

## A Breakthrough Process for the Production of Hydrogen

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The ability to use hydrogen as an energy source for consumers requires technology to produce and distribute the hydrogen cost-effectively and efficiently. Though achieved in large-scale industrial applications, e.g., in the petrochemical industry, cost-effective hydrogen manufacture and distribution has not been demonstrated convincingly for mobile and small-scale distributed production. In this paper we present a novel method of hydrogen production - suitable for mobile, small-scale, and also large-scale manufacture - that can potentially overcome many of the current performance issues in hydrogen production. We show how the system can be used for an on-board system integrated within a fuel cell vehicle, and in larger scale.

The Pressure Swing Reformer (PSR) is a steam reforming process yielding high-pressure, undiluted syngas using low-pressure air at very high efficiency and with the compactness of an autothermal reformer. PSR is a cyclic, reverse-flow reactor process that alternates a low-pressure combustion step that heats the reforming catalyst bed with a high-pressure reforming step that cools the bed. During this cycle the center of the catalyst bed remains quite hot - the peak temperature can be 1000-1200°C - but the inlet and exit to the reactor, as well as the metal reactor wall remain relatively cool - typically below 400°C.

The fundamental element of the PSR is a packed bed heat exchanger, which is described in reference to Figure 1. In a packed bed heat exchanger, the heat capacity of a bed of solids is used to change the temperature of a gas passing through the bed. In the example of Figure 1, the bed is initially at a cool temperature (red line), and the gas is initially at a higher temperature (blue line). Gas is cooled as it passes through the exchanger, transferring heat to the packing material, and heating up of the bed. The shape of the temperature profiles depends on the rate of heat transfer. When heat transfer is relatively slow, shallow profiles shown in Figure 1a are observed. When heat transfer rate is relatively fast, the sharp gradient shown in Figure 1b is observed. This gradient moves across the bed as heat transfer continues, until breakthrough occurs and the outlet temperature begins to rise.

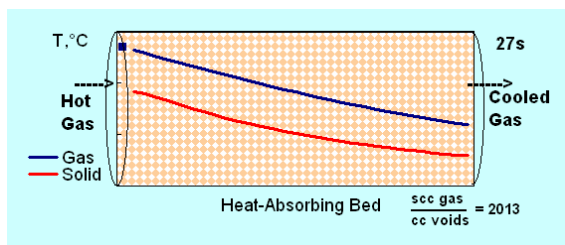


Figure 1a

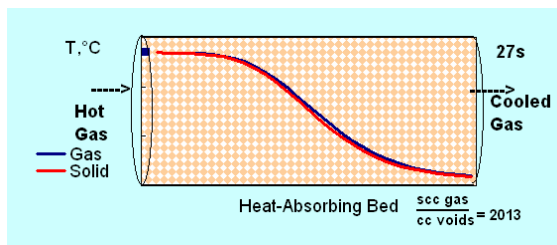


Figure 1b

An important feature of packed bed heat exchangers is that there is a large difference between the heat capacity of the gases and the solids. This means that, compared to the void volume in the bed, there is a large volume of gas that moves through the bed. For the profiles of Figure 1, the volume of gas that has passed through bed is over 2000 times the bed void volume. In PSR, the bed is designed to provide high heat transfer coefficients, so that the temperature profiles behave as in Figure 1b.

Figure 2 demonstrates the use of the packed bed heat exchanger in PSR. Two of these exchangers are placed back to back, with the hot ends together, as shown in Figure 2a. The left bed is roughly twice the size of the right, and it includes reforming catalyst applied to the heat transfer solids. During the regeneration phase of PSR, shown in Figure 2b, air and fuel flow from right to left. Combustion occurs near the interface between the two beds, and the hot fluegas travels through the reforming bed creating a temperature wave and heating the catalyst bed. During the reforming phase, shown in Figure 2c, hydrocarbon and steam flow from left to right. The feed is converted to syngas by the catalyst in the bed, with the sensible and reaction heat being drawn from the bed. Hot syngas leaves the reforming bed and is cooled in the non-catalytic bed on the right, depositing its sensible heat in that bed.

