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

Project ID #PD111

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Project team:

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6/8/2016

Overview

Timeline

- ☐ Start – November 2014
- ☐ End – October 2017
- ☐ 60 % Complete

Budget

- ☐ Total Project Budget – $2,755K
- ☐ Total Recipient Share – $555K
- ☐ Total Federal Share – $2,200K
- ☐ Total DOE funds spent* – $1200K

  *as of 4/5/2016

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

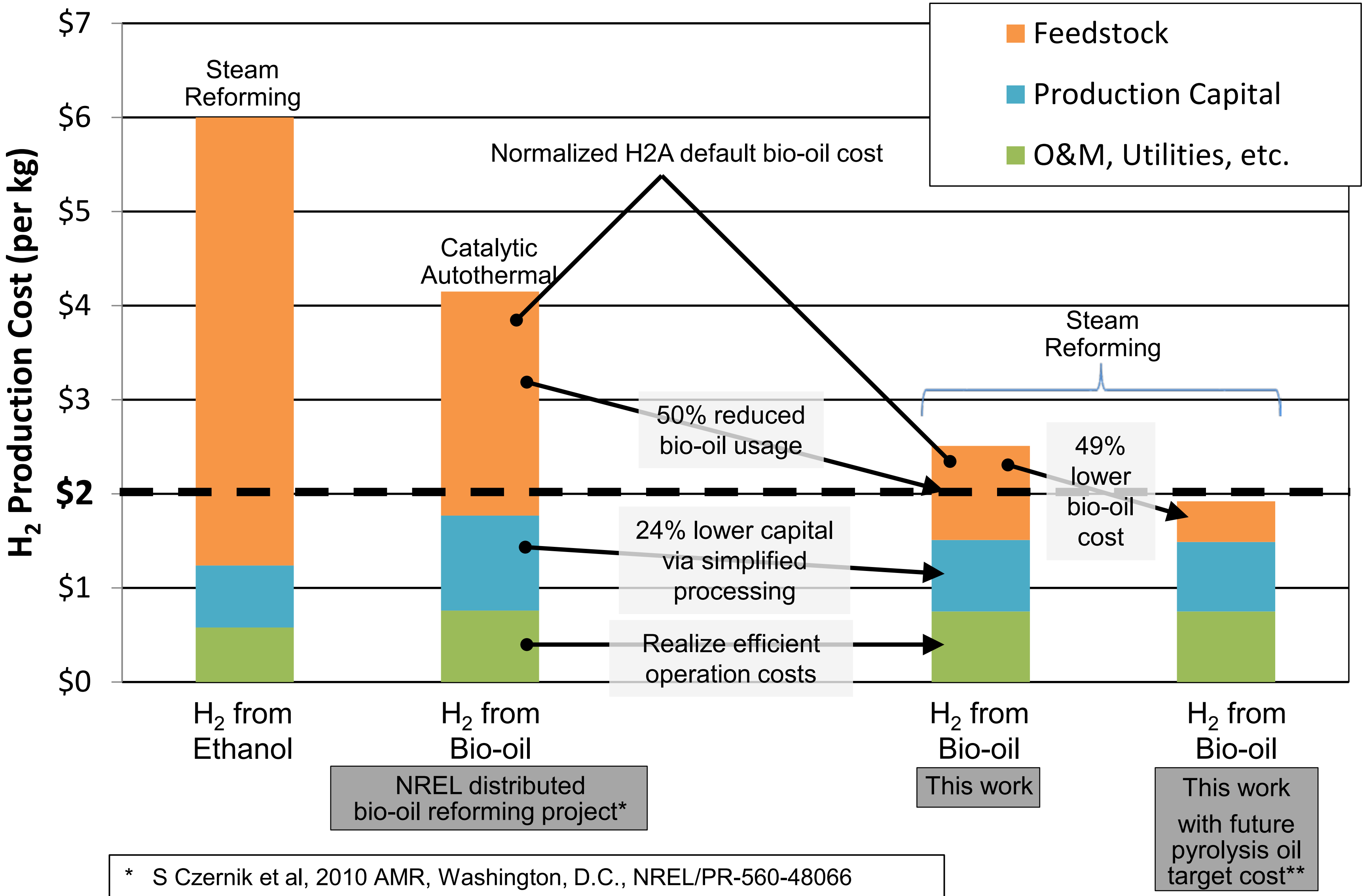
Project Objective

Advance H_2 production technologies from bio-liquids such as bio-oil

1. **Reduce 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. **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
   - 80% energy conversion efficiency achievable
     (versus 71.4% for methane reforming, 2011 status)
3. **Increase operating flexibility and durability**
   - Reduced O&M (operations & maintenance) requirements
   - Directly addresses coking & catalyst deactivation
   - Modular, compact reactors to make unit turn-around easier

Relevance - H2A analysis

Impacts of production technology innovations on H_2 cost



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

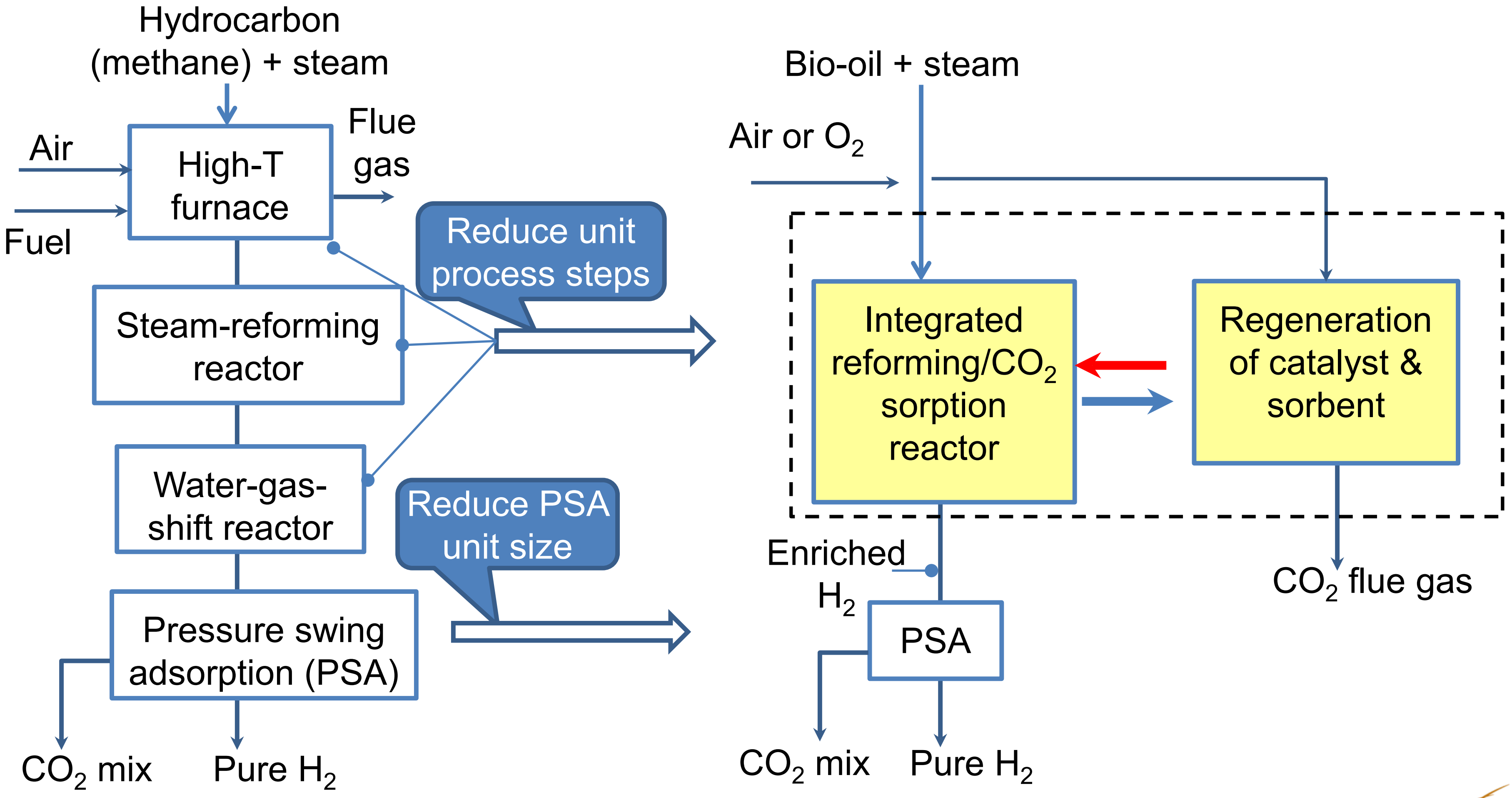
Approach – our process innovation

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



Hydrocarbon (methane) + steam

Air

Fuel

High-T furnace

Flue gas

Steam-reforming reactor

Water-gas-shift reactor

Pressure swing adsorption (PSA)

CO_2 mix

Pure H_2

Reduce unit process steps

Reduce PSA unit size

Bio-oil + steam

Air or O_2

Integrated reforming/CO_2 sorption reactor

Regeneration of catalyst & sorbent

Enriched H_2

PSA

CO_2 flue gas

CO_2 mix

Pure H_2

Approach - rapid swing reactor operation of integrated reactor

Endothermic steam-reforming (SR) reaction:

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

Coking & de-oxygenation reaction:

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

Exothermic carbonation reaction:

$CO_2 + MO \longrightarrow MCO_3$

Exothermic coke combustion for catalyst regeneration:

