

II.F.1 Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions

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- With WSU, develop a fundamental understanding of the impact of the TiO₂ monolith support on SR reaction performance, and an assessment of the impact of sorbents with different promoters on bio-oil reforming (and vice versa).
- Effectively scale up CO₂ sorbent preparation to hundreds of grams scale.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production (from Renewable Liquid Feedstocks) section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) Reformer Capital Costs and Efficiency
- (B) Operations and Maintenance (O&M)

Technical Targets

This project is focused on developing: (1) a nano-composite SR catalyst, (2) a dolomite-based CO₂ sorbent, and (3) a method of integrating in monolithic reactor form, for effective coupled operation in SEHP fashion employing PNNL's novel swing reactor operation concept. The advancements made in this development effort will allow for economic and durable reforming of biomass-derived liquids in the forecourt that achieve the following DOE distributed hydrogen production 2020 targets as they relate to biomass-derived renewable liquids:

- Hydrogen Production Cost: \$2.30/gge (kg H₂)
- Production Equipment Total Capital Investment: \$1.2 million
- Production Energy Efficiency: 75%
- Production Equipment Availability: 97%

FY 2016 Accomplishments

- The K-NiCu-Ce(D)-Al-O [D = Mg or La] metal oxide nano-composite catalyst has been demonstrated as an active and novel catalyst system for the SR of bio-oil with periodic regeneration by combustion.
- TiO₂ monoliths (supplied by CormeTech) loaded with the composite catalyst show exceptionally higher SR activity after certain activation, which is believed to result from the interaction with TiO₂ and the formation of highly active catalytic structures/phases inside the monolith channel walls.

Overall Objectives

- Develop a compact reactor unit for the production of hydrogen from biomass-derived liquids at a high enough efficiency and low enough capital cost to be economically attractive for distributed application, while resulting in lower net greenhouse gas emissions compared to natural gas reforming.
- Develop low-temperature steam reforming (SR) nano-composite catalysts and rapid regeneration methods to address catalyst deactivation challenges.
- Integrate the in situ capture of CO₂ formed during SR to produce a hydrogen-rich stream in one step, and couple catalyst and sorbent in monolithic reactor form.
- Demonstrate the sorption-enhanced hydrogen production (SEHP) swing-reactor concept at 2 kg/day scale.

Fiscal Year (FY) 2016 Objectives

- Optimize the metal oxide composite catalyst and monolith compositions to improve hydrogen selectivity and productivity for bio-oil reforming.
- Understand the impacts of monolith catalyst structures and reaction conditions on bio-oil reforming performance.
- Routinely prepare sets of monolith catalysts for Dason for bio-oil reformation testing.

- The integrated reactor testing unit constructed by Dason Technology has been commissioned and allows bio-oil reforming reaction tests at oil feed rates 10–100 times higher the bench-scale testing units at PNNL and WSU; Dason's new flow distributor design has been successfully demonstrated to distribute bio-oil evenly into the monolith catalyst channels under reaction conditions.
- Bio-oil reforming tests of the monolith catalyst modules at both PNNL and Dason Technology confirm that the monolith channels are not fouled during bio-oil reforming reactions.



INTRODUCTION

Biomass is a renewable resource that is produced over a wide range of territory in the United States. The conversion of bio-mass thermally or thermo-catalytically to bio-oil in centralized fashion presents an attractive potential energy carrier for distributed hydrogen production to support many facets of the economy, but most importantly transportation. However, the unstable nature and chemical characteristics of neat bio-oil presents some unique challenges for hydrogen production from bio-oil relative to conventional hydrocarbon SR processes.

A significant fraction of bio-oil is nonvolatile, and bio-oil is also highly reactive. This combination results in coking and charring as major obstacles to the effective reforming of bio-oil. Additionally, bio-oil contains higher amounts of oxygen and lower amounts of hydrogen than conventional hydrocarbon resources. This dictates that reforming strategies will need to be highly energy efficient in order to be economically viable.