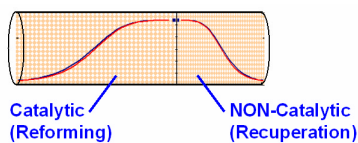


Figure 2a

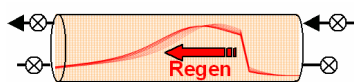


Figure 2b

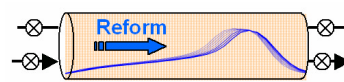


Figure 2c

Overall, this scheme results in a "heat bubble" within the bed system. During regeneration, air (and regeneration fuel) enter at a relatively cool temperature, are heated by the recuperator, then combust to fluegas near the interface of the two beds. This heat generation expands the bubble, and the fluegas is finally cooled by the heat transfer properties of the reform bed such that fluegas leaves at a relatively cool temperature. Similarly, reform feed enters at a relatively cool temperature, picks up heat and reforms with a relatively high final temperature, and then the product syngas deposits its heat into the recuperator packing before leaving at a relatively low temperature.

This reactor system is one example of a broader class of reactors called "reverse flow reactors" that have been a topic of recent academic interest (Boreskov & Matros, Kolios et al.). PSR also bears a strong resemblance to "regenerative cyclic reforming", which has been known for the better part of the 20th century. For example, Earl Riblett of the M.W. Kellogg company patented, in 1940, reverse-flow cyclic process for reforming methane with  $\text{CO}_2$ , using catalyst and checker-brick for heat recuperation. In the early 1980's, Richard Sederquist of United Technologies Corporation patented an updated cyclic reformer as used to provide feed to a fuel cell. Historic cyclic reforming processes typically operate at  $C_1$  space velocity near about  $100 \text{ hr}^{-1}$  and with the reform step at approximately ambient pressure. By  $C_1$  space velocity ( $C_1\text{GHSV}$ ) we mean the space velocity of carbon (as if it were a gaseous species), during reforming, and considering the entire reactor bed volume.

We have made two key advances in this technology. First, we have added the concept of a pressure swing, wherein the bed is operated at substantially higher pressure during the reforming step than during the regeneration step. This pressure swing is accomplished by pressurizing the bed with reform feed prior to opening the reform gas outlet. Second, we have identified key chemical engineering features of the bed that enable the technology to be operated at higher space velocity. Most important is to increase the bed heat transfer coefficient so that the heat required for reforming can be transferred in the requisite amount of time while keeping the gas/solid temperature difference small, and thus the temperature gradient sharp.

### Computer Simulation

The physics and chemistry of Pressure Swing Reforming have been programmed into a numerical simulation of the process. The model includes reforming kinetics (Xu and Froment for methane), heat transfer, pressure drop, axial conduction, and the relevant gas and solid properties. The computational approach is to divide the PSR bed into 30 cells, each representing 1/30<sup>th</sup> of the bed, to treat each cell as a perfectly stirred reactor, and to march the simulation forward in time. Figure 3 shows predicted temperature profiles at several key times in the simulated PSR cycle.

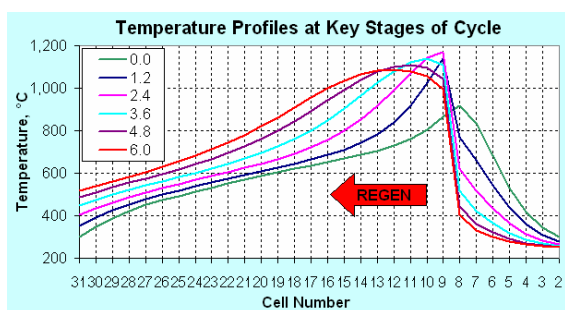


Figure 3a

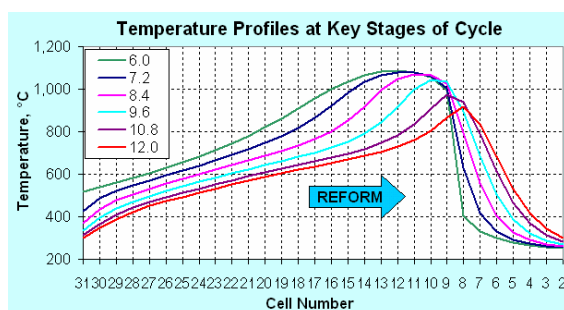


Figure 3b

This simulation is for methane reforming at steam/carbon 1.5 and 8000 hr<sup>-1</sup> C<sub>1</sub>GHSV in a 12 second cycle, with feed temperatures of 250°C and with reforming pressure at 10 atm and regeneration at 1 atm. Regeneration fuel is a separator purge stream comprised mostly of CO and H<sub>2</sub>, but also containing methane and diluents such as CO<sub>2</sub>. The bed material is a 1200 cells/inch<sup>2</sup> honeycomb monolith with 7-mil wall thickness. This simulation predicts 97% methane conversion and 92.6% recovery of feed and fuel heat of combustion ( $\Delta$ H<sub>C</sub>) as syngas heat of combustion. Exiting syngas (right side, Figure 3b) is at an average temperature of 269°C, while exiting fluegas (left side, Figure 3a) is at an average temperature of 443°C.