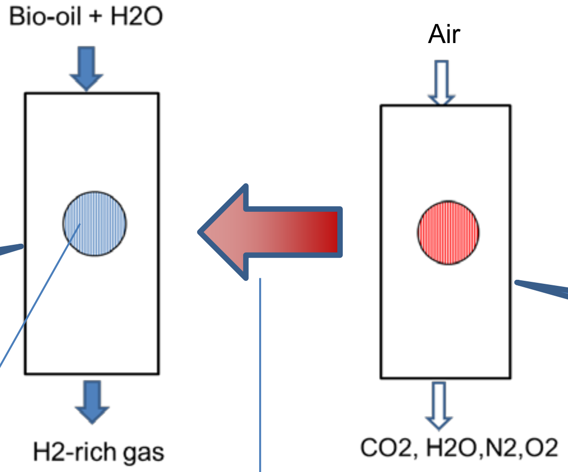
$C_nH_{n-2k}(\text{coke})\text{-cat} + 0.5(2.5n-k)O_2 \longrightarrow 0.5(n-2k)H_2O + nCO_2 + \Delta H(<0)$

Endothermic carbonate decomposition:

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

Reforming conditions:

- Lower temperature (500 - 700°C)



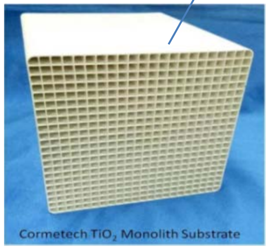
Regeneration conditions:

- Higher T (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



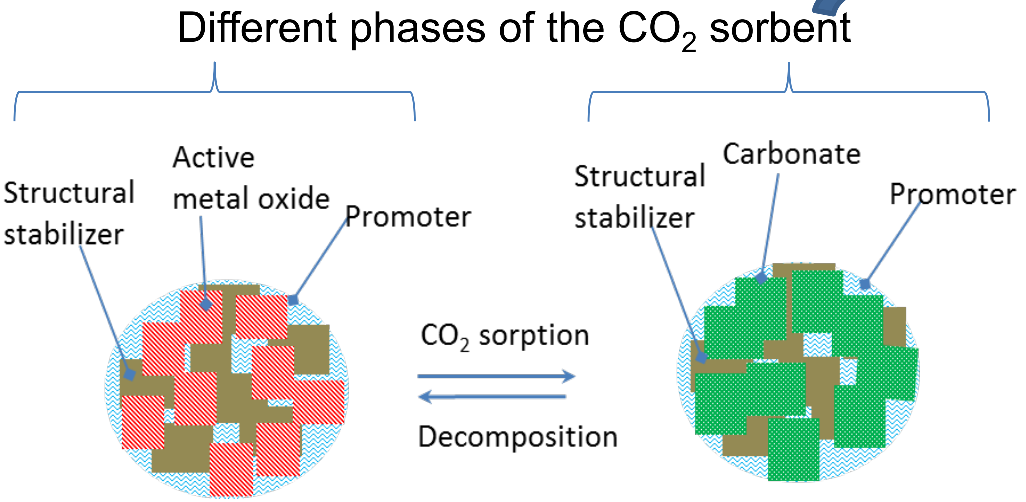
Approach – new composite sorbent for CO_2 capture under steam-reforming conditions

Performance characteristics: adequate working capacity, rapid kinetics, stability

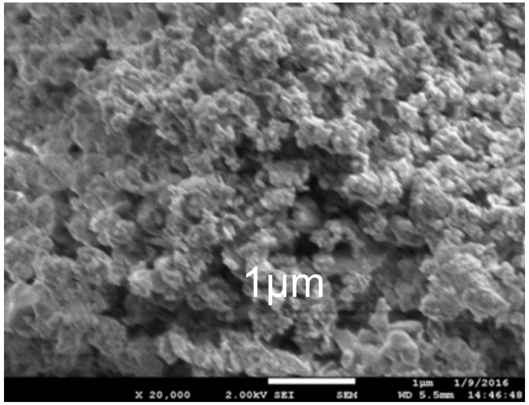
Features of present composite sorbent designs:

- CaO (active metal oxide) stabilized by MgO (structural stabilizer) during sorption & de-sorption
- Eutectic carbonate (i.e., promoter) used to catalyze CO_2 sorption and subsequent carbonate decomposition
- Stability results from reversible transformation between the active and carbonated states

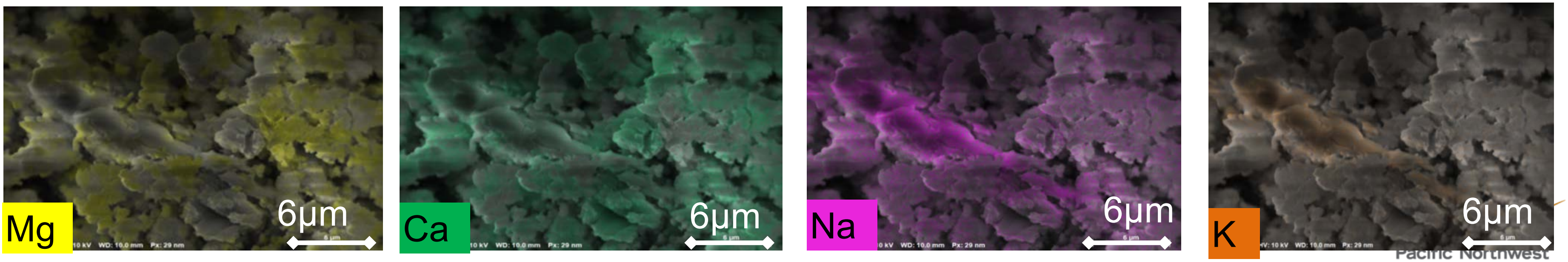
Different phases of the CO_2 sorbent



Intimate mixing at nano-&micro-scales



Elemental distribution in Dolomite-derived composite sorbent



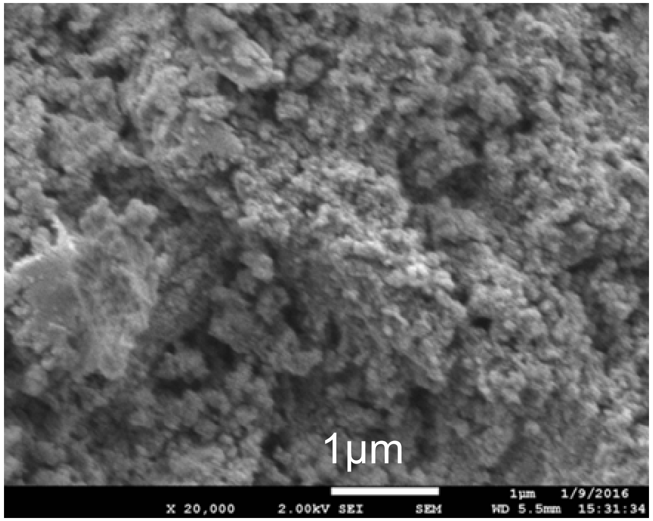
Approach – nano-composite catalyst for steam reforming reactions of bio-liquids

Performance characteristics:

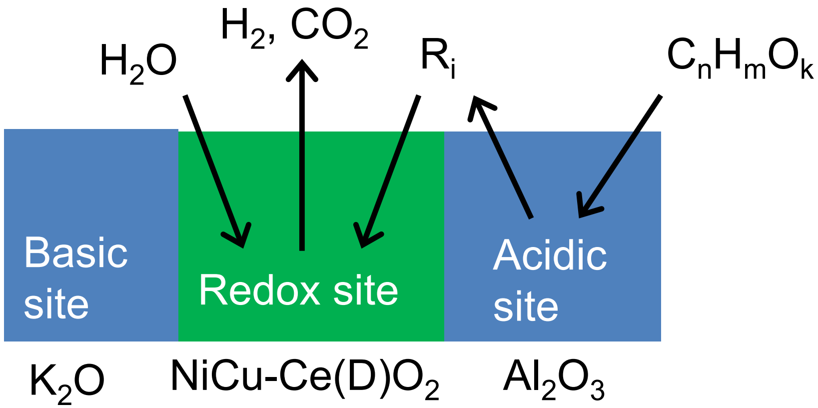
- Catalyst can be rejuvenated by calcination
- Catalyst is resistant to coking and fouling

Features of present nano-composite catalysts:

- Synergistic effects result from combination of different catalytic materials
- Redox sites are for reforming reactions
- Basic and acidic sites are for breakdown of large bio-oil molecules (or polymers)



Composite catalyst made as powder



H_2O

H_2, CO_2

R_i

$C_nH_mO_k$

Basic site

Redox site

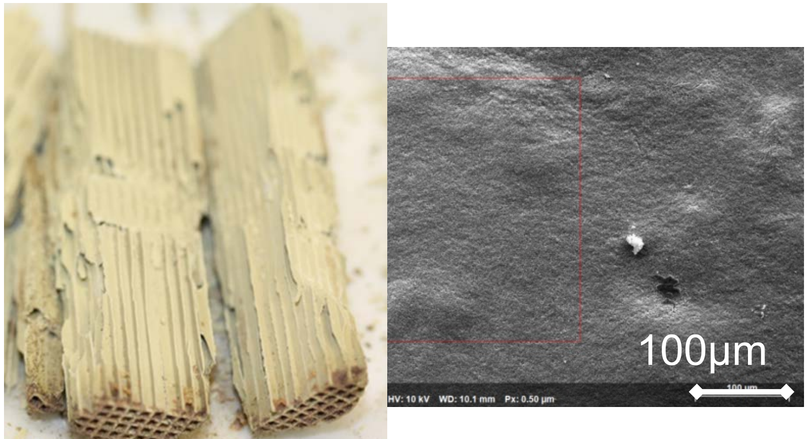
Acidic site

K_2O

NiCu-Ce(D)O_2

Al_2O_3

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



Composite catalyst deposited on and in monolith channel walls

Approach - milestones addressing three critical challenges

Milestone 1 (FY15) – **material innovation**:

- ✓ Composite catalyst demonstrated for steam reforming reactions with simulated bio-oil:
  - Stability in repeated reforming/regeneration cycles
  - H_2 productivity >0.6 [kg-H_2/h]/kg of catalyst
- ✓ Composite CO_2 sorbent demonstrated with $CO_2/H_2/H_2O$ gas mixtures
  - Stability in repeated sorption/regeneration cycles
  - CO_2 capture productivity >0.2 [kg-CO_2/h]/kg of sorbent

Milestone 2 (FY16) – **monolithic reactor innovation**:

- ✓ Monolith catalysts demonstrated for steam reforming of actual bio-oil:
  - Stability in repeated reforming/regeneration cycles
  - H_2 productivity >0.6 [kg-H_2/h]/kg of catalyst
- ➢ Demonstration of bio-oil flow distribution and integration of reforming reactions with CO_2 capture – next

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, high purity H_2 after PSA

Accomplishment & Progress

Responses to Previous Year Reviewers' Comments

	Critical issue/challenge	Response
1	• Consider devoting more resources to address the technical challenges associated with the catalyst, especially poison and coking tolerance when running on bio-oil, and translation of laboratory discovery to successful monolith. Clearly, catalyst performance has high project showstopper potential • Catalyst poisons in bio-oil have not been addressed.	1. The project focus was shifted toward catalyst development and reaction tests for bio-oil reforming • Catalyst particle bed tests at WSU • Monolith catalyst preparation and intrinsic performance studies at PNNL • Setup of reactor testing system at high flow rates and evaluation of flow distributors at Dason Tech • Supply of a large number of monolith supports by CormeTech 2. Both model compounds and pure bio-oil are used for reaction tests
2	• Would also like to see high priority given to assessing the relative kinetics of H_2 production, CO_2 diffusion into sorbent, and mass transfer through the monolith	• Composite sorbents have been tested in packed bed in particle forms under various conditions, in parallel to TGA screening tests • Some kinetics addressed in this talk; some diffusion/mass transfer effects to be addressed later
3	• Tackling very significant technical challenges on all three fronts simultaneously. Overly optimistic timeline.	• We are trying our best to solve the most significant problems to develop a step-out H_2 production technology, and will adjust the plan if necessary

Accomplishment & Progress

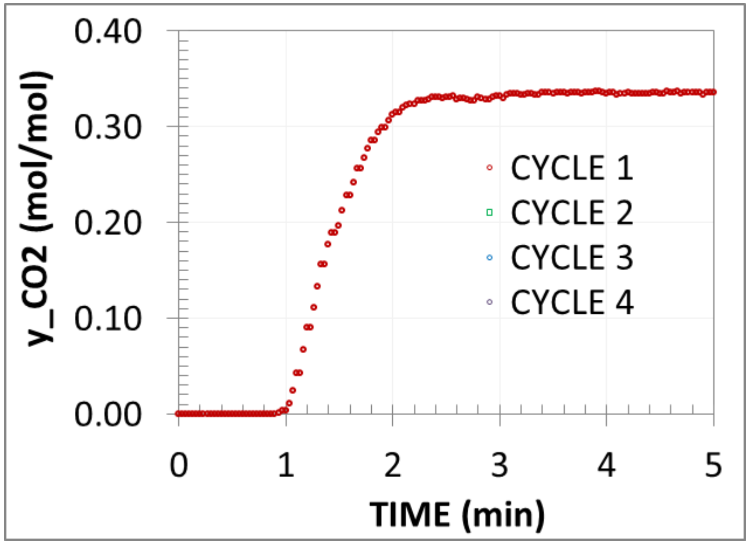
Rapid kinetics and >11 cyclic stability of the composite CO_2 sorbent

Stability testing of the packed sorbent particle bed under one set of conditions

Sorption: 500°C, 1 bar, GHSV=11,0001/h, H_2O/syngas (H_2/CO_2=2/1) =1:1

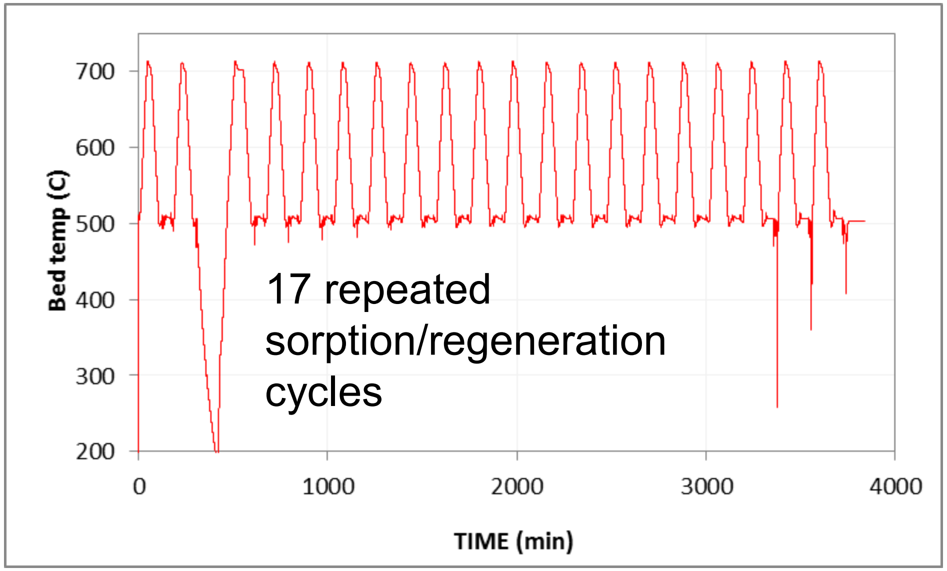
Regeneration: 700°C, 1 bar, air

CO_2 breakthrough curves

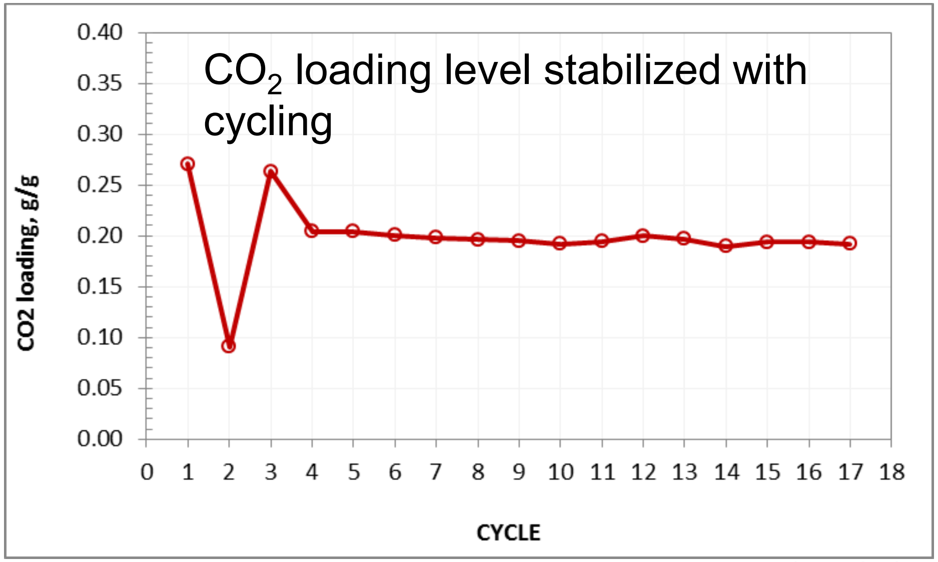


- 90% of the sorption capacity is reached in breakthrough time of 1.4min – rapid sorption kinetics

