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

Project ID #PD111

PI: Chaitanya Sampara

Project team:

Ken Rappé (presenter), Shari Li, Richard Zheng/PNNL

Yong Wang/Washington State University
Bang Xu/Dason Technology
Chris Bertole/Cormetech

6/7/2017

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

Overview

Timeline

- Start – November 2014
- End – October 2017
- 83 % Complete

Budget

- Total Project Budget – $2,755K
- Total Recipient Share – $555K
- Total Federal Share – $2,200K
- Total DOE funds spent* – $1745K

  *as of 3/31/2017

Barriers

- MYRDD Tech. Barriers addressed:
  - A: Plant Capital Costs and Efficiency (unit scale of economy)
  - B: Operations and Maintenance (O&M)
- Target:
  - *Production* cost of distr. H_2 <$2/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

Facilitating DOE's H_2 Production Cost Goal <$2/gge

Project Objective

Advance H_2 production technologies from bio-oil

1. **Reduce capital costs of plant**
   - Minimizing unit operations, process simplification
2. **Increase energy conversion efficiency**
   - In situ heat exchange between reaction & regeneration to minimizes heat loss
   - In situ CO_2 capture, push thermodynamics of reforming to higher conversion
3. **Increase operating flexibility and durability**
   - Reduced O&M requirements, directly addresses coking & catalyst deactivation

Current Year Focused On

A. **Scalable synthesis (of CO_2 sorbent)** – *achieved*

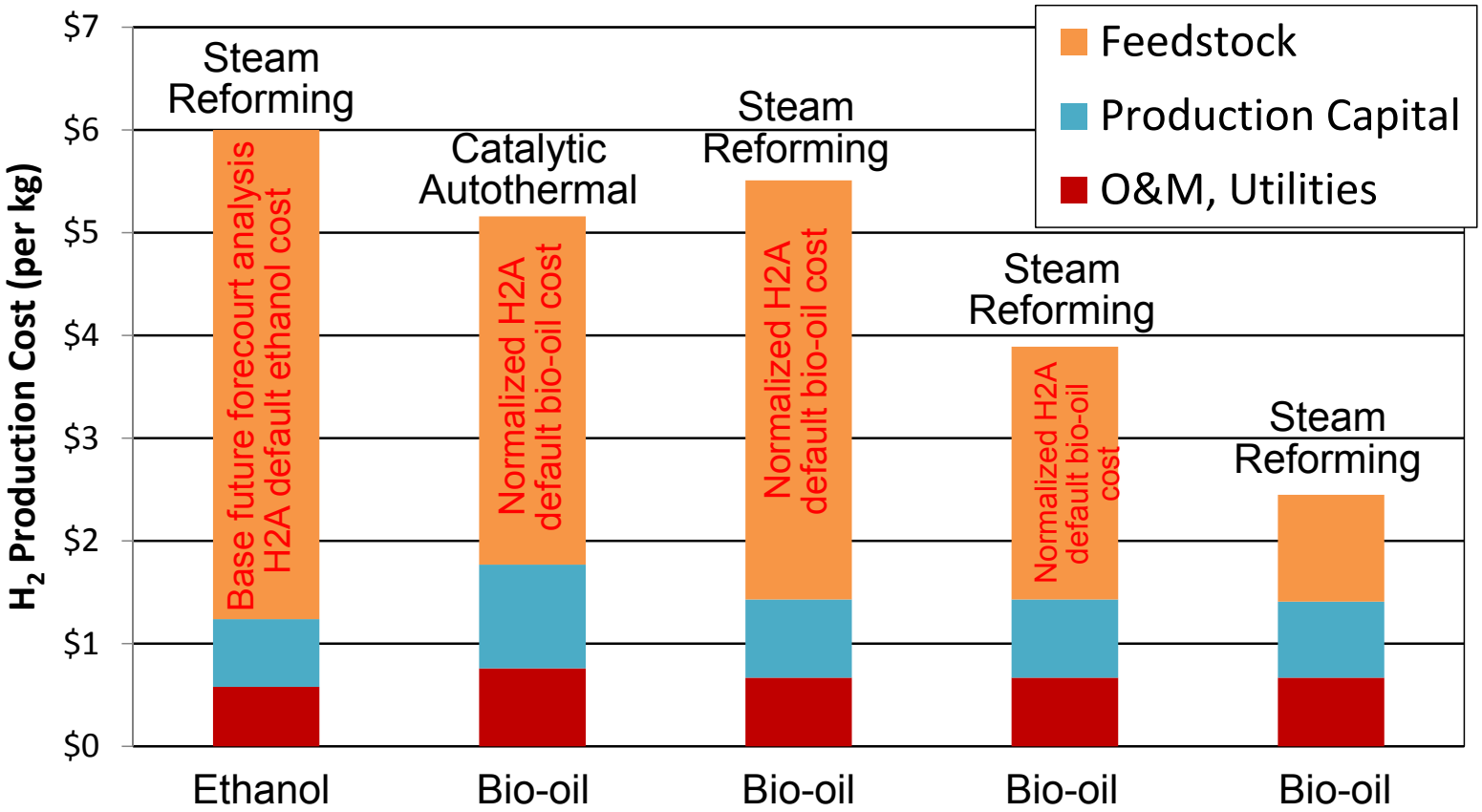
B. **Stable integration of functionalities** – *achieved*

