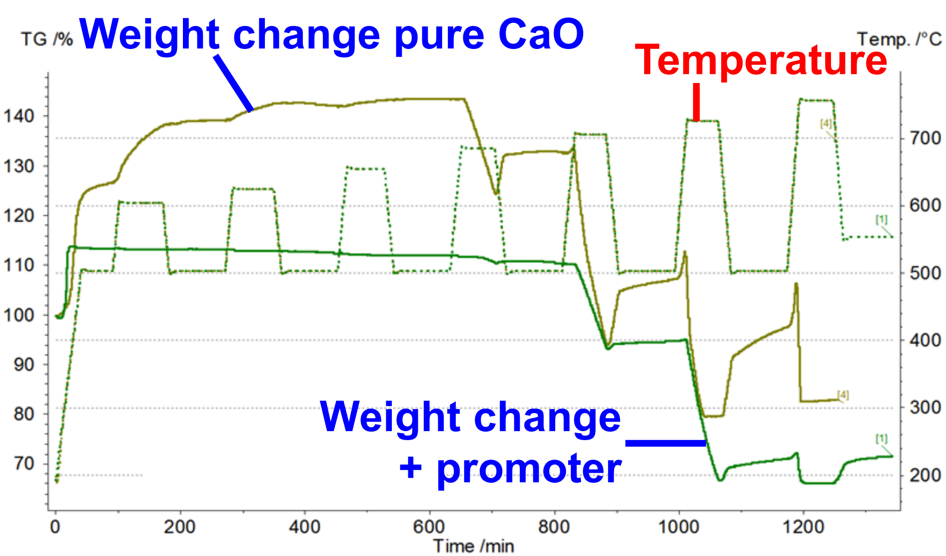
Technical Accomplishments – Task 1

MgO/Na_2CO_3 (in-house) and CaO sorbent performances



$MgO + CO_2 + Na_2CO_3 \leftrightarrow Na_2Mg(CO_3)_2$

- A stable sorbent at 400/500°C working/regeneration temp.



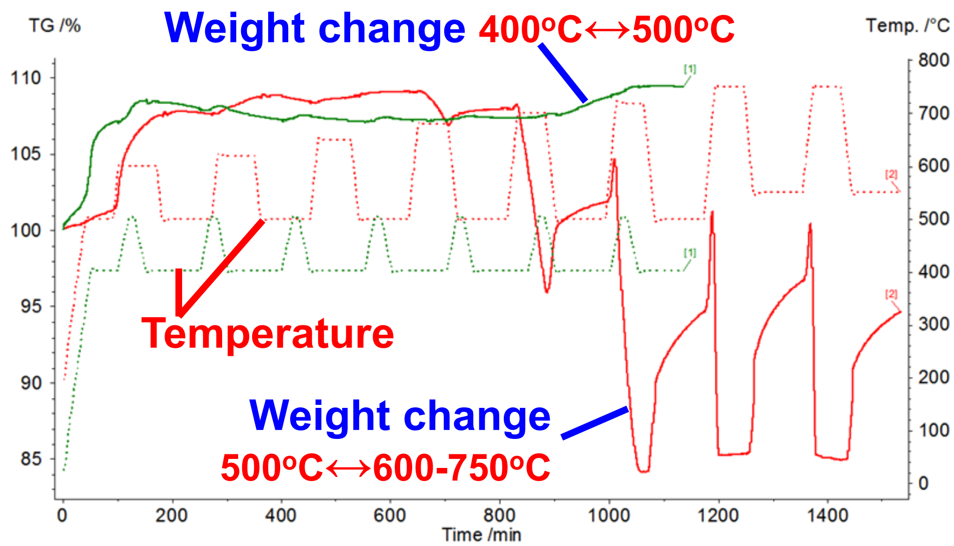
$CaO + CO_2 \leftrightarrow CaCO_3$

500°C ↔ 600-750°C

- >700°C regen required
- Addition of carbonates
  - decreased working capacity
  - did ***not*** lower regeneration temperature

