

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

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Overall Objectives

- Develop a compact reactor unit that can be readily transported and installed, and quickly turned around for distributed hydrogen production from biomass-derived liquids, as a pathway for reaching the DOE target of <\$4/kg H₂
- Realize the unit-based scale of economy rather than the capacity-based scale of economy
- Develop an integrated, mobile test unit and demonstrate the critical technical performances

Fiscal Year (FY) 2015 Objectives

- Set up research agreements with collaborators
- Conduct process designs of the integrated reactor testing system and install the first version of the unit
- Develop low temperature steam reforming catalysts suitable for rapid reaction/regeneration cyclic operation
- Develop sorbent materials suitable for capturing CO₂ under steam reforming conditions
- Identify preparation methods to load the sorbent and catalyst materials into monolith structures

Technical Barriers

This project addresses the following technical barriers from the 3.1.5 (Distributed Hydrogen Production from Renewable Liquid Feedstocks) section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

- (A) Reformer Capital Cost and Efficiency
- (B) Operations and Maintenance (O&M)
- (C) Biomass Feedstock Issues
- (D) Forecourt Footprint and Storage
- (E) Control and Safety

Technical Targets

The main goal of this project is to develop a hydrogen production technology that enables utilization of low cost bio-derived liquids. Ethanol is valuable for liquid transportation fuel blend. It is clean and mass produced in the United States (U.S.) As shown in Table 1, its current cost is fairly high as a feedstock for hydrogen production. The other bio-derived liquids such as bio-oil are projected of much lower costs. But, there are no proven technologies for hydrogen production from this kind of feedstock. The compact reactor technologies will be developed to substantially lower the feedstock cost without significantly increasing the capital and operation costs.

TABLE 1. Progress towards Meeting Technical Targets for Distributed Bio-Derived Renewable Liquids

Characteristics	Units	2015–high-T ethanol reforming ^a	Present bio-oil reforming approach
Production unit capital cost contribution	\$/kg	0.70	0.93
Feedstock cost contribution	\$/kg	5.10 ^b	2.07 ^c
Production fixed O&M cost contribution	\$/kg	0.10	0.42
Production of other variable O&M cost contribution	\$/kg	0.10	0.37
Hydrogen levelized cost (production)	\$/kg	5.90	3.81

^aValues from Table 3.1.3 in MYRDD plan

^bEthanol cost = \$2.15/gallon

^cBio-oil cost = \$0.219/kg, ref: PNNL-23053, NREL/TP-5100-61178

T - temperature

FY 2015 Accomplishments

- A new CO₂ sorbent material system, made of inexpensive materials, is invented and demonstrated with superior performances for applications to CO₂ capture over a wide range of process conditions, such as 300–700°C. The sorbent shows rapid sorption kinetics, high working capacity and stability in repeated sorption/regeneration cycling tests in the presence of steam. These performance characteristics make it possible to integrate CO₂ capture with steam reforming reaction into one reactor vessel so that the hydrogen production process can be greatly simplified.
- A metal oxide composite catalyst, made of inexpensive materials, is identified to conduct bio-oil reforming reactions at much lower temperatures than what was typically used in the previous studies (600–800°C). Lowering the reforming temperature is beneficial to reducing the reactor vessel cost, increasing the thermal energy efficiency, and prolonging the catalyst lifetime.
- Preparation methods are identified to load the CO₂ sorbent and reforming catalyst materials into monolithic structures for development of compact monolith reactors.
- A once-through, small laboratory-bench reactor system has been built to evaluate sorbent and catalyst materials for respective sorption and reforming processes and to conduct quick tests of new reactor/process concepts.
- Designs for the integrated reactor system are done and major pieces of equipment are acquired to erect the first version of the reactor system, which enables process tests and development at much larger feed rates than the laboratory apparatus.



INTRODUCTION

Biomass is a renewable resource and produced over a wide range of territories in the U.S. Some low cost processes can be used to convert biomass into liquids that are of high energy density and can be readily transported and stored. For example, bio-oils can be produced by pyrolysis and mixed oxygenates can be produced by hydrothermal deconstruction. These are attractive resource for distributed hydrogen production. The produced hydrogen or syngas can be used to generate electricity using fuel cells or gas turbines. Such a distributed power generation capability would help mitigate energy storage issues associated with other renewable energies such as solar and wind. Thus, distributed hydrogen production from biomass-derived feedstock is important to long term energy and environmental sustainability in the U.S.