### Process Consequences of PSR

PSR avoids the critical heat-transfer issues of conventional steam reforming by performing heat transfer internal to the reactor within the catalyst bed. As in conventional, large-scale steam reforming, the high-pressure product enables high-purity separation systems such as pressure-swing adsorption or membranes, resulting in a high-purity hydrogen product. However, PSR accomplishes this in a manner that improves efficiency and enables hydrogen production at smaller scale. PSR would typically be utilized as shown in Figure 4:

Two or more PSR beds are combined with appropriate valves to achieve continuous flow of feeds and products. Syngas can be shifted to adjust  $H_2$ ,  $CO$ , and  $CO_2$  composition, and then separated into product and off-gas streams. Typically, the off-gas would be used as at least part of the fuel for PSR regeneration. The choice of separation is based on the intended application. If high-pressure syngas is desired (i.e. for Fischer-Tropsch or Methanol synthesis) then a hydrogen-permeating membrane might be used to reduce the  $H_2$  content of the syngas. If high pressure hydrogen is desired (i.e. for refinery use), then pressure swing adsorption (PSA) would be a preferred separation. If the object is hydrogen for low-pressure utilization (i.e. for fuel cell consumption), then either PSA or membrane could be applicable.

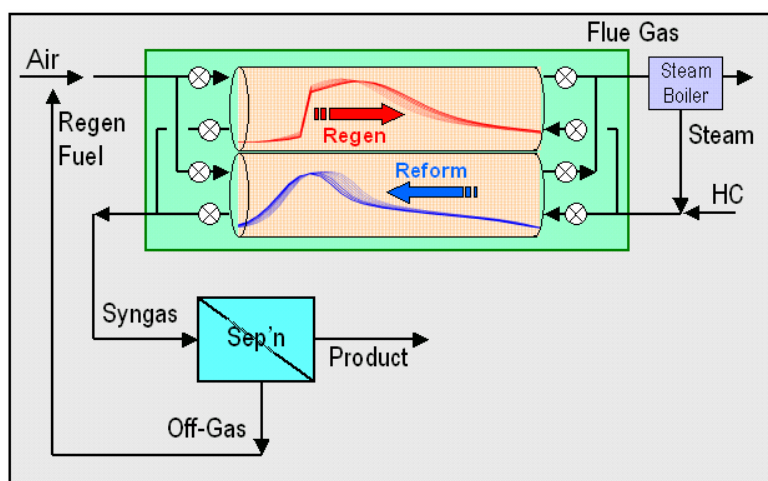


Figure 4

Because of the internal heat exchange that occurs in PSR, the process releases very little excess heat. Exiting syngas is at temperatures appropriate for further processing in high temperature shift, and exiting fluegas is at temperatures just about right for production of the steam needed for reforming. In conventional steam reforming, only about 70% of the  $\Delta H_C$  of the feed and fuel are recovered as hydrogen, with another 10-15% appearing as exported steam. But processes based on PSR recover over 85-90% of feed  $\Delta H_C$  into the hydrogen product, resulting in significant improvement in the economics of the process.

The cool inlet and outlet temperatures, combined with heat transfer based on catalyst heat capacity, removes metal components from regions of high temperature. The temperature of reforming is not limited by the ability to transfer heat through metal walls that must also serve as pressure-containing barriers at the temperature of reforming. This allows operation at thermodynamically desired high temperature for syngas generation, without paying penalties in materials of construction or in wasted heat.

The "pressure swing" is critical to the economics for many applications. For example, in a fuel cell vehicle, ample air is available for the regeneration step at the pressure of the fuel cell cathode system. But this air is available only at 1-3 atmospheres, and there can be a substantial economic debit for higher-pressure air. In contrast, hydrogen is most valuable if provided at higher pressure. Although the fuel cell itself does not need high-pressure hydrogen, it does need high purity hydrogen. The most economic, efficient, and rapid-starting approaches to high-purity hydrogen take advantage of syngas at pressure to effect a separation that provides the purity.

In summary, PSR achieves high efficiency because of the internal heat transfer and high recovery of stream enthalpy. PSR achieves attractive economics because it eliminates furnaces and high temperature metal parts (relative to steam reforming) and eliminates air separation (relative to autothermal reforming). PSR enables high space velocity, highly compact reactors, because the heat required for reforming is available in-situ on the catalyst. PSR enables liquid feed reforming because the cyclic regeneration removes carbon deposits.