C. **Demonstration of extended operation in pilot plant** – *currently on-going*

D. **Optimization of reforming catalyst performance** – *following C.*

Relevance - H2A analysis

Impacts of current production technology on H_2 cost



NREL distributed bio-oil reforming project 2010/ID# PD04

Demonstrated in this work <u>without process optimization</u>

This work with process optimization to 10 wt% H_2 production

This work with process optimization and future pyrolysis oil cost $6/GJ

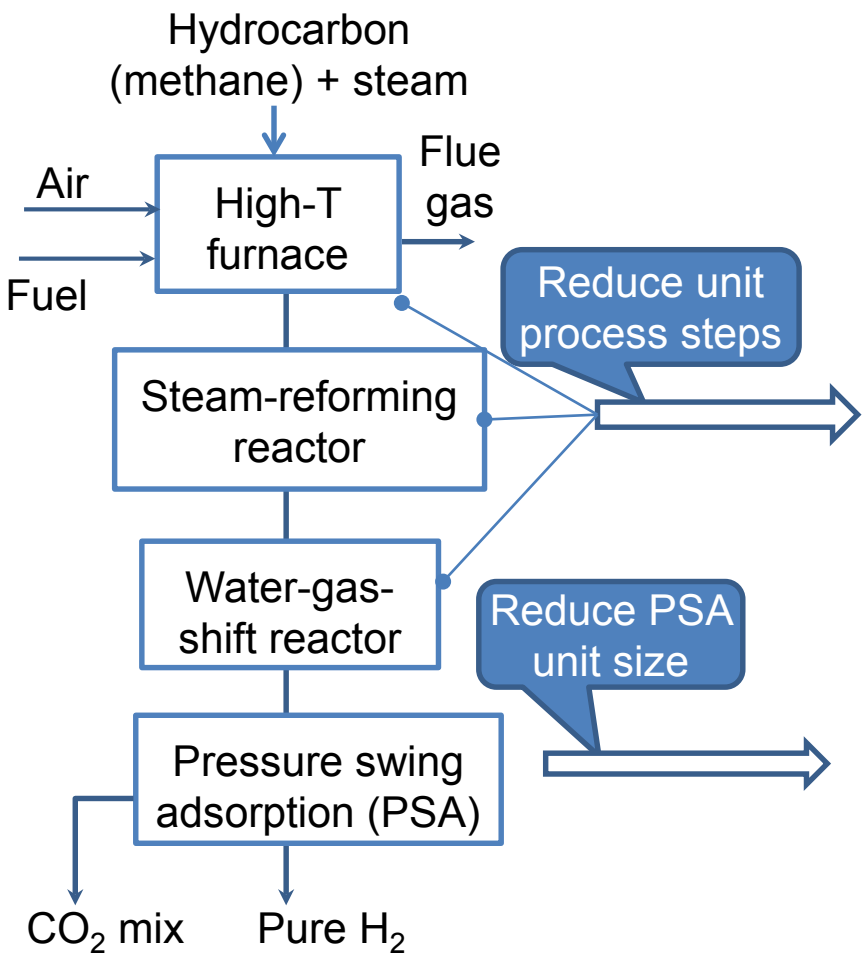
H2A default feedstock costs
- Ethanol = $26.7/GJ
- Bio-oil = $14.1/GJ