However, there are no technologies available for economic conversion of the bio-liquids into hydrogen. Because of its complex compositions, almost all the catalysts reported so far for steam reforming of bio-oil showed rapid deactivation or limited lifetime. Even if the catalyst deactivation issue can be addressed, the conventional hydrogen production process involves a complex process diagram that can make the hydrogen production cost-prohibitive because of small process capacity for distributed production.

APPROACH

This project pursues several innovative approaches toward addressing critical problems associated with practical process development of distributed bio-oil reforming for H₂ production. First, low temperature reforming catalysts and rapid catalyst regeneration methods will be developed to address the catalyst deactivation issue. Second, novel sorbents will be developed for in situ capture of CO₂ produced during reforming to produce a H₂-rich stream in one step, eliminating the need for separate water-gas shift and reducing the hydrogen purification unit size. Third, monolithic modular-type reactors will be developed to minimize mass and heat transfer so that the reaction and regeneration (both the catalyst and sorbent) can be conducted via rapid cycling (in the order of minutes).

A project team of combinatory expertise and experiences is formed to achieve the project objectives, which include PNNL, Washington State University, Dason Technology, and Cormetech. The project team undertakes five major tasks, (i) monolith reactor technology development, (ii) model analysis and process design, (iii) development of monolith supports, (iv) catalyst characterization and development, and (v) reactor system tests and process development. Three major milestones will be achieved. The first-year milestone is about material innovations. The steam reforming catalyst and in situ CO₂ sorbent are developed that work effectively under the same reaction (~500°C) and regeneration (~700°C) conditions. Both high productivity and stability for rapid cyclic operation are the important performance criteria. The second-year milestone is mainly about monolithic reactor innovations. The optimum CO₂ sorbent and reforming catalyst materials will be integrated into monolith structures and demonstrated for one-step production of pure H₂. The sorption and reforming reaction processes need to be synchronized in one reactor vessel to achieve cyclic stability and high H₂ productivity. The third-year milestone is mainly about process innovations. The materials and monolith reactors will be demonstrated on an integrated reactor apparatus for long time stability, production >99% pure H₂, and ≥10 wt% H₂ yield at H₂ production capacity of about 2 kg/d.

RESULTS

To simplify the hydrogen production process (Figure 1), we want to integrate CO₂ sorption with steam reforming reaction into one reactor vessel. In this way, CO₂ is captured on metal oxide sorbents upon its formation from the reforming reaction so that pure or enriched H₂ gas is produced in one process step. The heat released from exothermic carbonation reactions can compensate the endothermic reforming reaction. Once the sorbent is saturated and/or the catalyst is deactivated, the reactor is switched to regeneration by air. During the regeneration, the endothermic carbonate decomposition can absorb the heat released from catalyst coke combustion. The regeneration is conducted at higher temperatures than the reforming reaction. Thus, the reactor provides thermal mass for subsequent reforming reaction. To realize this process design concept, we need to have a CO₂ sorbent that can work effectively under the reforming reaction. Both sorbent and catalyst need to be quickly regenerated by air calcination.

The literature reports and in-house studies [1-3] on CO₂ capture over a temperature range of 200–800°C have been reviewed. No existing sorbent materials were found suitable for the present application in terms of stability, kinetics, and capacity. Thus, a sorbent design model was proposed to guide preparation of a number of new sorbents. The sorbent materials were screened on thermogravimetric analyzer apparatus [4]. The promising candidates have been tested on a packed bed [5-6]. A novel sorbent system

is found that provides high CO₂ working capacity over a range of CO₂ partial pressure, temperature, and steam partial pressure, which cover the likely operation windows of the bio-oil reforming. Rapid CO₂ sorption kinetics was observed under all the sorption conditions tested. As illustrated by the breakthrough curves in Figure 2, >95% CO₂ loading is completed within breakthrough time of 2 min. With dry feed gas (H₂/CO₂ = 2:1), the CO₂ loading tended to decrease with sorption/regeneration cycling. With wet feed gas of H₂O/dry gas = 1.0, the breakthrough curves for four sorption cycles completely overlapped. The results clearly show the positive effect of steam on the sorbent stability. The sorbent appears to be more stable in the presence of steam. Such performance characteristic is highly desirable for CO₂ capture applications under reforming conditions and for most practical applications as well, since the presence of steam is ubiquitous. The sorbent stability was assessed by conducting the sorption tests of the same bed for many cycles between 500°C sorption and 700°C regeneration. The CO₂ loading was stabilized at 19 wt% in the 17 cyclic testing. The rapid sorption kinetics and high working capacity are necessary to develop a compact reactor of high productivity.

