

## **SORPTION ENHANCED REACTION PROCESS (SERP) FOR THE PRODUCTION OF HYDROGEN**

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### **Abstract**

The novel Sorption Enhanced Reaction Process has the potential to decrease the cost of hydrogen production by steam methane reforming. Current effort for development of this technology has focused on adsorbent development, experimental process concept testing, and process development and design. A preferred CO<sub>2</sub> adsorbent, K<sub>2</sub>CO<sub>3</sub> promoted hydrotalcite, satisfies all of the performance targets and it has been scaled up for process testing. A separate class of adsorbents has been identified which could potentially improve the performance of the H<sub>2</sub>-SER process. Although this material exhibits improved CO<sub>2</sub> adsorption capacity compared to the HTC adsorbent, its hydrothermal stability must be improved.

Single-step process experiments (not cyclic) indicate that the H<sub>2</sub>-SER reactor performance during the reaction step improves with decreasing pressure and increasing temperature and steam to methane ratio in the feed. Methane conversion in the H<sub>2</sub>-SER reactor is higher than for a conventional catalyst-only reactor operated at similar temperature and pressure. The reactor effluent gas consists of 90+% H<sub>2</sub>, balance CH<sub>4</sub>, with only trace levels (<50 ppm) of carbon oxides.

A best-case process design (2.5 MMSCFD of 99.9+% H<sub>2</sub>) based on the HTC adsorbent properties and a revised SER process cycle has been generated. Economic analysis of this design indicates the process has the potential to reduce the H<sub>2</sub> product cost by 25-31% compared to conventional steam methane reforming.

A second experimental process test unit has been designed which will permit investigation of the fully cyclic H<sub>2</sub>-SER process in FY99.

### **Novel Sorption Enhanced Reaction Process**

The goal of this work is to develop a novel, more efficient steam-methane reformation (SMR) process for the production of hydrogen. The overall SMR reaction is given by:



The novel concept is called the Sorption Enhanced Reaction Process (SERP). The reactants, steam and methane, are fed at 300-500°C and 50-300 psig into a tubular reactor containing an admixture of commercial reforming catalyst and an adsorbent for removing carbon dioxide from the reaction zone. A reactor effluent consisting of relatively pure hydrogen (90-98+%) is produced during this step. The primary impurity is methane with traces of carbon oxides. Once the adsorbent is saturated with CO<sub>2</sub>, it is regenerated in situ by using the principles of pressure swing adsorption (PSA) at the reaction temperature.

The key benefits of producing H<sub>2</sub> by the SERP concept are: (i) reformation at a significantly lower temperature (300-500°C) than conventional SMR process (800-1000°C), while achieving the same conversion of methane to hydrogen, (ii) significantly lower capital cost, (iii) production of hydrogen at feed gas pressure (200-400 psig) and at relatively high purity directly from the reactor, (iv) significant reduction or even elimination of downstream hydrogen purification steps, (v) elimination of CO in the hydrogen product, (vi) minimization of side reactions, e.g., coking, and (vii) reduction of the excess steam used in conventional SMR.

### **APCI/DOE Program Goals for FY98**

The key program goals and milestones for the cooperative APCI/DOE SER Project during the current year are listed below:

- (1) Evaluate sensitivity of H<sub>2</sub>-SER process steps to process variables.
- (2) Refine the initial H<sub>2</sub>-SER design/economic analysis based on experimental data.
- (3) Design and begin construction of a cyclic SER process test unit.
- (4) Identify and demonstrate improved CO<sub>2</sub> adsorbents for H<sub>2</sub>-SER process.

### **Experimental**

Experimental equipment used to characterize the performance of various CO<sub>2</sub> adsorbents and for investigating the H<sub>2</sub>-SER process steps have been constructed and described by Hufton et al. (1997). Adsorbent screening is performed with a thermal gravimetric adsorption unit (for measurement of dry CO<sub>2</sub> working capacity), a binary desorption unit (to determine CO<sub>2</sub> capacity

in steam environments), and a hydrothermal stability unit (to assess physical and chemical stability of adsorbents in steam/CO<sub>2</sub> mixtures at elevated temperatures). Procedures and equipment have also been developed for the production of pelletized forms of the synthesized adsorbents. Process experiments have been carried out in an electrically-heated fixed bed tubular reactor (SER#1). These experiments have focused on individual steps of the process, rather than the fully cyclic operation of an industrial SER process unit.