APPROACH

Catalyst deactivation challenges (associated with coking and charring) along with heat transfer challenges are addressed by using a multi-bed reactor system with rapid switching between endothermic SR and exothermic regeneration operation. A monolith reactor provides the basis for multi-scale engineering of a catalyst bed of different functions, including reforming catalyst and CO₂ sorbent, forming a SEHP system. During endothermic SR, CO₂ produced by the reaction is captured by a metal oxide sorbent via an exothermic carbonation reaction that supplies heat to the endothermic SR process. During regeneration, air is introduced to burn off coke and char in exothermic fashion which subsequently provides energy to the carbonate decomposition sorbent regeneration process.

Bio-oil SR is conducted at intermediate temperatures (<700°C) to benefit the long-term stability of the catalyst

and sorbent. The metal oxide nano-composite catalyst is a promising catalyst system for the low-temperature SR process, and consists of, amongst other additions, transition metal oxides, alkaline earth metal and cerium oxide, and aluminum oxide.

RESULTS

Efforts were undertaken to begin to develop an understanding of the micro-structure characteristics of the composite CO₂ sorbents. Scanning electron microscopy imaging indicates that the sorbents have a porous structure with grains or dense crystals less than 1.0 μm. Furthermore, elemental mapping of Mg, Ca, Na and K conducted in concert with scanning electron microscopy (shown in Figure 1 for a spent sorbent, which reflects what is observed in the fresh sorbent) shows uniform distribution of all four elements. The crystal phases of the composite sorbent were also measured by X-ray diffraction; Figure 2 shows X-ray diffraction peaks for the fresh (no CO₂, top) and activated (with CO₂, bottom) sorbents. The major crystal phases are Ca(OH)₂, MgO, CaCO₃, and CaO. The MgO phase remains predominantly unchanged, indicating that its role is as a structural stabilizer under the present set of testing conditions, whereas CaO is predominantly the active phase for CO₂ sorption as indicated by its disappearance and emergence of CaCO₃ in the activated sorbent. These results indicate that uniform elemental distribution, relative particle size, and crystal phases can be used as tools for evaluating sorbent relative activity and potential degradation mechanisms.

Efforts are also underway to increase the production scale of the composite sorbent, and subsequently load the active sorbent into the TiO₂ monolith. Initial trials of sorbent manufacture at increased scale have identified challenges associated with segregation of the Na and K components of the eutectic phase of the sorbent; to form an active eutectic phase, Li, Na and K carbonates need to coexist in durable fashion. These efforts will continue to identify an active and durable eutectic phase of the composite sorbent. A method has been developed for loading CO₂ sorbent into the TiO₂ monolith channels. Reproducibility was demonstrated with nine monolith samples prepared using this technique.

Efforts were also undertaken to develop a consistent method for preparing the reforming catalyst in monolith form. An impregnation method has been developed that shows durable formation of active catalyst in monolith form, and is shown to be superior and more durable than coating with slurry. The monolith catalyst stability was assessed by conducting repeated reforming and regeneration cycles under constant flow conditions. The monolith catalyst prepared showed excellent stability as illustrated by hydrogen productivity performance exceeding the project target value of 0.6 g H₂/h/g cat over 11 cycles. This represents