Technical Accomplishments – Task 1

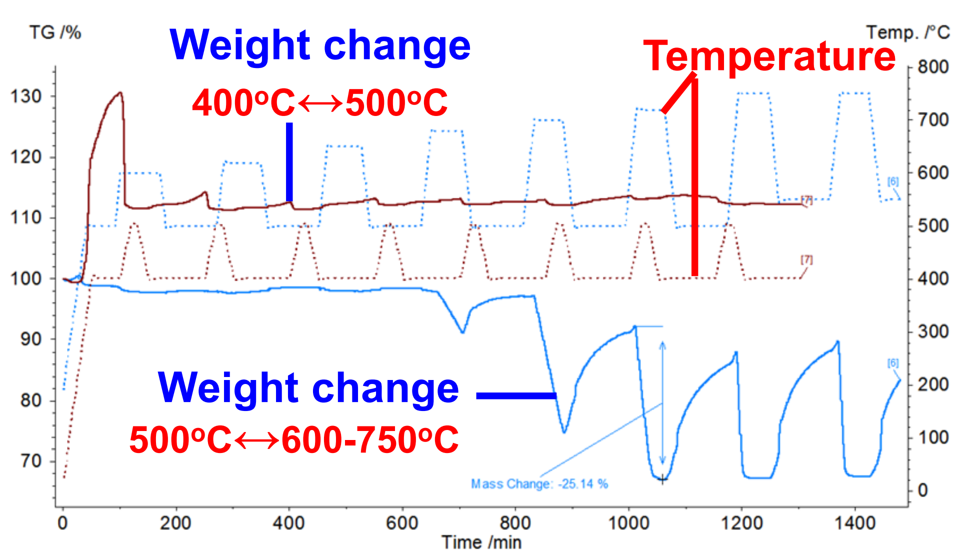
Performances of dolomite-derived CO_2 sorbent at high T



Dolomite-derived sorbent

$MgO + CaO + 2CO_2 \leftrightarrow MgCa(CO_3)_2$

- Only CaO component works at high temperature !



Dolomite-derived sorbent with addition of promoter

- did not lower regeneration temperature
- ***Increased*** working capacity

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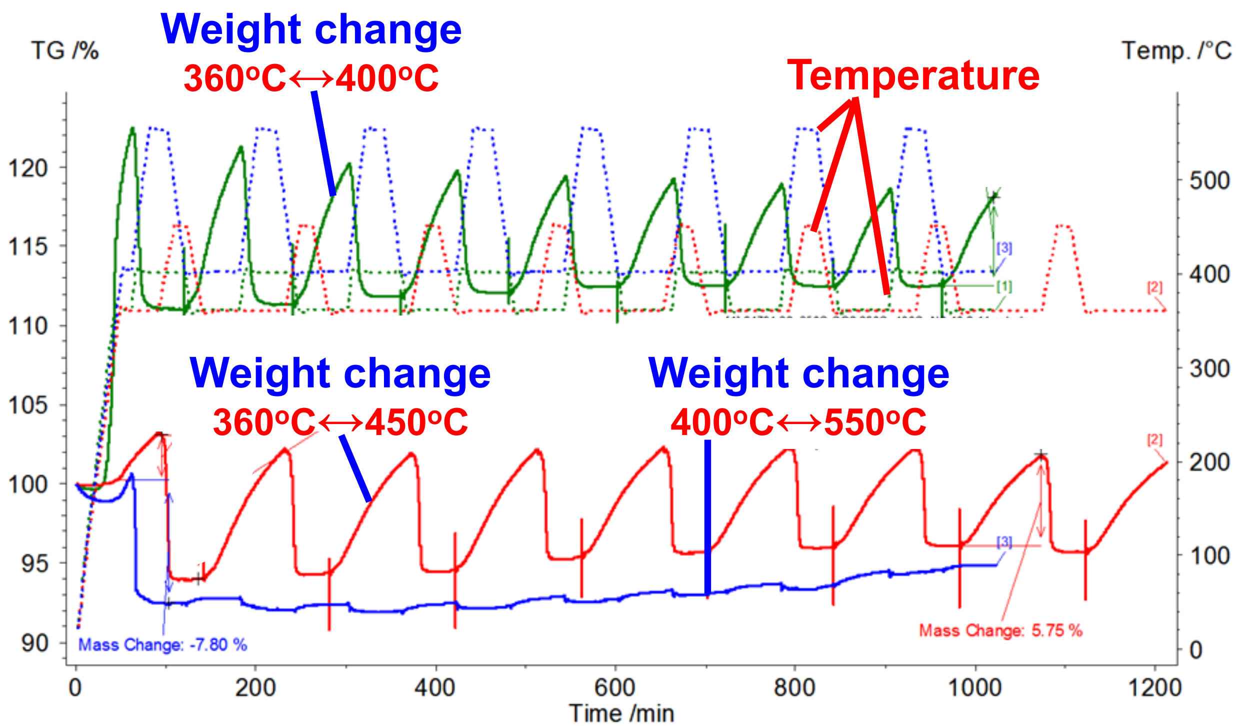
Technical Accomplishments – Task 1