$CaO\text{-}MgO + CO_2 \leftrightarrow CaCO_3\text{-}MgO$



17 repeated sorption/regeneration cycles

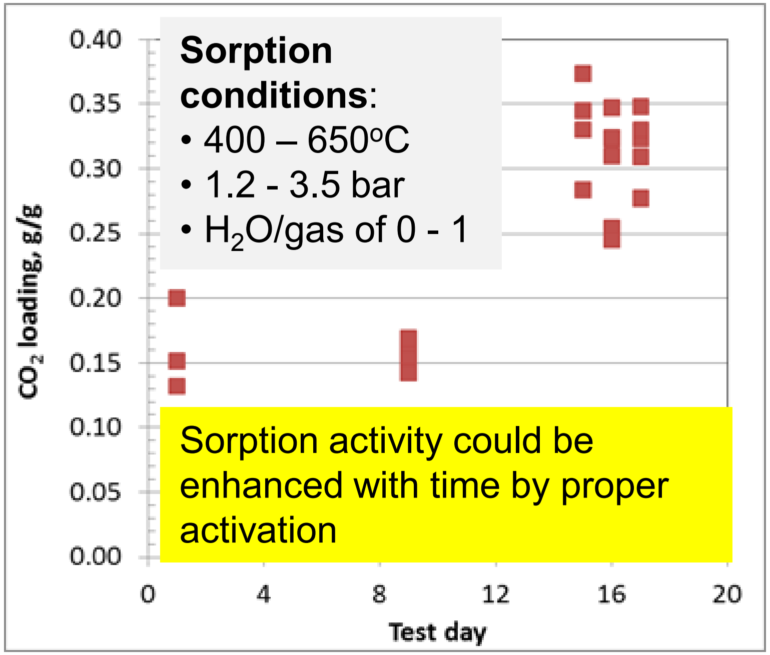


CO_2 loading level stabilized with cycling

Accomplishment & Progress

Three-week stability of the composite sorbent tested under various conditions

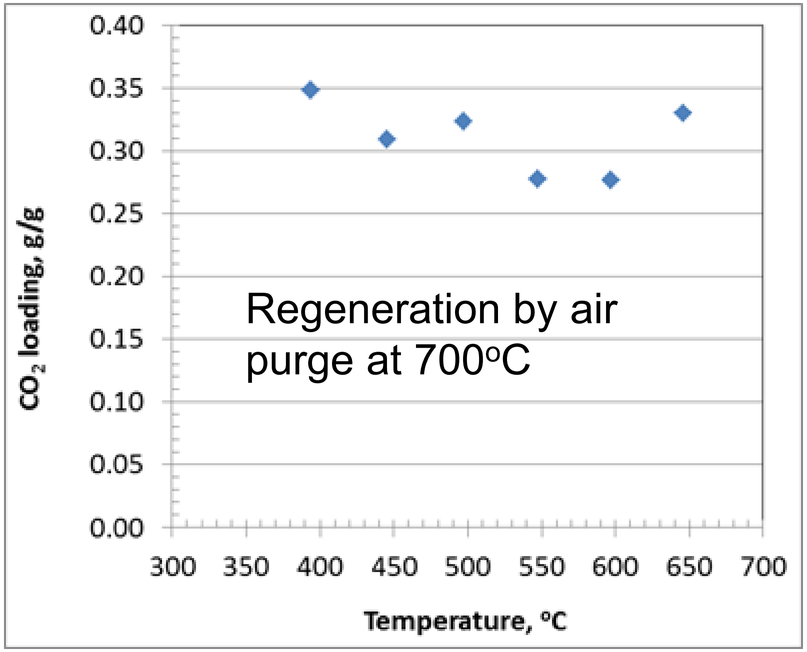
Parametric tests in different days



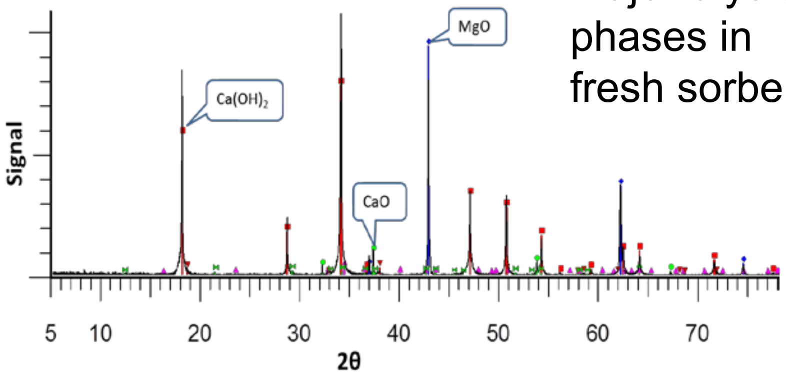
Sorption conditions:
- 400 – 650°C
- 1.2 - 3.5 bar
- H_2O/gas of 0 - 1

Sorption activity could be enhanced with time by proper activation

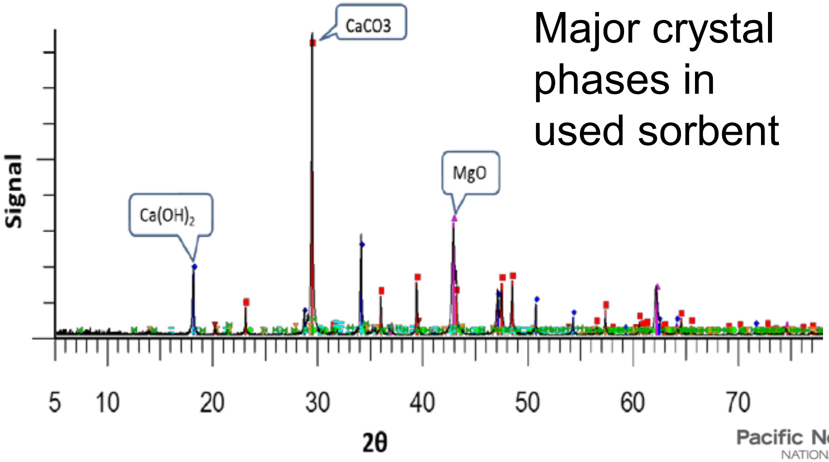
Sorbent works over a range of temperature



Regeneration by air purge at 700°C



Major crystal phases in fresh sorbent



Major crystal phases in used sorbent

Pacific Northwest
NATIONAL LABORATORY

Accomplishment & Progress

Cyclic stability of K-NiCu-Ce(Mg)-Al-O composite reforming catalyst

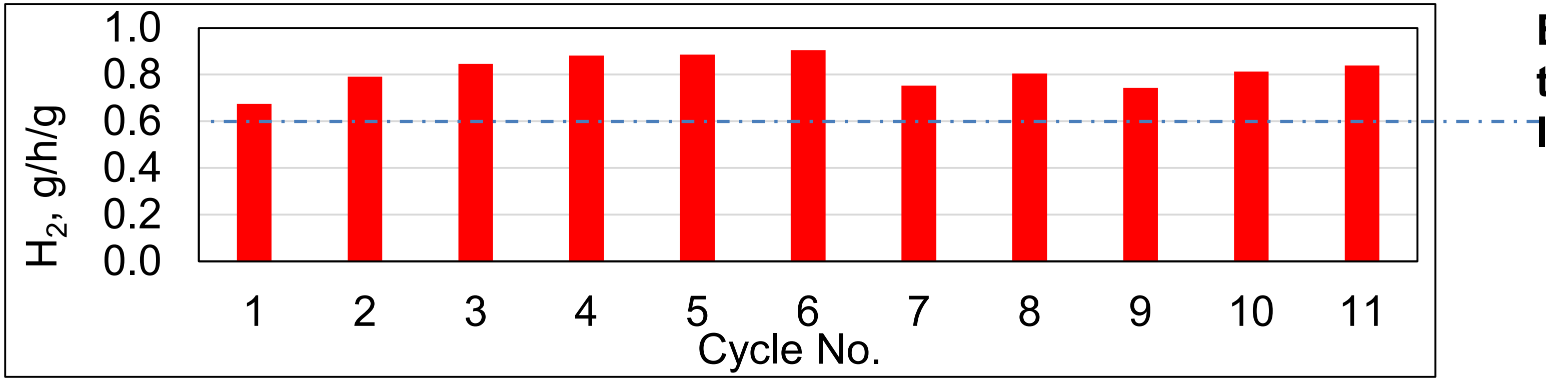
Test of the catalyst particle-packed bed:

Simulated bio-oil: Ethanol:Acetone:Acetic Acid: Phenol =1:1:1:1

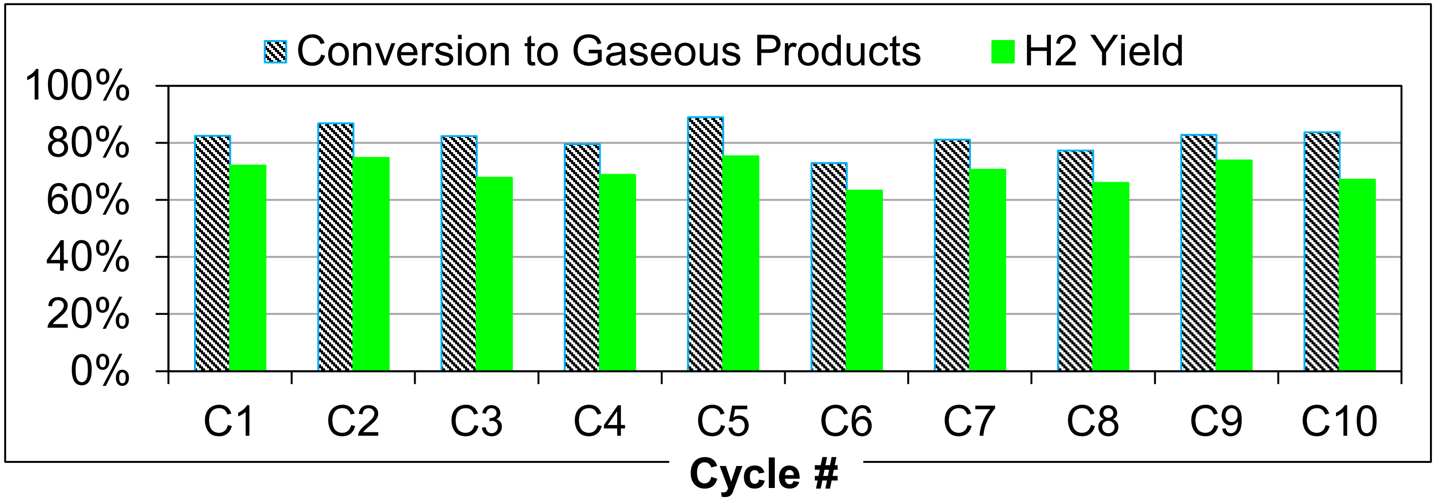
Reforming conditions: 500 °C, steam/carbon= 3.3, SV = 10,000 h^{-1}