Pacific Northwest NATIONAL LABORATORY

Approach

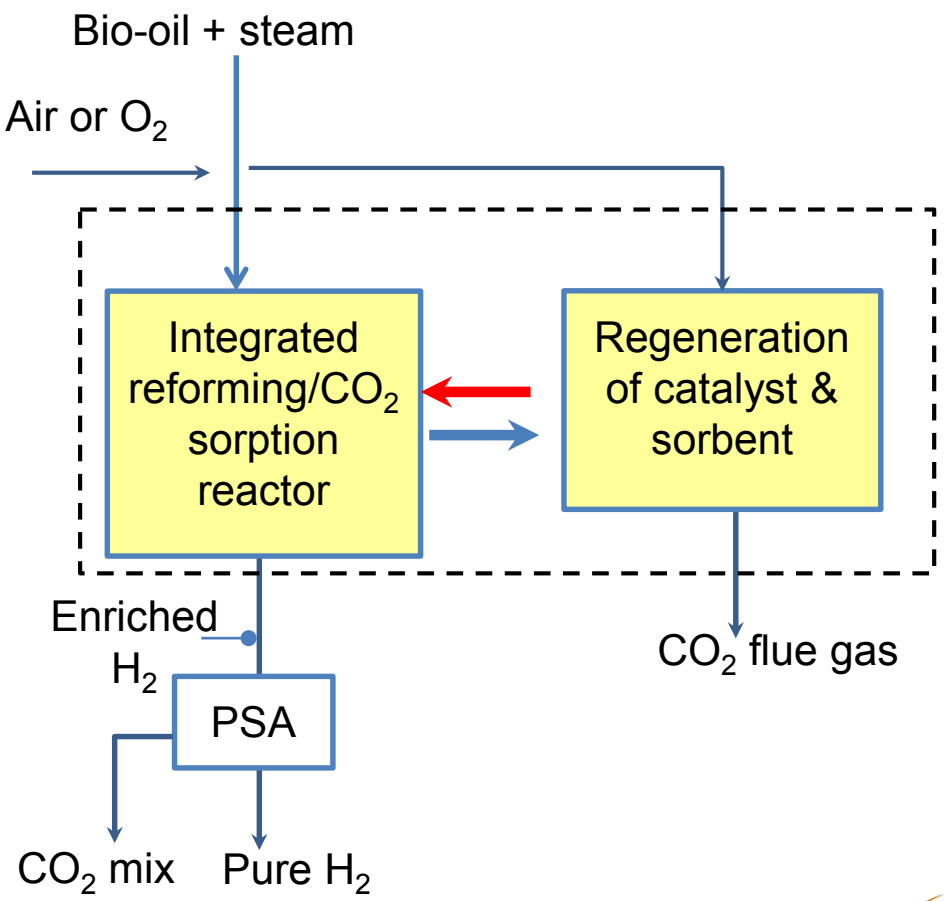
Reduce unit process steps and intensify heat/mass transfer

Typical commercial processes



Present process:

- Conduct rapid reaction/regeneration swing operation
- Capture CO_2 during reforming reaction



Pacific Northwest NATIONAL LABORATORY

Approach

*Rapid swing reactor 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:

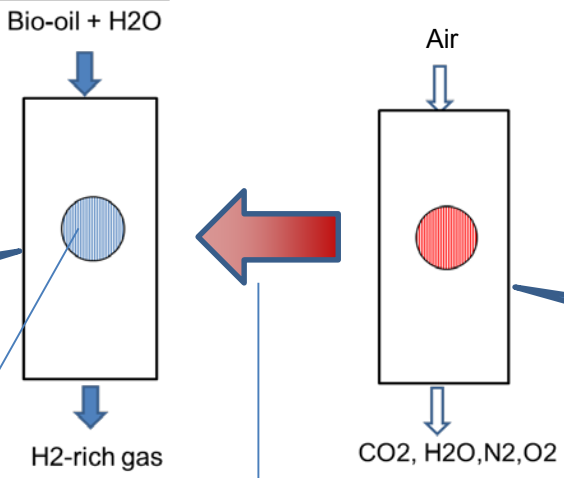
$C_nH_{n\text{-}2k}(coke)\text{-}cat + 0.5(2.5n\text{-}k)O_2 \longrightarrow 0.5(n\text{-}2k)H_2O + nCO_2 + \Delta H(<0)$

Endothermic carbonate decomposition:

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

Reforming conditions:

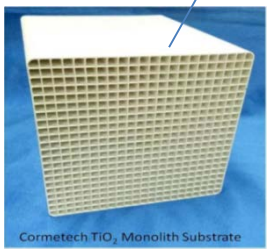
- Lower temp (500-700°C)



Regeneration conditions:

- Higher temp (700-750°C)

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

Pacific Northwest NATIONAL LABORATORY

Approach

Pilot-scale integration for stable process demonstration

Structures with integrated catalyst and sorbent functionality prepared by PNNL and currently being tested by Dason

Features of present composite sorbent and catalyst designs:

- Catalyst is resistant to coking and fouling
- Catalyst – synergistic redox, basic and acidic sites for promoting reforming and cracking reactions
- Scalable and stable sorbent synthesis methodology developed by PNNL

Dason pilot-scale test platform:

- Observed catalyst/sorbent deactivation successfully addressed
- Temperature monitoring required improvement to understand actual operating temperature
- System calibrations performed to tightly control operating temperature
- ***The result: stable materials demonstration with actual bio-oil***

Milestone 3 (FY17) – process innovation:

- Development of an integrated reactor system with technical readiness level ≥ 4
  - Demonstration of ≥10 wt% H_2 yield, >90% H_2 in reactor
  - Status – on-going ~60% complete

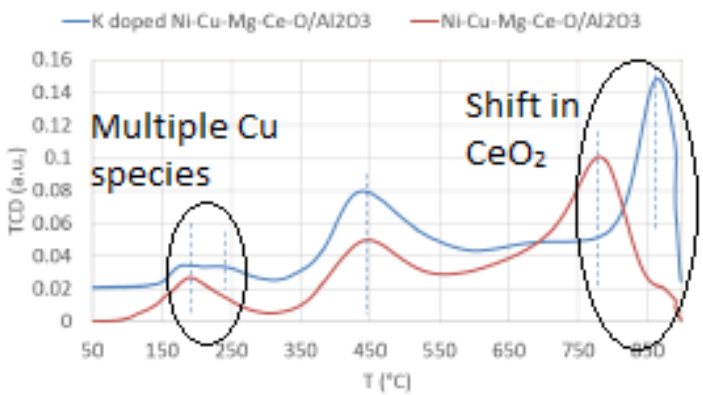
Accomplishment & Progress

Reforming catalyst optimized with K addition

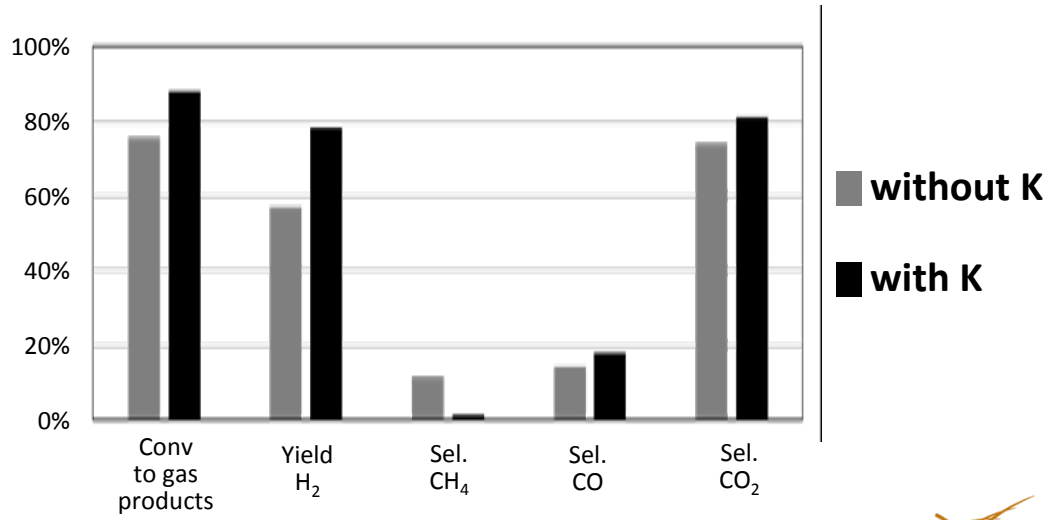
- Catalyst composition improved by modification with two elements
  1. **Addition of Potassium (K)**
  2. Lanthanum (La) in place of Magnesium (Mg)

1. Addition of Potassium (K)

- Reduces the selectivity to methane (CH_4)
- Modifies reforming sites on Copper (Cu)
  - Two distinct copper sites (versus one)
- Improves the reducibility of CeO_2
  - Increased C—C bond cleavage energy
- Optimal Ni^0/Ni^{2+} distribution effecting CO activation



TPR profiles of catalysts with and without K-doping



Pacific Northwest NATIONAL LABORATORY

Accomplishment & Progress

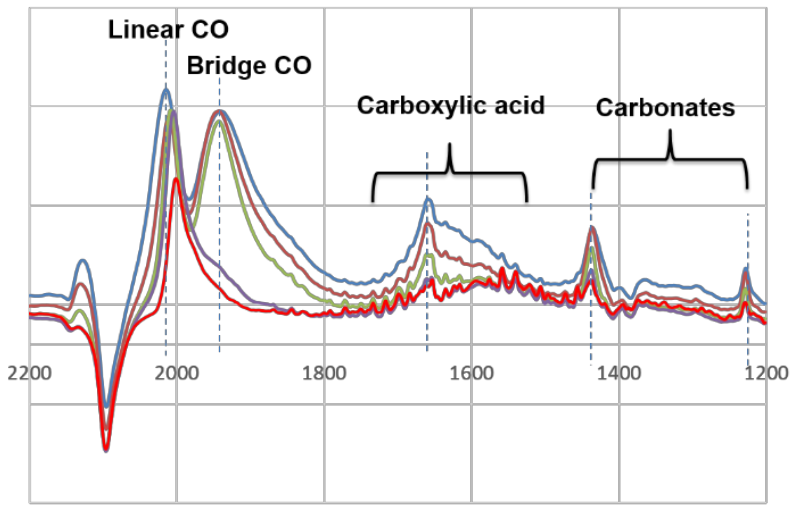
Reforming catalyst optimized with K addition