### Experimental Validation

Pressure Swing Reforming is being experimentally explored in two bench-scale units at ExxonMobil. One unit is a single-reactor system designed for methane feed. The second unit is a dual-reactor system designed for liquid feed. A photo of the methane unit and diagram of one internal configuration is shown in Figure 5.

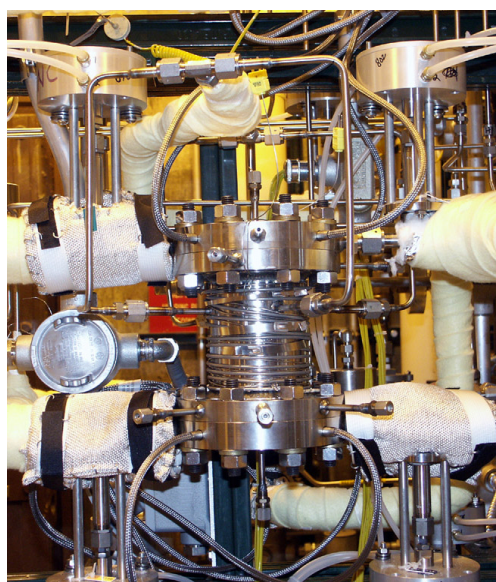


Figure 5a

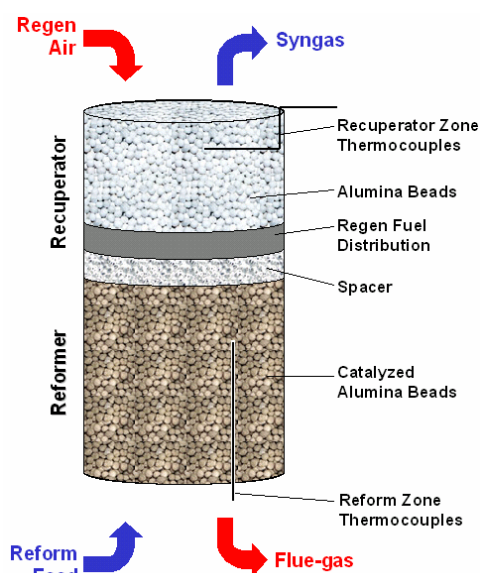


Figure 5b

In the methane unit, the beds are configured as cylinders with vertical axis. The reforming zone is on the bottom, with up-flow reforming. The unit is configured to operate with either monolithic catalyst or with particulate catalysts. The difference is only in how the thermocouples enter the reactor. Packed beds provide more flexibility in testing support materials, while honeycomb monoliths are preferred for reducing pressure drop. Several experiments include a regeneration fuel distributor located near the end of the recuperator to set the location of combustion during regeneration.

Temperature profiles from experimental operation of the methane pressure swing reformer are shown in Figure 6. Reactor locations for this 30-second cycle have been translated to the same distance scale as the simulation. The data are more granular because there are fewer thermocouples in the reactor than there are cells in the simulation. In addition, the experimental recuperator is a little longer than the particular model simulation shown in Figure 3. Nonetheless, the profiles bear a strong resemblance to the model prediction.

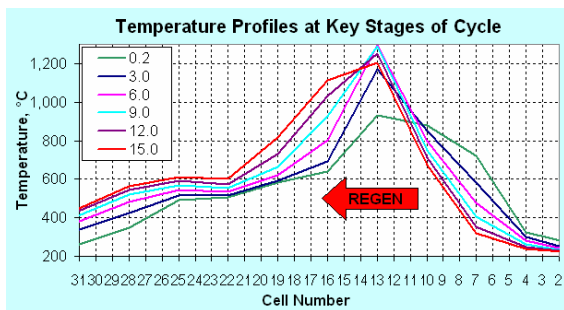


Figure 6a

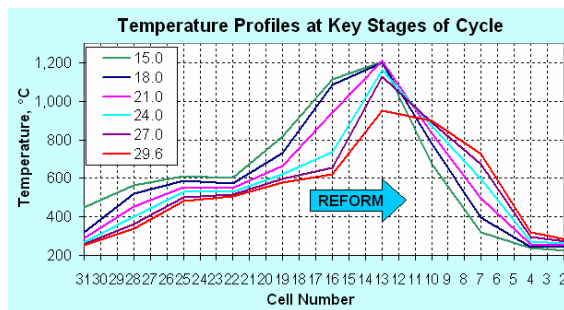


Figure 6b

The products are characterized by mass spectrometry for transient observation of products, and by gas chromatography for more quantitative analysis. When sampling frequency is properly accounted for, the MS results agree well with GC results. For selected experiments, the computer simulation has been operated at conditions matching the experiment. Table 1 compares experiment to model for one such experiment.