## Results and Discussion

### High Temperature Sorbents for CO<sub>2</sub>

The following criteria were developed for an acceptable CO<sub>2</sub> sorbent for performing steam-methane reforming by the SER concept:

- (a) CO<sub>2</sub> working capacity > 0.3 mmole/g at 300-500°C in the presence of steam at high partial pressure and at low partial pressures of CO<sub>2</sub> ( $P_{\text{CO}_2}$ , 0.1 to 1 atm ;  $(P_{\text{H}_2\text{O}})/(P_{\text{CO}_2}) > 20$ );
- (b) Adequate ad(de)sorption kinetics for CO<sub>2</sub> at reaction and regeneration conditions;
- (c) Stable CO<sub>2</sub> sorption capacity after repeated sorption/desorption cycles;
- (d) Adequate mechanical strength of adsorbent particles after cyclic exposure to high pressure steam.

Previous efforts have identified a preferred adsorbent, potassium carbonate-promoted hydrotalcite (referred to as HTC), which satisfies the above requirements. It exhibits a stable CO<sub>2</sub> working capacity of -0.45 mmole/g in the presence of 0.3 atm CO<sub>2</sub> and 10 atm steam at 400°C. The adsorption/desorption kinetics were measured in fixed bed experiments and found to be relatively fast. The active ingredient was found to be non-leachable in steam, and the CO<sub>2</sub> capacity was not negatively influenced by combination with the SMR catalyst. Production of this material was scaled up to the kilogram range for process testing.

A second class of materials, referred to as the 'H' family of adsorbents, was also identified last year. These adsorbents were characterized by much higher CO<sub>2</sub> working capacities than the HTC. Modification of the processing procedures was found to change the shape of the CO<sub>2</sub> isotherm of the 'H' adsorbents to a more linear shape (preferred) at low partial pressures of CO<sub>2</sub>. This class of materials held promise as an improved second generation adsorbent for the H<sub>2</sub>-SER process.

Current year efforts in the adsorbent development area has been focused on improving\_ the properties of the HTC adsorbent, understanding methods to manipulate the properties of the 'H' family of adsorbents, and developing methods for the production of larger batches of the desired adsorbent for process development study.

An additional experimental screening capability was developed to qualitatively asses the apparent desorption kinetics of small (mg) samples of adsorbents. The technique was based on the thermal gravimetric adsorption (TGA) approach and could be used to benchmark apparent CO<sub>2</sub> desorption kinetics against the promoted HTC material.

A series of  $K_2CO_3$  promoted HTC adsorbents was examined for working  $CO_2$  capacity (dry) at  $400^\circ C$  as a function of the carbonate loading. As illustrated in Figure 1, the data indicate that the  $CO_2$  working capacity does not appreciably change when the HTC is impregnated with a solution containing 2.0-4.0 M  $K_2CO_3$ . All of the materials tested in the process test unit, described later in this report, were prepared using 2.0 M solution.

Approximately five kilograms of 20%  $K_2CO_3$ /HTC was prepared for continuing engineering evaluation. Each 1 kg batch was produced by promoting the base HTC with carbonate solution, and the  $CO_2$  capacities of each batch were checked with the TGA unit. Plans were made with an external vendor to produce larger batches (100 lbs) of 1/8" HTC pellets with larger scale extrusion equipment. Initial samples prepared with this equipment have adequate crush strength. Additional work is required to further reduce the pellet aspect ratio to our target of 1:1. Fifty to one hundred pounds of adsorbent will be needed for process testing experiments planned for the later part of this year.