- Catalyst composition improved by modification with two elements
  1. **Addition of Potassium (K)**
  2. Lanthanum (La) in place of Magnesium (Mg)

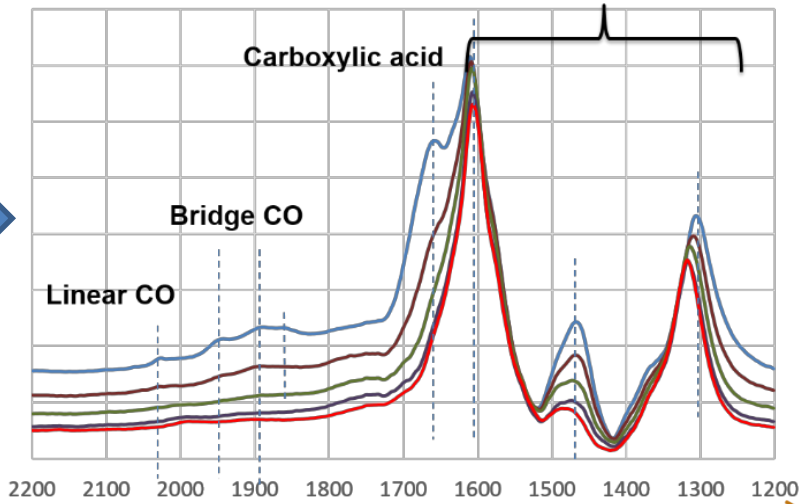
1. Addition of Potassium (K)

- Reduces the selectivity to methane (CH_4)
- Modifies reforming sites on Copper (Cu)
  - Two distinct copper sites (versus one)
- Improves the reducibility of CeO_2
  - Increased C—C bond cleavage energy
- Optimal Ni^0/Ni^{2+} distribution effecting CO activation

without K



with K



Accomplishment & Progress

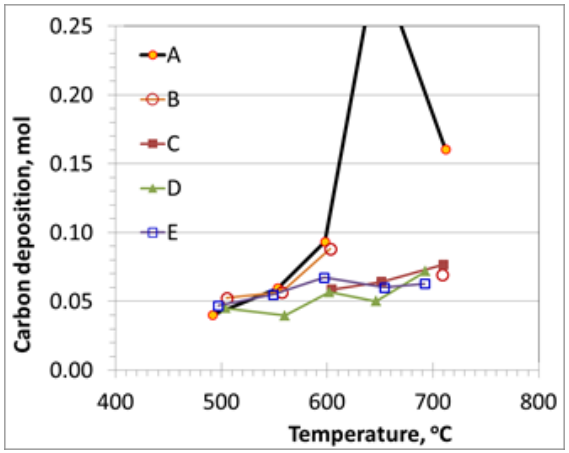
Reforming catalyst optimized with La in place of Mg

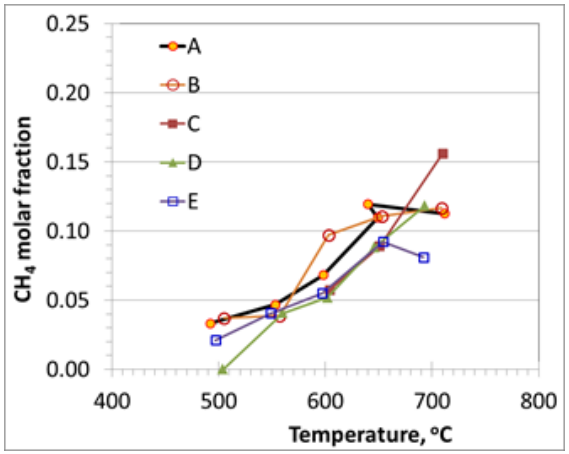
- Catalyst composition improved by modification with two elements
  1. Addition of Potassium (K)
  2. **Lanthanum (La) in place of Magnesium (Mg)**

2. Lanthanum (La) in place of Magnesium (Mg)

- Reduced CH_4 selectivity
- Reduced carbon (coke) formation

- … with presence of Al
  - Inhibits crystal growth inside TiO_2 pores
  - Improves dispersion of metal oxides – higher reaction rates