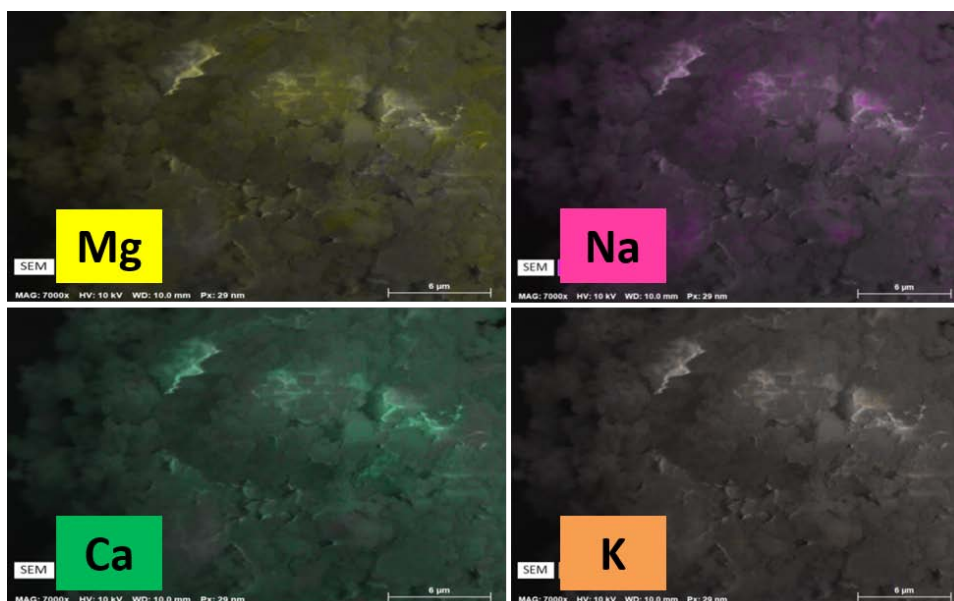


FIGURE 1. Scanning electron microscopy elemental mapping of spent sorbent

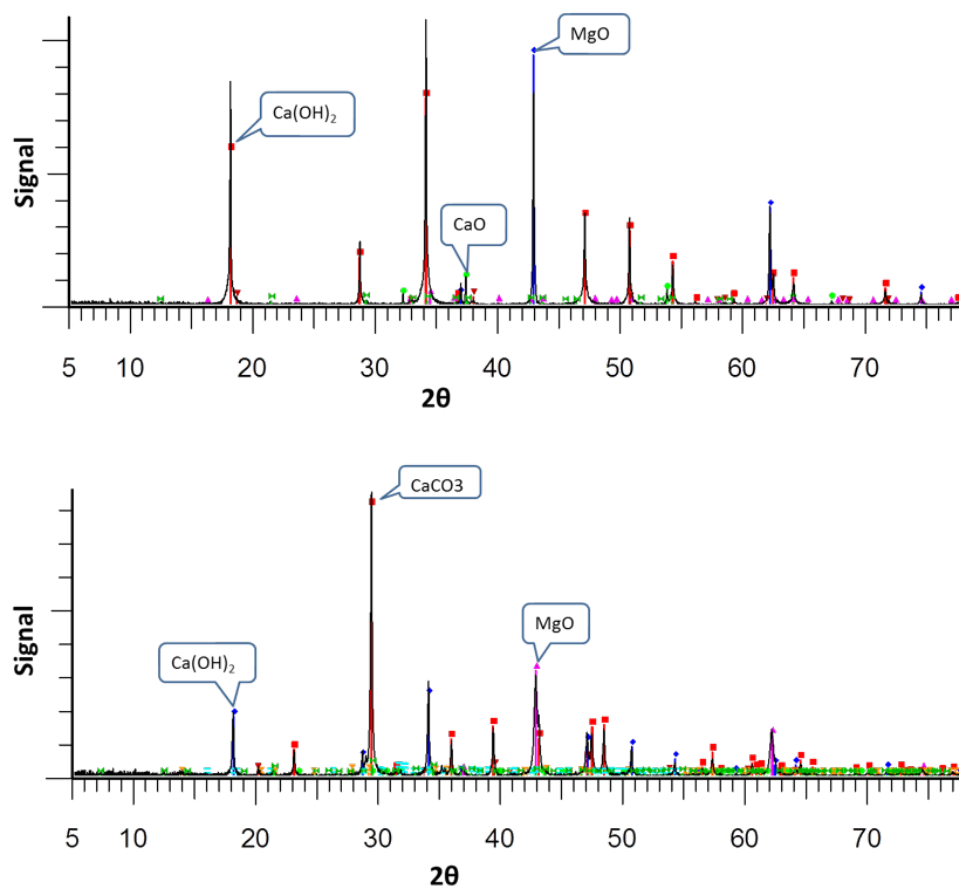


FIGURE 2. X-ray diffraction patterns of dolomite composite sorbent containing 5 wt% eutectic LiNaK-carbonate with (bottom) and without (top) CO_2