The bio-oil reforming catalysis literature was reviewed and analyzed. No existing catalyst materials [7] were demonstrated to work under the presently desired conditions. The temperatures used in most vapor phase bio-oil reforming studies are higher than what is targeted for the present application (400–500°C). Lowering the reforming temperature is desired from points of views of achieving high

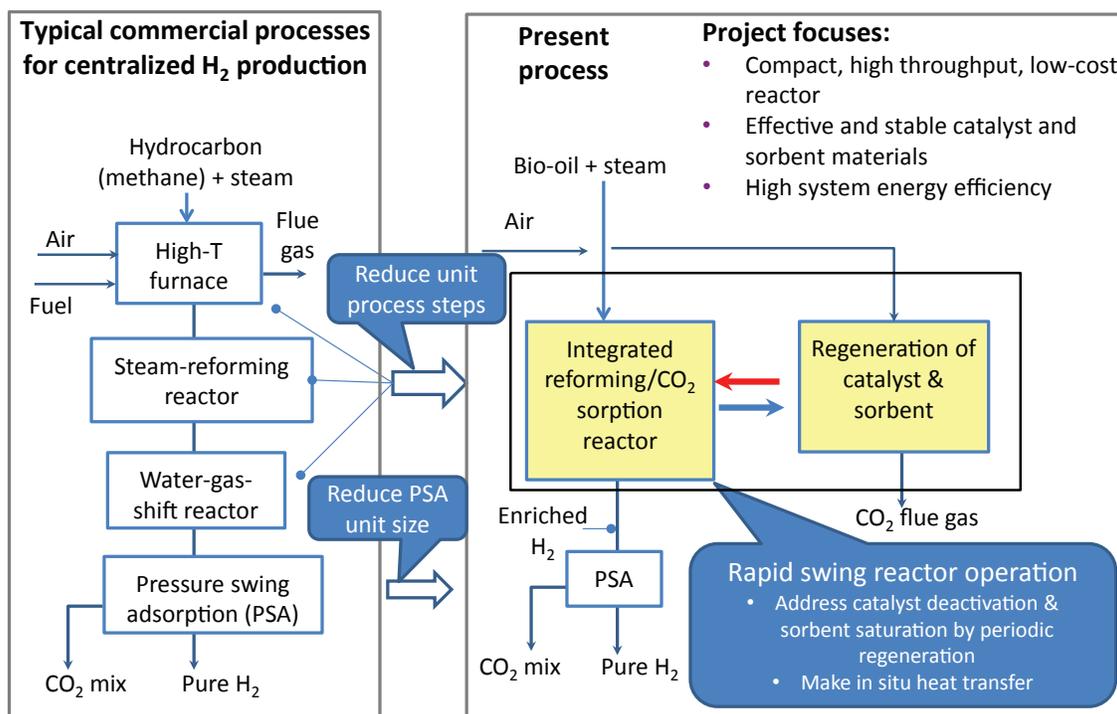


FIGURE 1. Process flow diagram of present hydrogen production technologies

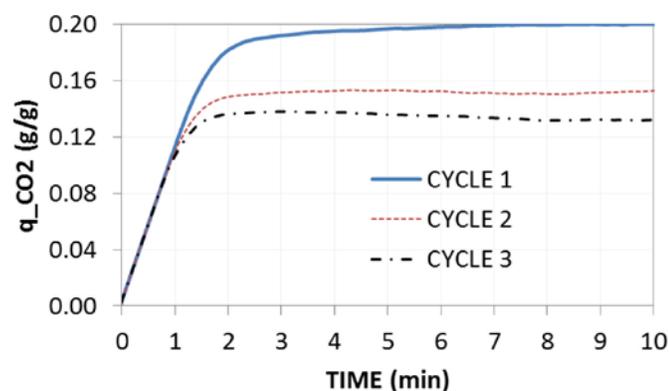
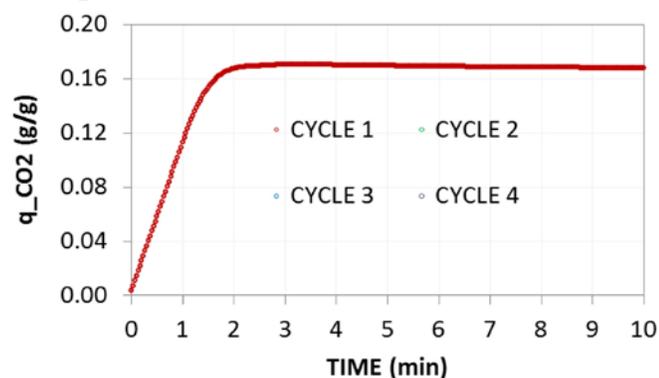
(a) $H_2O/dry\ gas = 0$ (b) $H_2O/dry\ gas = 1.0$

FIGURE 2. CO_2 sorption breakthrough curves of the packed sorbent bed with dry feed gas (a) and with wet feed gas (b) (sorption conditions: $500^\circ C$, 1.0 bar, gas hourly space velocity = 6,000 v/v/h based on standard dry gas flow rate, dry gas of H_2/CO_2 molar ratio = 2/1, wet gas of $H_2O/dry\ gas$ molar ratio = 1/1; regeneration: $700^\circ C$, 1.0 bar, air purge)