Even though the 'H' series of adsorbents exhibited higher  $CO_2$  working capacity in the presence of steam than the HTC, these adsorbents are not very stable in continuous contact with steam. A number of characterization techniques were employed to understand how the variables for synthesis of 'H' series adsorbents affect the chemical, physical and adsorptive properties of these adsorbents. Systematic changes were found to occur in the composition, surface area, porosity,  $CO_2$  adsorption isotherm shape and  $CO_2$  desorption rate as the 'H' adsorbents were post-treated. Transmission electron microscopy analysis of the post-treated adsorbents indicated the presence of extremely small grains of 'active ingredient' in the adsorbent matrix. This unique morphology was not observed in the untreated samples. The presence of these small domains was postulated to be the key to the high reversible  $CO_2$  sorption capacity of the post-treated material, and perhaps also to the adverse effects of steam, which tend to sinter the smaller domains into larger clusters with less effective adsorptive properties.

Several different material compositions and synthesis routes for 'H' adsorbents were pursued in order to improve their steam stability. The general idea was to fix the grains of 'active ingredient' into a substrate which will stabilize the grains and prevent them from sintering. Samples of bound, extruded pellets derived from 'H' material were prepared using 5, 10 and 20 wt.% HTC, bentonite and atapulgite binders. The sorbent bound with 20% atapulgite showed the best performance with a crush strength of over 2 lbs/mm and a reversible  $CO_2$  capacity of 1.33 mmol/g at  $375^\circ C$ . The samples bound with 10-20 wt.% bentonite and atapulgite showed substantially improved resistance to degradation with respect to  $CO_2$  working capacity after one week of exposure to hydrothermal aging conditions relative to the unbound sample. After 4 weeks of steam testing, however, all of the bound H adsorbents had inferior  $CO_2$  capacity/kinetic combinations relative to the promoted HTC.

## **H<sub>2</sub>-SER Process Experiments**

The goal of this, work was to experimentally investigate the effect of various process variables on the performance of the H<sub>2</sub>-SER process steps. Initial experimental efforts were focused on

performing the reaction step with a reactor initially cleaned of both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and filled to reaction pressure with pure hydrogen. Table 1 contains detailed descriptions of the SERP process steps.

During the last year, reaction step experiments with hydrogen pressurization were carried out at various conditions (temperature ranging from 350 to 450°C, pressure ranging between 55 and 250 psig, adsorbent/catalyst ratio ranging between 1:3 and 3:1, and  $\text{H}_2\text{O}/\text{CH}_4$  ratio in the feed gas ranging between 3:1 to 8:1). In all cases, the SER reactor produced higher purity hydrogen (a mixture of hydrogen and methane, with only trace levels of carbon oxides) at significantly higher methane conversion than a catalyst-only system operating under the same temperature and pressure. The results also indicate that both the hydrogen purity of the effluent gas and the methane conversion increase as the reactor pressure is decreased and the reactor temperature and  $\text{H}_2\text{O}/\text{CH}_4$  ratio are increased. These are exactly the same trends one would expect based on the thermodynamics of the SMR reaction.

The impact of variations of the original  $\text{H}_2$ -SER process steps (Table 1) have been evaluated by process design analysis, and the most attractive approaches have been tested in the laboratory. These include the utilization of different pressurization gases and different purge conditions, while varying the reaction pressure, temperature, feed gas composition, and adsorbent to catalyst ratio. Figure 2 shows some of the promising SERP reactor performance obtained from these studies. It reports the net average  $\text{H}_2$  purity (%) in the reactor effluent (product) and the  $\text{CH}_4$  conversion to  $\text{H}_2$ , as a function of the specific  $\text{H}_2$  product (mmole/g of catalyst and adsorbent). The experiment was carried out with 6:1  $\text{H}_2\text{O}/\text{CH}_4$  in the feed gas, 1:1 adsorbent (HTC) / catalyst in the reactor, 55 psig reactor pressure, and reactor temperatures of 400-450°C.

Table 2 reports examples of the  $\text{H}_2$  product purity and  $\text{CH}_4$  to  $\text{H}_2$  conversion at two levels of  $\text{H}_2$  production (0.4 and 0.8 mmole  $\text{H}_2/\text{g}$  adsorbent and catalyst) at 400 and 450°C as measured in our 3.5' long SER#1 reactor. The table also compares the corresponding properties for the catalyst-only SMR reactor operated under identical conditions. The superiority of the SERP concept is obvious. The table also shows that the operation of SERP at 450°C is significantly better than at 400°C.