advancement in the state-of-the-art with regards to hydrogen productivity from bio-oil SR. It has been discovered that the monolith catalyst activity can be enhanced by conditioning treatment in situ. Figure 3 shows that hydrogen productivity increased by ~10X following activation which was accompanied by significantly improved selectivity. This mechanism will be investigated further in the project. And finally, catalyst performance sensitivity to different feed stream and oil rates were investigated and is shown in Figure 4. The sensitivity of productivity to space velocity is high, indicative of high overall conversion; if conversion is small, the productivity would be close to the rate constant of the reaction and minimally affected by space velocity. Additionally, the SR reaction on the catalyst tested shows

excellent versatility over a wide range of steam to oil ratios, as indicated by Figure 4.

CONCLUSIONS AND FUTURE DIRECTIONS

Efforts will continue to identify an active and durable eutectic phase of the composite sorbent. Preliminary studies have identified negative synergy between CO₂ capture and reforming functionalities. A path forward for integrating CO₂ capture and reforming in concerted fashion will be developed and reduced to practice with the help of Dason Technology. Preliminary improved fundamental understanding of SR catalyst functionality and structure–activity relationship will be developed with the assistance of WSU to inform the path

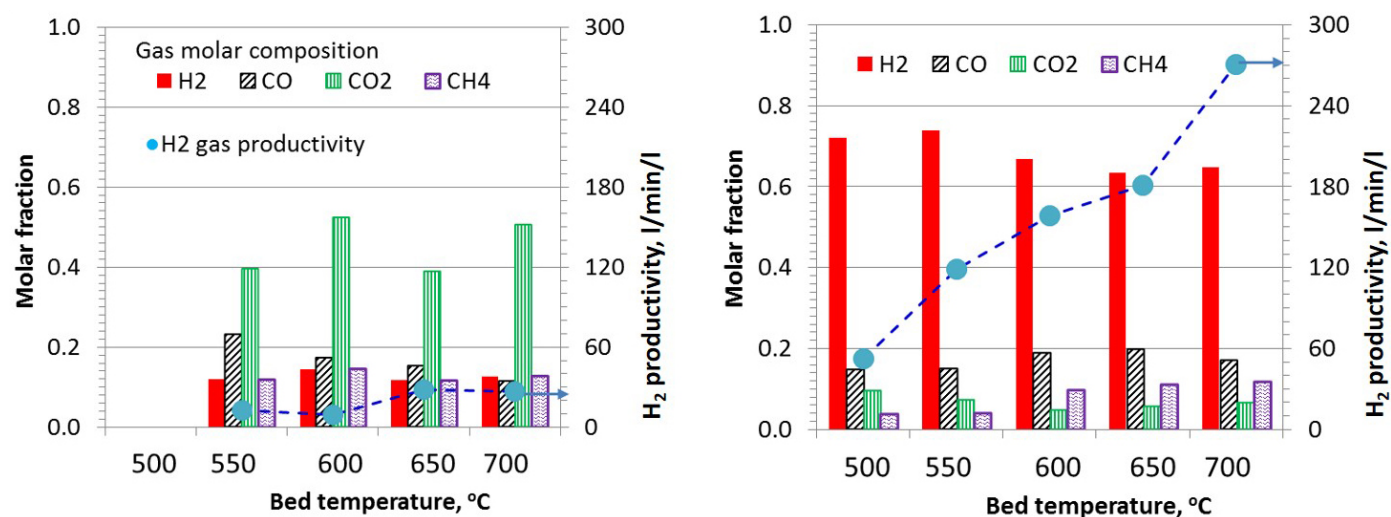
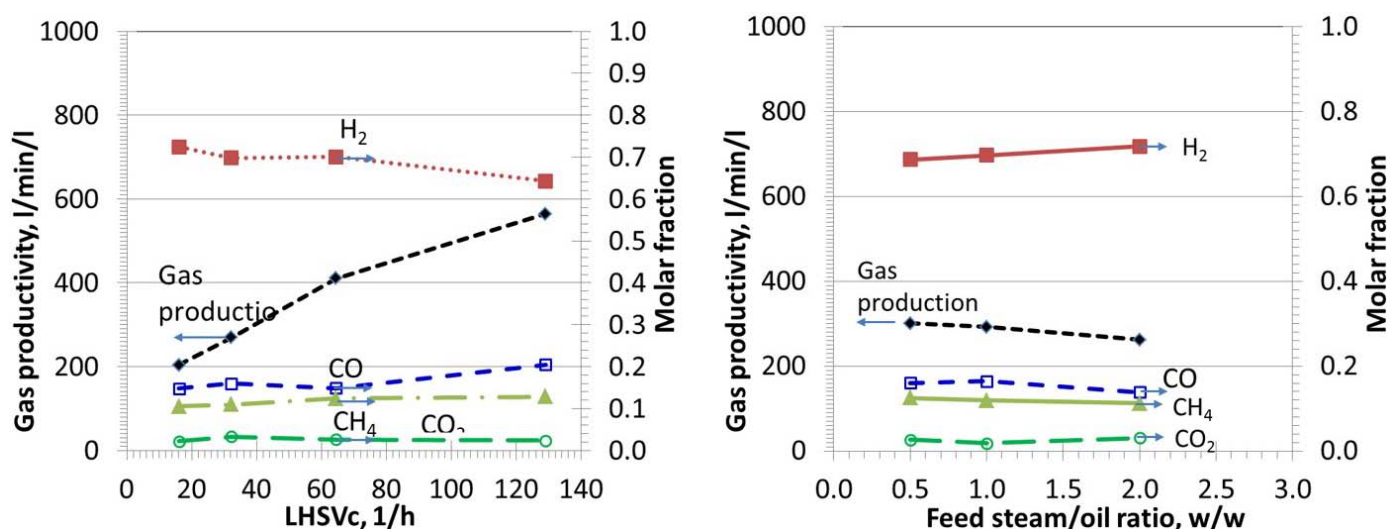