thermal energy efficiency, reducing the reactor vessel cost, and prolonging catalyst lifetime. Almost all the catalysts deactivated or showed limited lifetime. Coking is the leading cause of catalyst deactivation. The information about catalyst regeneration and long term stability is missing. Thus, we conceived a new catalyst design model and formulated a number of new catalyst compositions, including zeolite-supported ones, zeolite/oxide composites, and metal oxide nano-composites [4]. The catalyst materials were screened by reforming reaction tests on a micro-reactor apparatus with phenol as a model feed. Preliminary tests of a few metal oxide composite catalysts were conducted with actual bio-oil reforming [5]. Both the model reaction and bio-oil reaction tests suggest that the M-Ce(D)-Al-O nano-composite is an active catalyst system for low temperature reforming reactions ($400\text{--}500^\circ C$), where M = transition metal and D = dopant. Figure 3 shows that 70% conversion of phenol to gases and more than 80% of theoretical hydrogen yield was obtained with this composite catalyst at a high space velocity. This catalyst can be regenerated by air calcination. Further testing of this catalyst system with simulated bio-

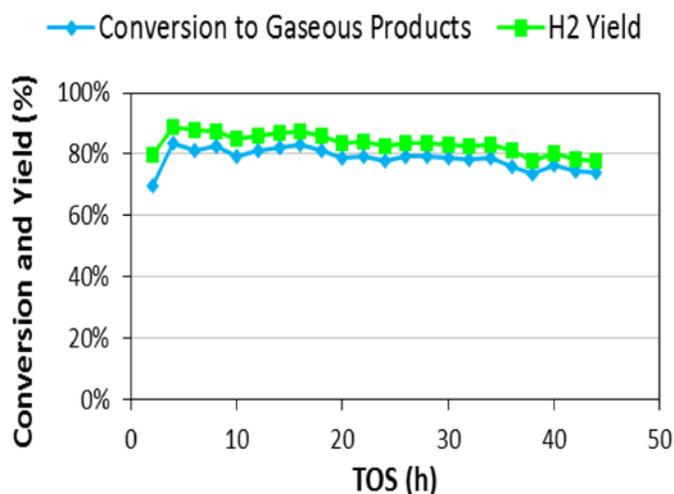
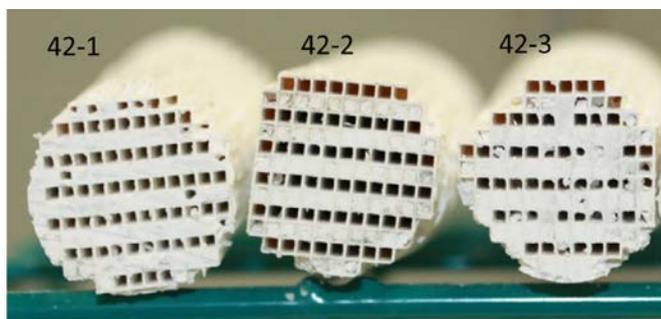
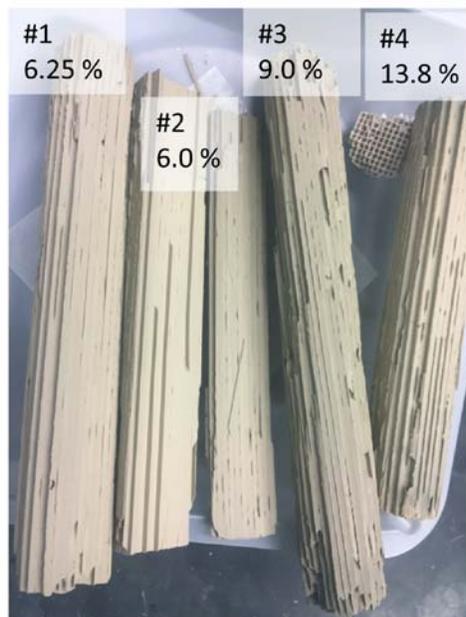