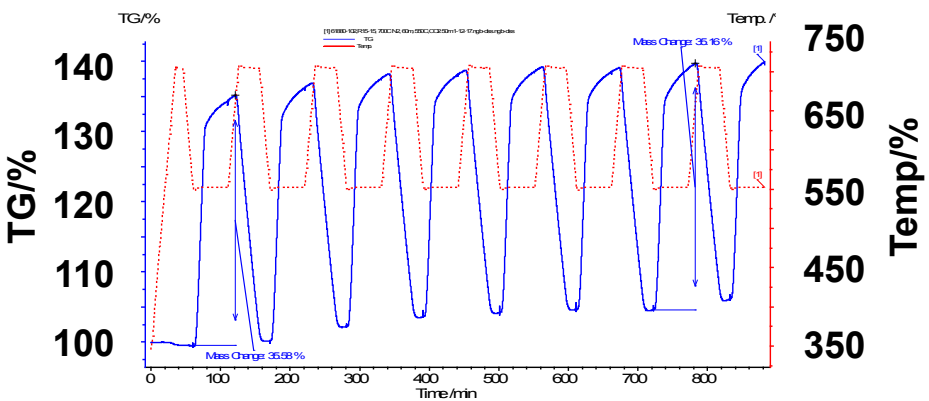


Catalyst #	Composition
(A)	K-NiCu-Ce(Mg)-Al-O
(B)	K-NiCu-Ce(Mg)-Al-O (higher loading)
(C)	K-NiCu-Ce(Mg)-Al-O (with additives)
(D) ***	K-NiCu-Ce(**La**)-**Al**-O
(E)	K-NiCu-Ce(La)-O

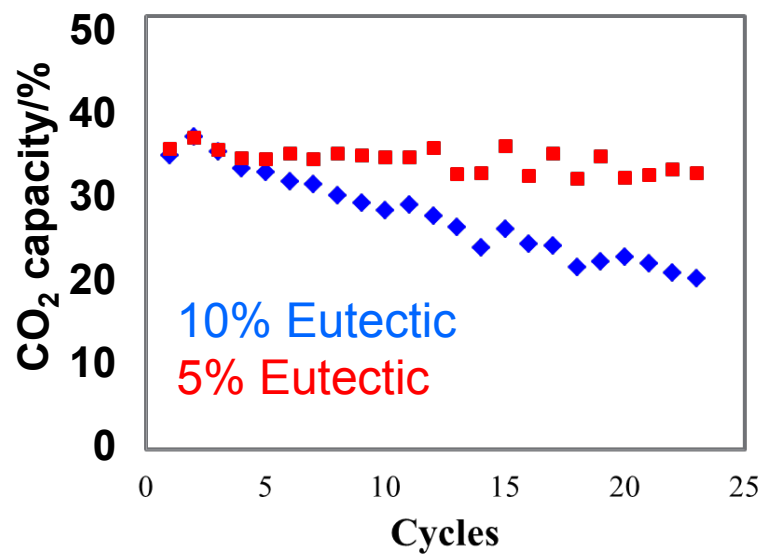
Accomplishment & Progress

Sorbent successfully optimized for scaled synthesis and stability

- Simple synthesis method developed to facilitate scale-up
  - Direct impregnation of Li, Na, and K carbonate eutectics on dolomite
  - Synthesis time reduced by 75%
- Sorbent loading optimized to address stability
  - 10 wt% versus 5 wt% $LiNaKCO_3$/dolomite



Stable sorbent performance during CO_2 TGA – large scale synthesis batch

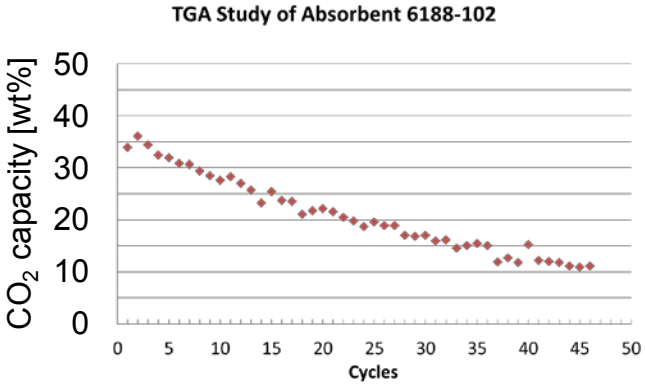


Stability addressed via optimized Eutectic loading on dolomite

Accomplishment & Progress

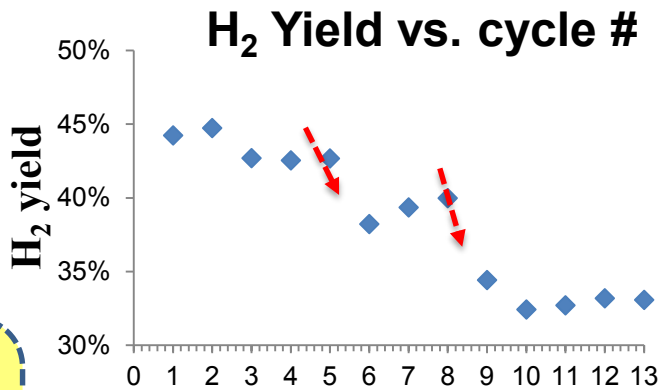
The barrier to stable catalyst/sorbent integration & operation identified