Regeneration conditions: 700 °C, 40 sccm of air, TOS = 8 min/cycle

Stable H_2 productivity demonstrated through reforming/regeneration cycles



Exceeded the target level



Accomplishment & Progress

The composite catalyst is more stable in monolith for reforming 100% bio-oil

Catalyst in packed particle bed configuration:

Reforming: 600°C, $WHSV_{cat}$ = 82 h^{-1}

steam/oil (S/O) = 3

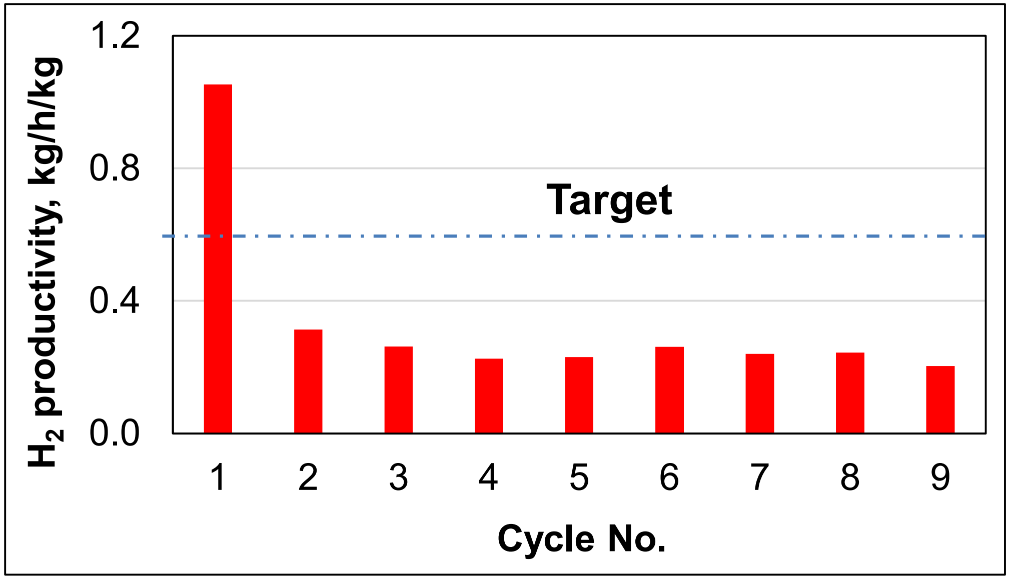
Regeneration: 700 °C, air

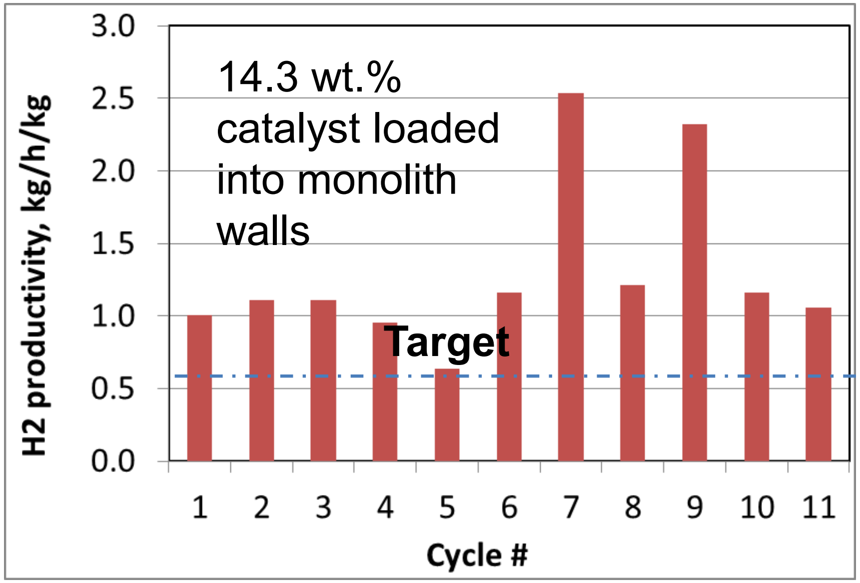
Catalyst loaded into walls of TiO_2 monolith

Reforming: 550°C, S/O=1

$WHSV_{cat}$ = 237 h^{-1}, $LHSV_c$= 56 h^{-1}

Regeneration: 700 °C, air,





14.3 wt.% catalyst loaded into monolith walls

$$WHSV_{cat} = \frac{G_{oil}(g/h)}{W_{cat}(g)}$$

Active composite catalyst in the monolith channel wall exposed to feed oil

$$LHSV_C = \frac{F_{oil}(cc/h)}{V_C(cc)}$$

Volume of monolith reaction channels exposed to feed oil

Accomplishment & Progress

Dramatic enhancement of the monolith reactor volume-based productivity

H_2 productivity is enhanced about 10X with the activated TiO_2 monolith-supported K-NiCu-Ce(Mg)-Al-O catalyst

$$R_{Bed} = R_c \cdot \varepsilon_c$$

Channel volume fraction

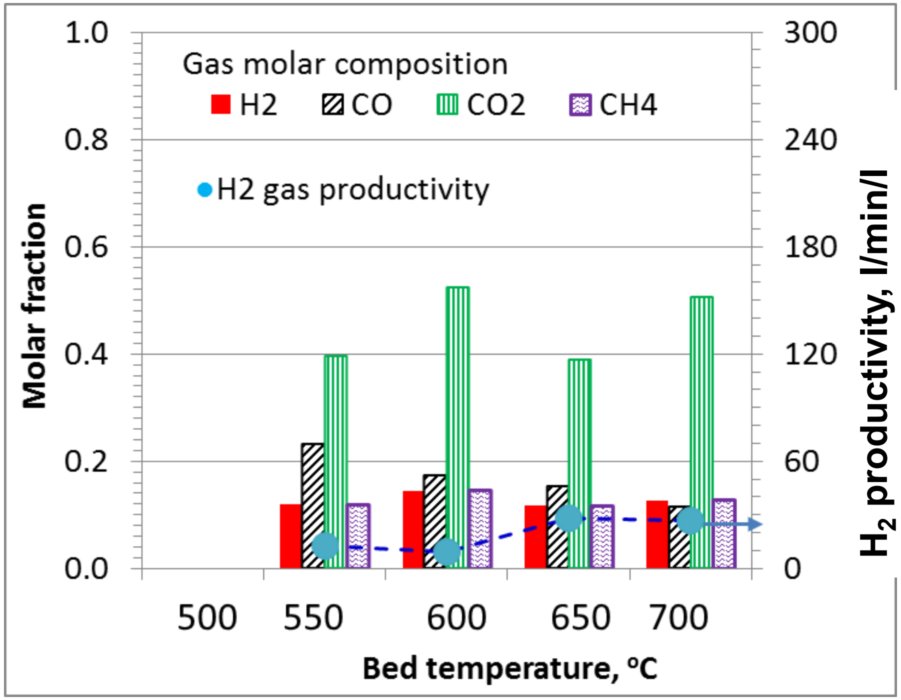
$$R_c = \frac{F_{H2}(cc/\min)}{V_c(cc)}$$

Produced H_2 flow rate

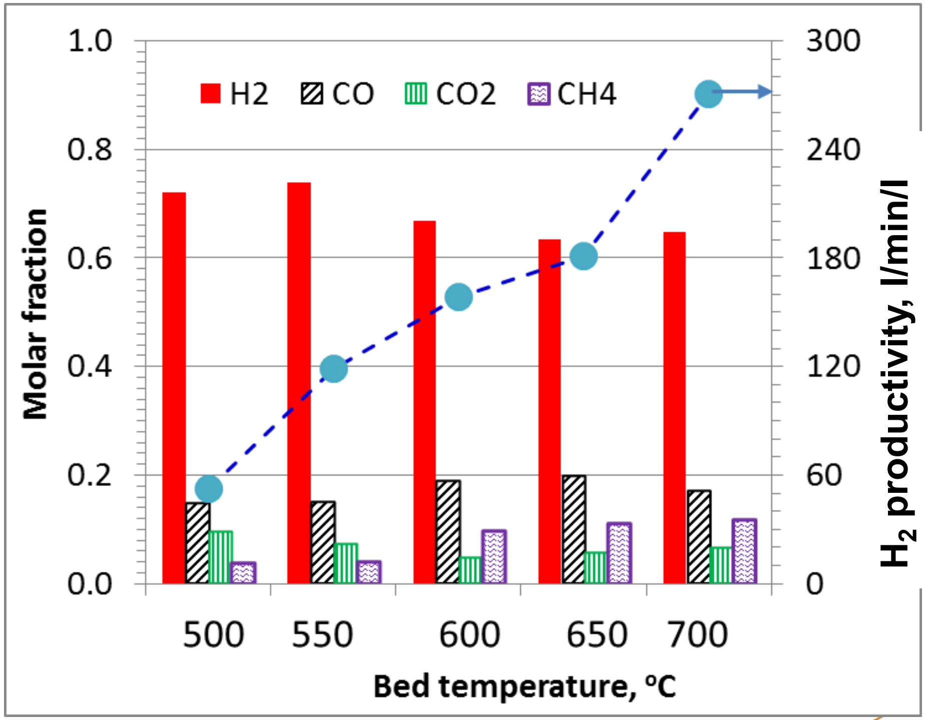
Reaction channel volume

Syngas composition and H_2 productivity of the same monolith catalyst module:

Before activation



After activation



Cat #60193-41-3, 18.5cm long; Reforming: S/O=1,LHSV$_c$= 32 h^{-1}; Regeneration: 700 °C, air

Accomplishment & Progress

Monolith reactor enables usage of low steam/oil ratio in the reactor feed

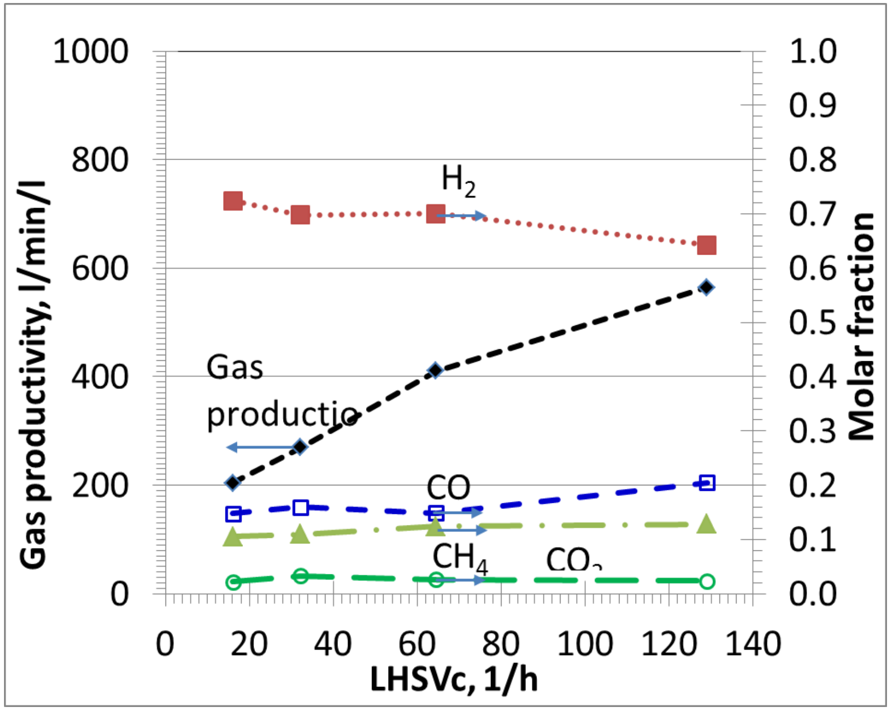
- The reforming can be effectively conducted at low feed steam/oil (S/O) ratio
- Syngas productivity increases with LHSV, while H_2 molar fraction in the syngas slightly decreases

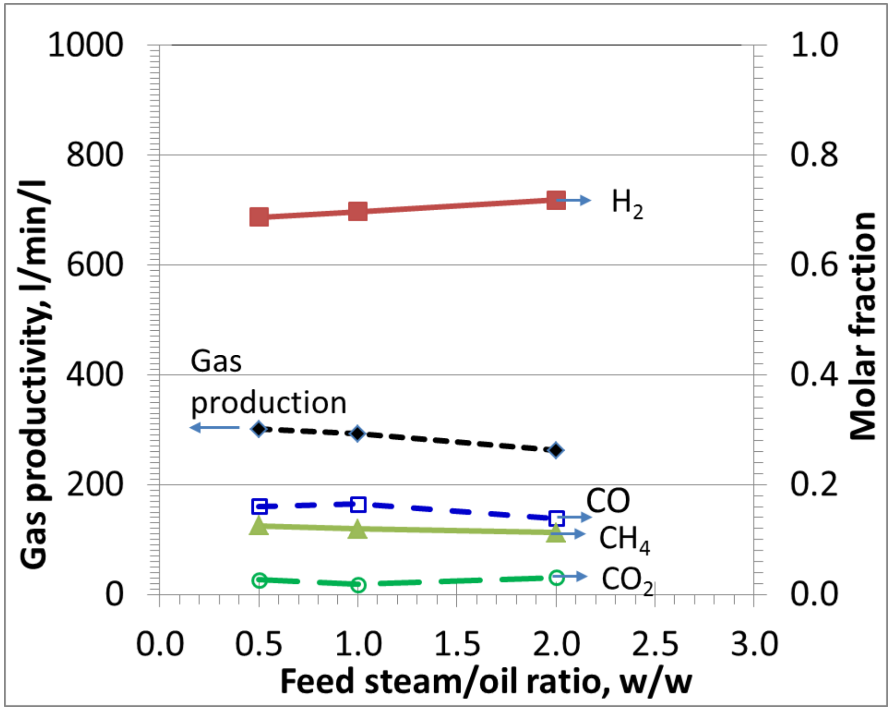
Reforming: 640°C, S/O=1

Regeneration: 700 °C, air

Reforming: 640°C, $LHSV_c$= 32 h^{-1}

Regeneration: 700 °C, air,





Cat #60193-41-6, 18.5cm long

Accomplishment & Progress

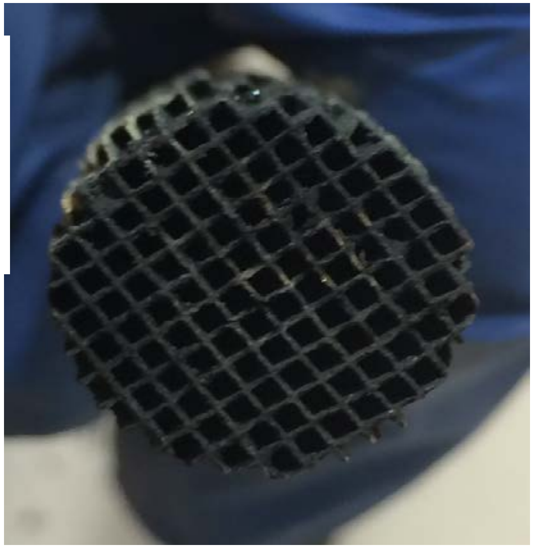
Promising steam/bio-oil flow distributor identified

- ✓ Dason's integrated reactor skid is commissioned for tests at feed rates 10-100 times higher than PNNL's reactor

- ► The system was debugged with ethanol reforming over a commercial steam-reforming catalyst
- ► PNNL's monolithic catalyst is more active at ~100°C lower temperature versus commercial catalyst

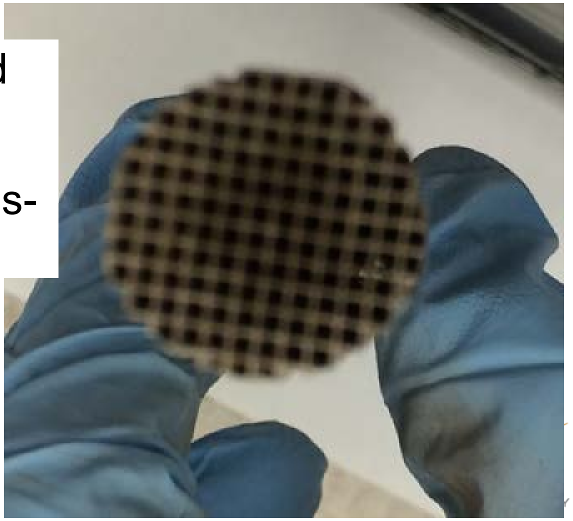
Feed nozzle positioned above the monolith at designed distance:

Bio-oil spread evenly over cross-sectional area of the monolith



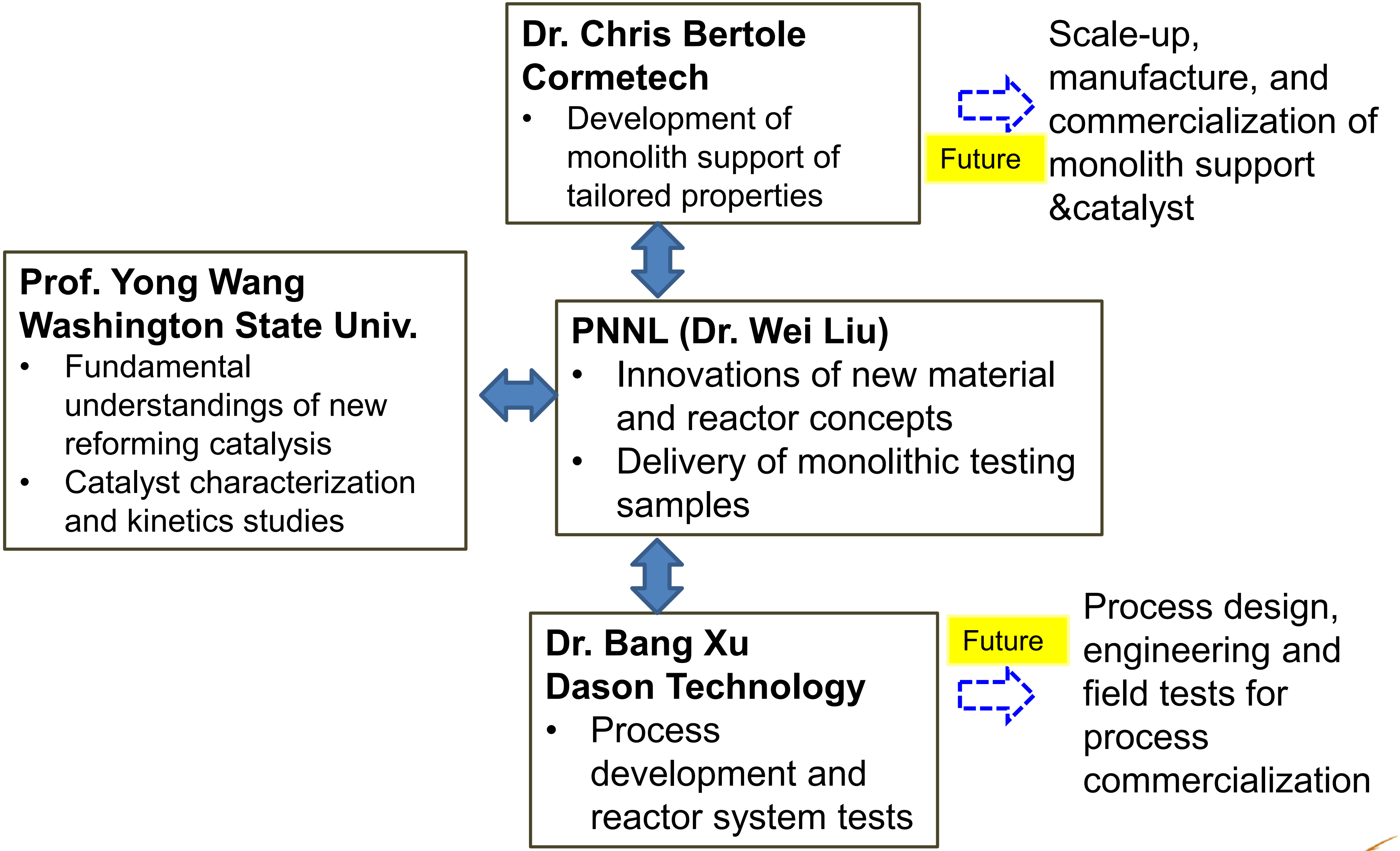
Feed nozzle positioned too close to the monolith:

Bio-oil spread mostly into middle of the monolith cross-section



Collaboration and technology transfer

PNNL filed patent application 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. Wei Liu)

- 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

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	• Synchronization of reforming and CO_2 capture processes • Preparation and testing of the composite CO_2 sorbent in larger quantities • Negative chemical interactions between the sorbent and reforming	• Systematic reforming tests with the bio-oil flow distributor to identify robust operation windows • Improving the sorbent formulations to tolerate large temperature variations • Understanding impacts of sorbents on reforming reactions • Evaluation of different catalyst/sorbent packing structures in the reactor tube
9/30/2017: Demonstration of an integrated reactor system for complete bio-oil conversion and production of 99% pure H_2	• Recycling of un-converted bio-oil and condensed water • Long-term, continuous swing reactor operation • Good material balances	• Making and delivering monolithic reforming catalysts and CO_2 sorbents of consistent quality • Upgrading of operation and control of the testing units • Chemical composition analysis of feed, liquid product, and gas product • Systematic process tests • Correlation of catalyst and sorbent properties with process performances

Summary

- ✓ Bio-liquids (e.g., ethanol, bio-oil) coke strongly on steam reforming catalysts
- ✓ The K-NiCu-Ce(D)-Al-O metal oxide nano-composite is an active, new catalyst system for steam reforming of bio-liquids with periodic regeneration by combustion
- ✓ TiO_2 monoliths (CormeTech) loaded with the composite catalyst show exceptionally higher activity after certain activation than the particle bed:
  - New active catalytic states are formed in the monolith channel walls
  - Bio-oil is more evenly spread on the channel wall; high steam/oil ratio not necessary
- ✓ The monolith swing reactor is promising to solve the catalyst deactivation associated with steam reforming of bio-liquids

  → To be further developed with higher (10-100-fold) oil feed rates to magnify hydrodynamics and heat transfer effects.
- ✓ Dolomite + eutectic carbonate composite is developed as a new sorbent system for capturing CO_2 in $CO_2/H_2/H_2O$ mixtures
  - Sorption over 400 to 700^oC, regeneration above 700 ^oC
  - Fast CO_2 sorption (carbonation) kinetics, comparable to CO_2 adsorption
- ✓ Both preparation and reactor loading of the sorbent need to be scaled up with larger quantities. Its chemical interactions with the reforming catalyst needs to be addressed for in situ CO_2 capture applications

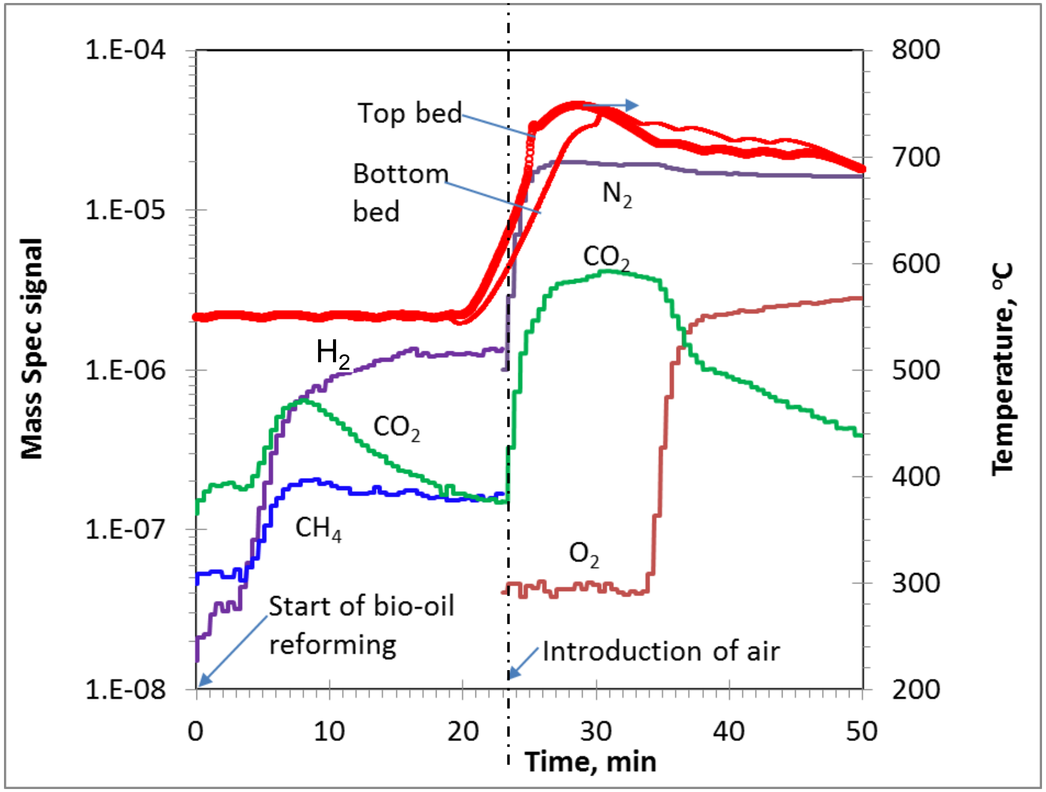
Technical Back-Up slides (optional)

Bio-oil steam reforming tests of monolith catalysts

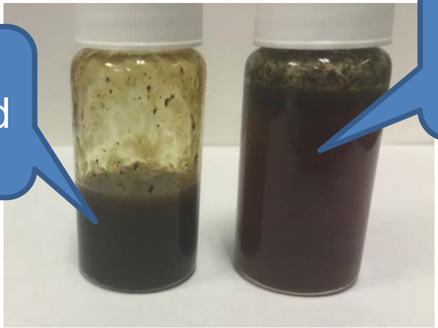
Gas production profiles during reforming and regeneration