FIGURE 3. Variations of conversion and H_2 yield with time on stream (TOS) for steam reforming of phenol on a M-Ce(D)-Al-O oxide composite catalyst (reaction condition: catalyst loading = 600 mg, temperature = $500^\circ C$, steam/carbon ratio = 3.8, space velocity = $13,000\ h^{-1}$)

oil is ongoing. We are planning to start with a preliminary mixture of 1:1:1:1 molar ratio of ethanol, acetic acid, acetone, and phenol and observe the effects of different reaction parameters such as temperature, partial pressure, and steam/carbon ratio. Then, we plan to add compounds into the feed which are more difficult to steam reform, such as glucose and furfural, in order to simulate more realistic bio-oil. After showing 80% H_2 yield, we will identify reaction conditions to achieve the project milestone of 0.6 kg $H_2/h/kg$. Catalyst productivity and stability will be demonstrated with more than 10 cycles of reforming/regeneration testing.

The monolith bed structures are pursued to develop a compact reactor for rapid reaction/regeneration swing operation. The monolithic structure enables the sorbent material to be fixed adjacent to the reforming reaction site so that rapid mass and heat transfer between the sorbent and reforming catalyst can be obtained. The straight flow channels of the monolith minimize the dead space and pressure drop so that the process streams can come in and out freely. In the first year, preparation methods for separate loading of sorbent and catalyst loading are identified. TiO_2 monoliths are used. For the sorbent loading, a sorbent material is prepared into slurry that is used to fill the alternate channels of the TiO_2 monolith. The results are illustrated with three monolith samples in Figure 4a. Almost all the channels in alternate rows are filled up for first and second samples. The results show the feasibility to load the sorbent material into the small monolith channels ($\sim 0.9\ mm$). However, the channel filling may not occur uniformly if the preparation procedures and conditions are not controlled well. As illustrated by the third sample, channel filling appeared randomly. The root causes for poor channel filling have been identified. We are in the process to standardize the channel

(a) Channel filling with CO₂ sorbent

(b) Channel wall catalyzed with reforming catalyst

FIGURE 4. Monoliths loaded with CO₂ sorbent (a) and reforming catalyst (b)

filling process and produce consistent samples. For catalyst loading into the monolith structure, a simple impregnation method is identified. The salt solution containing the metal precursors is prepared and used to impregnate the pores on the channel wall. After the impregnation, the monolith is dried and calcined so that the metal precursor is converted into respective oxides and fixed on the channel wall. Figure 4b shows four monoliths of different loading levels of the M-Ce(D)-Al-O composite catalyst. The first and second samples were impregnated once, while the third and fourth monoliths were impregnated two and three times respectively. The catalyst loading increased with the times of impregnation. All the monoliths appear uniform in color, indicating uniformity of the catalyst distribution. The second monolith sample was cut open to reveal uniformity inside the channels and along the monolith length. Thus, an active reforming catalyst can be loaded into the monolith structure. The amount of catalyst loading required for actual reforming

reactions will be determined by the reaction tests. If it is necessary to have high catalyst loading, channel coating may be used.