**Table 1**

Product:	Experiment	Model
CO <sub>2</sub>	4.2%	5.3%
CH <sub>4</sub>	0.7%	0.7%
CO	21.1%	18.0%
H <sub>2</sub>	74.1%	76.0%
Conversion	97.3%	97.1%
$\Delta H_c$ Recovery	89.2%	89.3%

When the simulation is run at conditions matching the experiment, similar yields are obtained. Differences in water gas shift are not surprising, because the model and experiment have subtle differences in both kinetics and temperature. The agreement in conversion and recovery of  $\Delta H_c$  are more important, because they address the heat balancing properties of the system.  $\Delta H_c$  recovery is ~3% lower here than in the simulation of Figure 3, partly due to heat losses through the reactor wall (about 1%) and partly due to higher outlet temperatures (about 2%). Most important is that these facets are reflected in model performance when the model is run at experimental conditions. When the heat balance is properly accounted for, the conversion follows, because the reactor has no place to put heat except into feed conversion.

Initial runs using typical, noble metal based steam reforming catalysts demonstrated high conversion (>95%) with reasonable (<1200°C) maximum temperatures. We have yet to have a run terminated due to catalyst deactivation. We have demonstrated many thousands of cycles on several different catalysts, including packed bed and honeycomb formulations. We have run with pressure swings up to about 100 psi (difference between reform and regen).

### Considerations for Fuel Cell Vehicles

When PSR is utilized to turn gasoline into hydrogen on a fuel cell vehicle, as described in Figure 7, there are several particular advantages. The material balance is ideally suited, in that

PSR makes no excess steam and provides a home for the separation off-gas and fuel cell purge. Compared to conventional schemes, there is a great reduction in metal heat exchange surface. PSR also saves weight and precious metals by enabling separations to replace downstream CO cleanup steps (low temperature shift and preferential oxidation). Compared to steam reforming, PSR saves weight and expensive alloys in high-temperature heat transfer tubes (or channels).

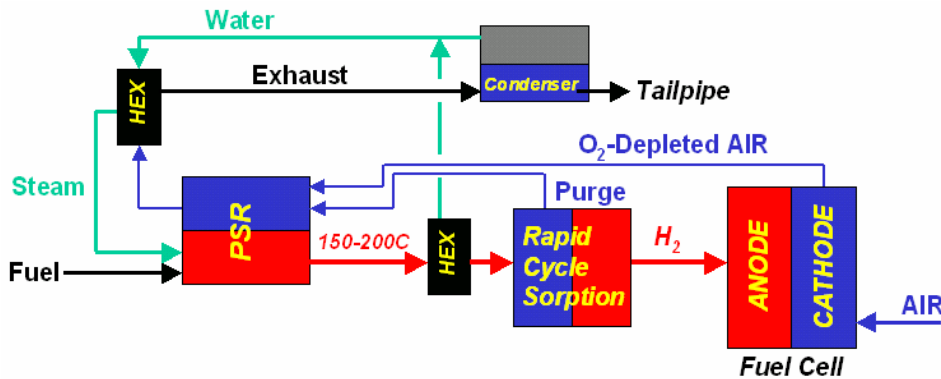


Figure 7

Just as important, PSR is a fundamentally transient system. There are only minor differences between the temperature profiles at turndown and full power. Changing power level only requires cycle times to change in response to temperature profile position. Otherwise, the reform and regen rates can change power almost instantaneously. Furthermore, the only part of the system that needs to be hot to operate is the PSR bed itself, which can have relatively little heat capacity. Thus, the thermal energy needed to start the system can be very small, and can approach startup losses in today's IC engines.

This makes the system ideal for small-scale applications where the fuel cell may be moved (e.g., vehicles and distributed power). We have evaluated the potential of the PSR system against the on-board vehicle targets developed by the DOE for 2010 and 2015 by steady-state and dynamic system modeling. The results show an integrated PSR-based system has the potential to meet stringent targets for size, start-up time and energy, dynamic performance, and overall system efficiency. This technology may provide a path to deliver hydrogen to fuel cell systems in the near term, thus enabling the deployment of fuel cell vehicle power trains.

### Literature

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