FIGURE 3. Performance of the same K-NiCu-Ce(Mg)-Al-O/TiO₂ monolith catalyst before (left) and after (right) activation



LHSV – Liquid hourly space velocity

FIGURE 4. Impact of feed stream flow and conditions on K-NiCu-Ce(Mg)-Al-O/TiO₂ monolith catalyst performance

forward for final engineering of an active, highly selective, and durable reforming catalyst.

The final phase of the project will be focused on extended demonstration of the integrated monolith reactor system at 2 kg-H₂/d production capacity, 0.10 kg-H₂/kg-bio-oil yield, and 80% overall energy efficiency. The intent is to move the technology to a technology readiness level of 4 or above (i.e., TRL \geq 4).

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. W. Liu, S. Li “A Reactor, CO₂ Sorbent System, and Process of Making H₂ with Simultaneous CO₂ Sorption,” U.S. Patent application #15012791 filed on February 1, 2016.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Wei Liu, Shari Li, Richard Zheng, Paul Armatis, Erika Cutsforth. “Integrating CO₂ Capture with Steam-Reforming Reactions,” Presentation at the AIChE Annual Meeting, Salt Lake City, UT, November 8, 2015.
2. Wei Liu “Reversible Carbonate & CO₂ Reaction System for High-Temperature Thermo-Chemical Energy Storage,” Presentation at the AIChE Annual Meeting, Salt Lake City, UT, November 12, 2015.
3. Wei Liu, Shari Li, Feng Zheng “Enhancing stability and productivity of solid sorbents for CO₂ capture from hot humid gas,” cleared for Ind. Eng. Chem. Res.