We found that it is very difficult to make uniform bio-oil flow distribution on the small-bench reactor apparatus because of the low flow rate and high oil viscosity. It is necessary to build a reactor system with adequate flow rates and length to conduct monolith reactor tests for bio-oil reforming reaction and CO₂ capture. Thus, an integrated reactor system has been designed. Major pieces of equipment, including reactor tubes and furnaces, steam generator and super heater, and flow distributor, have been acquired. The control system has also been designed. It is planned that first version of the reactor apparatus will be erected and debugged by end of FY 2015. The reactor provides 1 m x 2 cm reactor tubes that allow sorbent and catalyst loading in the order of 100 g levels with 0.5 kg/d hydrogen production capacity. The final version of the reactor system will be refined in the third year to have 5 cm reactor tubes for loading of 1.0 kg level of catalyst and sorbent materials with 2.5 kg/d of hydrogen production capacity.

CONCLUSIONS AND FUTURE DIRECTIONS

The following are main conclusions drawn from the project work done so far:

- Demonstrated a new CO₂ sorbent material system with rapid kinetics, high working capacity, and good stability for applications to capturing CO₂ under the steam reforming conditions.
- Identified a M-Ce(D)-Al-O metal oxide composite catalyst system to conduct steam reforming reactions at moderate temperatures (400–500°C) with high productivity. The catalyst can be regenerated by air calcination. Catalyst coking is very significant for bio-oil reforming. The catalyst regeneration by air calcination is essential.
- Identified preparation methods to fill up alternate monolith channels with the sorbent material and to fix the reforming catalyst inside the porous channel wall.
- Observed that the low flow rate of the small-scale reactor and the strong propensity of the bio-oil to charring/coking make uniform bio-oil flow distribution very difficult. It is critical to develop an effective flow distributor and necessary to build a reactor system with sufficiently high bio-oil feed rates.

The following are important future approaches toward making significant technology progress:

- Demonstrate targeted productivity and stability of the promising reforming catalyst through >10 rapid reaction/regeneration cycles with simulated bio-oil

- Validate the reforming catalyst performances with bio-oil reforming
- Scale up promising CO₂ sorbent and reforming catalyst preparation to 100 g level
- Deliver 2 cm diameter monolith samples loaded with the CO₂ sorbent and reforming catalysts for respective CO₂ sorption and reforming reaction tests in a monolith reactor tube
- Identify an effective bio-oil flow distributor for reaction tests on the integrated reactor apparatus
- Demonstrate the CO₂ sorption and reforming reaction performances in the monolith reactor with performances comparable or better than what are achieved on the small reactor apparatus
- Prepare 2 cm diameter monolith samples with both the CO₂ sorbent and reforming catalyst being incorporated
- Demonstrate the performances of monolith reactors for production of pure H₂ with in situ CO₂ capture, achieving the targeted productivity and stability
- Scale up the sorbent and catalyst preparation to 1 kg level
- Scale up the sorbent and catalyst loading into 5 cm diameter monolith modules
- Upgrade the integrated reactor system with 5 cm diameter reactors, bio-oil recycle, and post hydrogen purification
- Demonstrate the integrated reactor system performances for production of 2.5 kg H₂/d with >99% pure H₂, >80% hydrogen yield, and complete bio-oil conversion
- Conduct systematic evaluation of different bio-derived liquids on the reaction performances
- Conduct process designs and H2A analysis for 1,500 kg/d commercial-scale H₂ production units based on the research results achieved from this project
- Develop designs and plans for follow up field demonstration of the integrated reactor skid

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. W. Liu “An integrated reactor unit for H₂ production,” provisional patent application (IP ID No. 30726-E).

FY 2015 PUBLICATIONS/PRESENTATIONS

1. W. Liu, “Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions,” presentation given at DOE/EERE HPTT Project Team Kick-off Meeting, NREL Golden, CO, August 25, 2014.
2. Wei Liu, Richard Zheng, Shari Li, Ken Rappé, David King, “Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions,” HPTT webinar, March 3, 2015.
3. W. Liu, “Monolithic Piston-Type Reactor for Hydrogen Production through Rapid Swing of Reforming/Combustion Reactions,” presentation at AMR review, Washington DC., June 11, 2015.

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