Cat #60193-41-6

Reforming: feed steam/oil = 1, LHSVc = 32 h^{-1}
Regeneration: 200 sccm air



Injection of steam/oil into two channels



As-received bio-oil

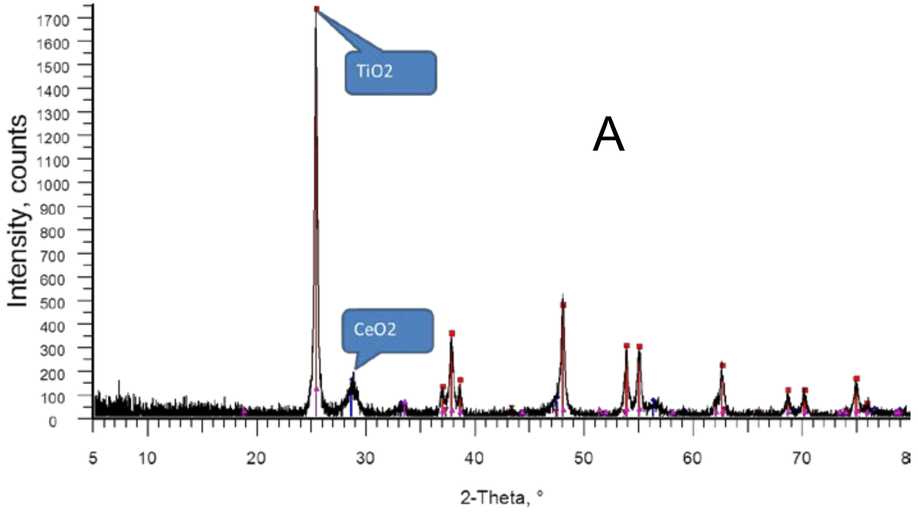
1:1 mix with water

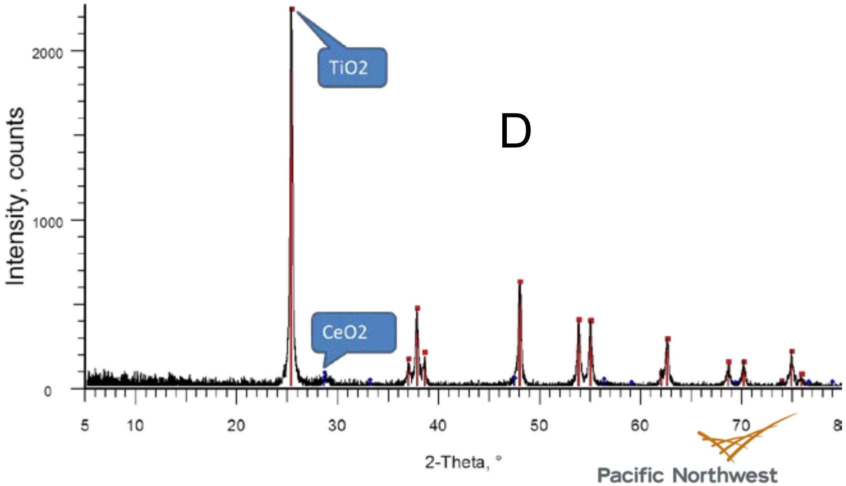
Liquid condensed from reactor effluent

Five TiO_2 monoliths impregnated with different solutions

K-NiCu-Ce(Mg)-Al-O nano-composite oxide

Cat #	Preparation condition	Loading wt %	Crystal phases in spent catalyst			
			Major	Minor		
A	1-time impregnation	12.5	TiO_2	rutile	CeO_2	K_2O
B	2-time impregnation	19.2	TiO_2		CeO_2	
C	2-time impregnation with additives	10.8	TiO_2		small CeO_2	
D	Replaced Mg with La	13.0	TiO_2			
E	Replaced Mg with La and removed Al	12.1	TiO_2	rutile	CeO_2	NiO

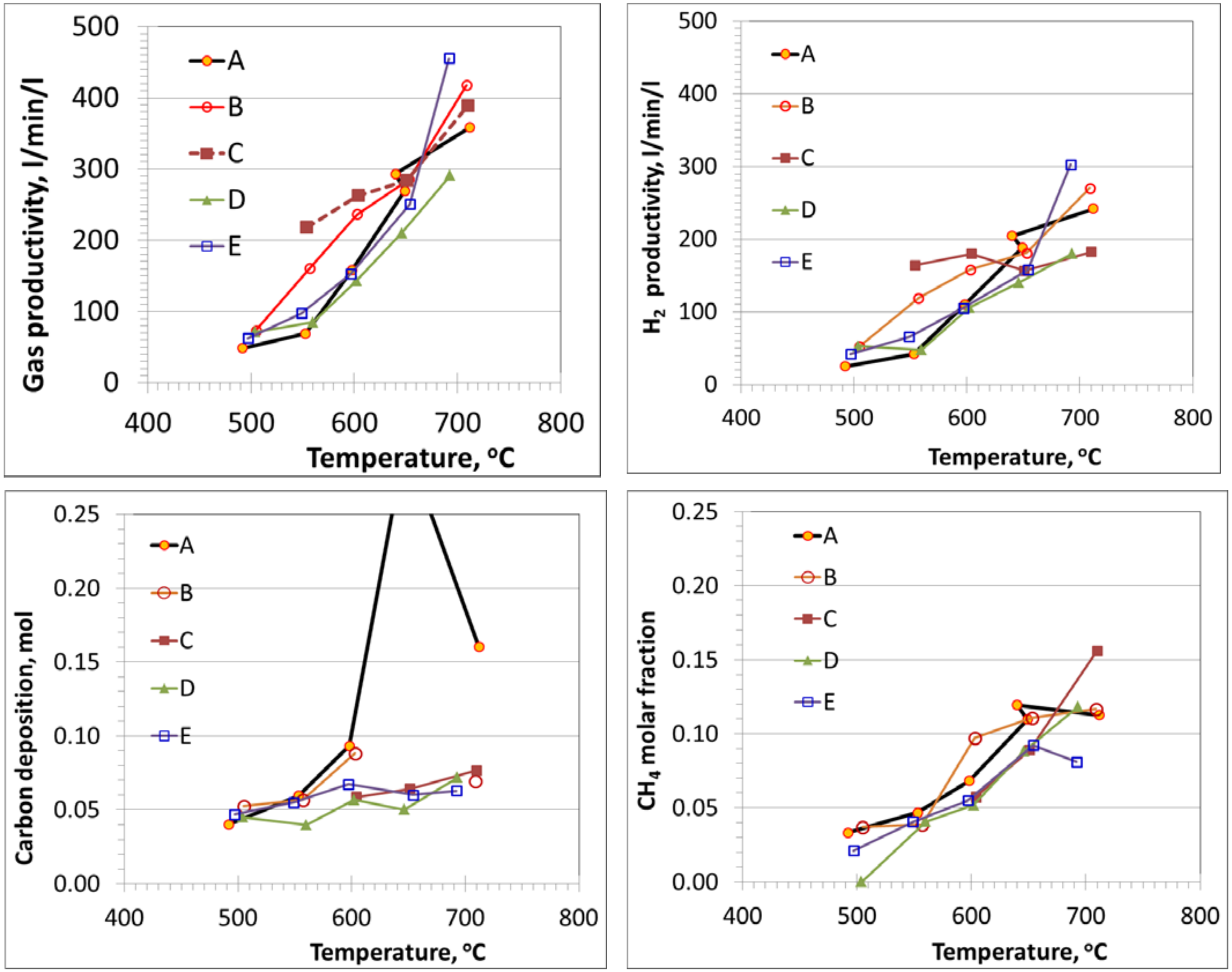




Impacts of composite catalyst compositions on bio-oil reforming performances

Five identical TiO_2 monoliths impregnated with different solutions:

- Syngas productivity increases with temperature for all 5 catalysts
- H_2 productivity increases with temperature except for Cat C
- CH_4 content in syngas increases with temperature for all the catalysts
- Coke deposition slightly increases with temperature



Reforming: S/O=1, LHSVc= ca. 32 h^{-1}

Regeneration: 700 °C, air

Improvement to the composite CO_2 sorbent using eutectic carbonates

TGA sorption/regeneration cyclic tests:

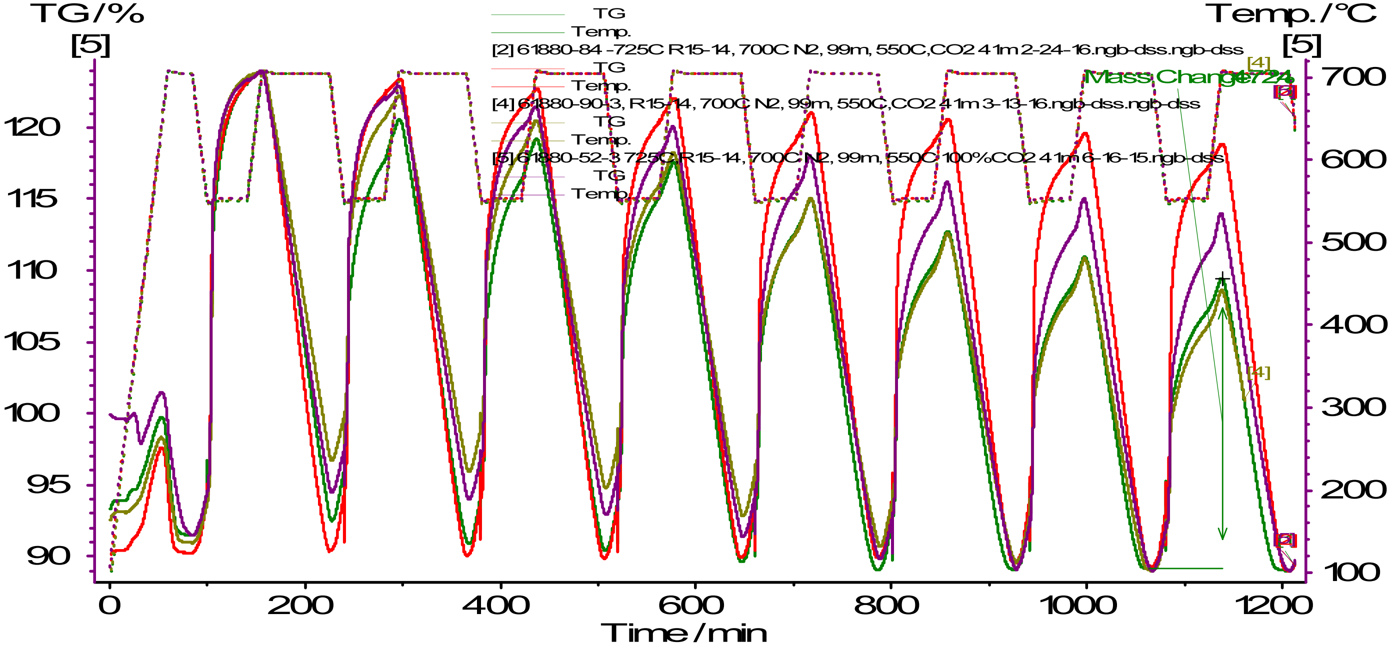
Sorption: 550°C in CO_2

Regeneration: 700°C in N_2

Dolomite added with eutectic carbonate of different melting point (°C):

Purple = 397, Red= 498, Green = 550, Yellow = 600

The eutectic carbonate of melting point slightly lower than the sorption temperature gives the best performance.



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Loading of the CO_2 sorbent powder into monolithic channels

Alternate channels of the monolith are filled with the sorbent fine