- TGA experiments performed with crushed catalyst + sorbent
  - Performance degradation with mixing
  - Catalyst + sorbent exposed to atmosphere after every 6 cycles



Performance degradation in terms of sorption when sorbent mixed with catalyst

- Monolith catalyst + sorbent loaded into Dason pilot reactor
  - Performance degradation after every 4 cycles – corresponding to frequency of opening reactor for servicing



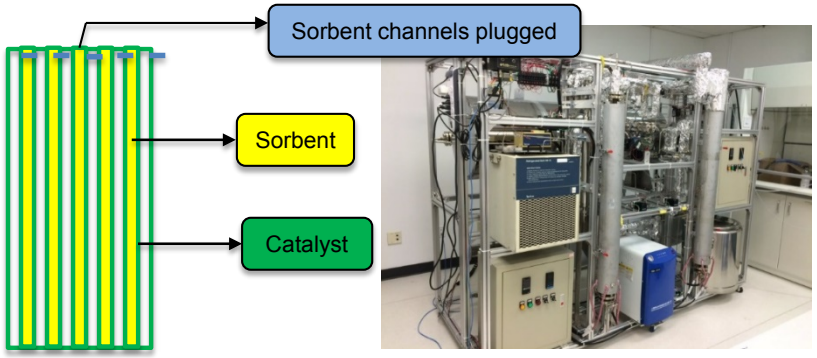
Performance degradation in pilot reactor with integrated catalyst+sorbent system

Stable operation achieved by eliminating reactor disassembly/reassembly during routine operation

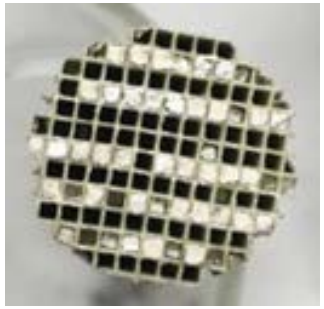
Believed to be linked to contamination of the catalyst/sorbent system

Accomplishment & Progress

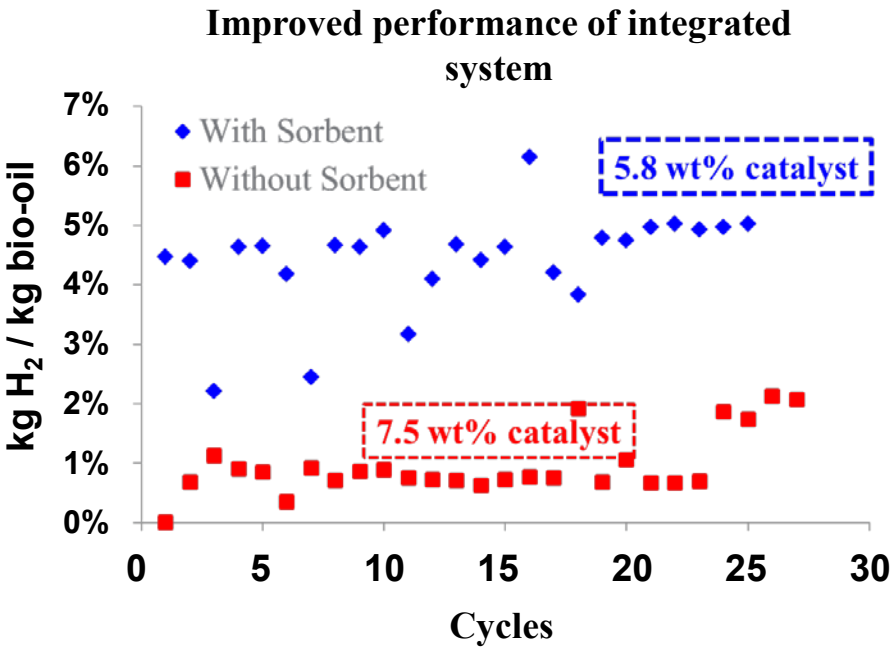
Integrated system demonstrated with improved performance



Pilot Reactor System at Dason



Integrated system catalyst +sorbent



Significantly improved H_2 yield (up to 5x) demonstrated with proposed system in Dason pilot reactor *with sorbent* versus without

Demonstrated with ***low*** catalyst and sorbent loading for calibration of Dason pilot reactor to address stability issues