Performances of dolomite-derived CO_2 sorbent at low T



Dolomite-derived sorbent with promoter at lower temperatures

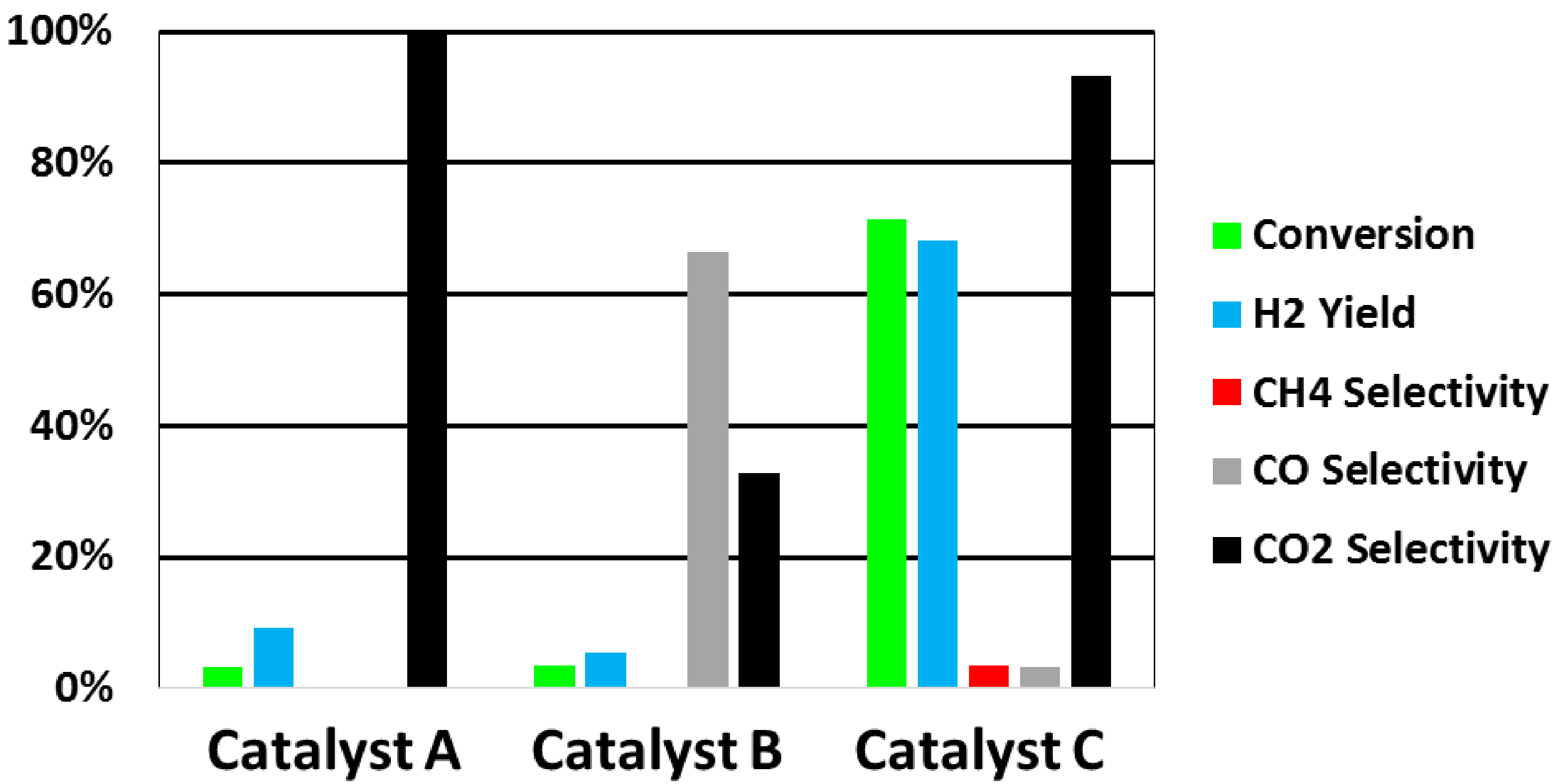
$$MgO + CaO + 2CO_2 \leftrightarrow MgCa(CO_3)_2$$

- *Only MgO component works at low temperatures!*

Accomplishment & Progress

Promising reforming catalysts identified from model reaction tests

- Identified catalyst composition which gives about 70% yield to H_2 using phenol as a model compound for pyrolysis oil
- Catalysts are stable for >30 mins and no activation is required.



Reaction Conditions:

T = 500 °C, S/C=10, P_{Phoh}= 0.81 mol%, SV= 3000 hr^{-1}