- *Highly confident that both catalyst and sorbent loading can be increased for significant improvement in performance*

Accomplishment & Progress

Responses to Previous Year Reviewers' Comments

	Reviewer Comment	Response
1	<u>CO_2 capture and matching with reforming</u> • Not enough consideration is given to potential non-matching conversion and kinetics of the competing reactions for both reforming and regeneration conditions, which are likely to have significant impact on overall system design and O&M costs. • Although not the primary goal of the project, there was not much discussion or analysis of the in situ CO_2 capture portion of the system.	• This is correct in that the matching of reforming and regeneration conditions is significant to O&M costs and process efficiency. Optimizing reforming and regeneration is currently occurring empirically. The current approach is for optimization only to occur as necessary to demonstrate at scale with favorable economics. • At the start of the project, the CO_2 capture technology (eutectic-promoted dolomite) has been studied in detail at PNNL and its partners. Apart from TGA, its currently being optimized empirically during demonstration.
2	<u>Coke formation and combustion</u> • The role of coke burn-off must be better understood. • Questions include how much coke is ideal and whether the feed composition can be related to the amount of coke that will be deposited; the latter will be critical for bio-oil since the composition will vary considerably depending on how it is made. The project should consider modeling (or even testing) the use of bio-gas instead of bio-oil	• Ideally, yes, it would be better understood. But materials durability is the current focus, and with that achieved the scope of the work only allows for empirically optimization of soot/char formation and combustion. Coke combustion is believed to be predominantly a thermal process, and thus warrants little attention at this stage of development assuming materials durability is demonstrated. • Variation in bio-oil composition is outside of the scope of the current program.

Collaboration and technology transfer

PNNL – patent application filed on the new materials & reactor concepts

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 of new reforming catalysis
- Catalyst characterization and kinetics studies

PNNL (Dr. Chaitanya Sampara)
- Innovations of new material and reactor concepts
- Delivery of monolithic testing samples

Dr. Bang Xu
Dason Technology
- Process development and reactor system tests

Future

Process design, engineering and field tests for process commercialization

Pacific Northwest
NATIONAL LABORATORY

Remaining barriers and challenges, and proposed future work

Milestone	Critical issue/challenge	Proposed approach
9/30/2016: Integration of reforming reactions with CO_2 capture in one reactor vessel	• Demonstration of extended operation (~100 cycles) of integrated reforming and CO_2 capture processes with actual bio-oil	• This work is underway and stable operation has been achieved. • Working towards a 100 cycle demonstration.
9/30/2017: Demonstration of an integrated reactor system for complete bio-oil conversion and production of 2 kg/day H_2 at 10% kg H_2/kg bio-oil	• Recycling of un-converted bio-oil and condensed water • Long-term, continuous swing reactor operation • Good material balances	• High quality chemical composition analysis of feed, liquid product, and gas product • Systematic process tests and optimization of catalyst - sorbent structures with the goal of achieving 10 wt% H_2 yield.

Any proposed future work is subject to change based on funding levels.

Pacific Northwest NATIONAL LABORATORY

Summary

Objective: To advance H_2 production technology from bio-oil to the DOE target of <$2/GGE

Relevance: Biomass is a renewable resource that presents an attractive resource for distributed hydrogen production. The conversion of bio-mass to bio-oil presents an attractive potential energy carrier for distributed hydrogen production for transportation, and is important to long-term energy and environmental sustainability in the US.

This project is in pursuit of several innovative approaches towards addressing challenges associated with process development of distributed bio-oil reforming for H_2 production

Approach: Use in-situ CO_2 capture to add heat and push thermodynamics to overall higher efficiencies, and directly address the use coking by operating in cyclic fashion where coke is combusted and its subsequent energy drives the endothermic reforming process

Accomplishments: The addition of K and La to the reforming catalyst is shown to reduce selectivity to methane, reduce coke formation, and increase reform rate(s) by increased metal-oxide dispersion

Sorbent successfully optimized for scaled synthesis and stability by optimizing eutectic weight-% in sorbent, and by a method of synthesis that includes direct impregnation of Li, Na, and K carbonate eutectics on dolomite; synthesis time reduced by 75%

The source of deactivation in the integrated system was identified this year that had compromised progress, and subsequently stable operation has been achieved.

Demonstration of stable bio-oil reforming with integrated CO_2 capture has occurred, and continues. CO_2 capture shown to significantly improve H_2 yield (up to 5x).

Collaborations: A highly versatile and committed team that includes a national laboratory (PNNL), academia (WSU), and small and large private industry (Dason, Cormetech, respectively).

Remaining Barriers: Optimization of catalyst - sorbent structures, combined with systematic and long-term process testing, with the goal of demonstrating 10 wt% H_2 yield.