Figure 3 shows the experimental analysis of reactor effluent gas of Figure 2. It is very important to note that the average carbon oxide ( $\text{CO}_2$  and  $\text{CO}$ ) concentration levels in the  $\text{H}_2$  product gas is negligible (<50 ppm). Thus, the SERP reactor effluent ( $\text{H}_2$  product) mainly consists of bulk  $\text{H}_2$  (>90% average) and  $\text{CH}_4$  (<10% average), which can be very easily separated to produce pure  $\text{H}_2$  by using a simple 3-4 column PSA system. This is a key advantage of the SERP which can lead to significantly lower PSA separation costs (less adsorbent inventory and  $\text{H}_2$  losses) compared to a conventional SMR-PSA system (which requires removal of ~20%  $\text{CO}_2$  and 1%  $\text{CO}$  from  $\text{H}_2/\text{CH}_4$  mixture) using 8-12 adsorption columns.

Carbon analysis of used catalyst and adsorbent indicated that no carbon was formed during the  $\text{H}_2$ -SER experiments.

In summary, the above reaction-step data indicate that relatively high-purity hydrogen (90+%) can be produced directly from the SER reactor at high conversion and much lower reaction temperature than a conventional reformer. The product is essentially a mixture of H<sub>2</sub> and CH<sub>4</sub>, with only trace levels of CO<sub>2</sub> and CO. The above results have been obtained with a relatively short reactor operated in a non-cyclic fashion. It is expected that the performance of the system will improve as the reactor length is increased since then the equilibrium zone will represent a larger fraction of the reactor volume.

## **Industrial-Scale SER Reactor Design**

Heat must be supplied to the reaction zone during the reaction and regeneration steps of the SERP process. Previous reports have described a 'condensing heat transfer fluid' approach where a high temperature organic fluid is vaporized and passed on the shell-side of a shell and tube reactor. Catalyst and adsorbent are packed on the tube side, and condensation of the heat transfer fluid in the shell-side provides energy for the reaction. This approach is characterized by a high shell-side heat transfer coefficient and nearly isothermal temperatures along the length of the reactor. Unfortunately, it is also limited to -400°C by the stability characteristics of the commercial heat transfer fluids.

The experimental data presented above clearly indicate that the lab-scale reactor performance improves with increasing temperature. An alternative reactor design has been developed based on indirect gas heating which has the potential to increase the operating temperature range to 450-500°C.

## **Preliminary H<sub>2</sub>-SER Process Design and Economic Analysis**

A best-case industrial H<sub>2</sub>-SER process design (2.5 MMSCFD of 99.9+% H<sub>2</sub>) was developed based on the experimental process data, SMR thermodynamics, and judicious engineering assumptions. This design was substantially different from that presented last year (Hufton et al., 1997) since it was based on a different adsorbent and process cycle. The process design utilized the condensing heat transfer fluid system operating at 400°C, and the adsorbent properties were those of K<sub>2</sub>CO<sub>3</sub>/HTC. The system consists of three shell and tube reactors operated in parallel, along with a number of heat exchangers, condensers, and vacuum equipment for subatmospheric regeneration. A H<sub>2</sub>PSA unit was included in the system for final purification of the product gas (H<sub>2</sub>/CH<sub>4</sub> separation). Economic analysis of this design indicates that the system has the potential to reduce hydrogen production costs by 25% compared to the conventional SMR route. Savings could increase to 31% if the CO<sub>2</sub> adsorbent capacity is increased by a factor of three (consistent with CO<sub>2</sub> capacities of the H-series adsorbents). It was also found that elimination of the H<sub>2</sub>PSA unit will yield similar savings. This approach would produce a product consisting of 95-98% H<sub>2</sub>, balance CH<sub>4</sub>, and only trace CO/CO<sub>2</sub>. Table 3 provides a breakdown of the relative capital and operating costs associated with the above processes. It is clear that the cost advantages of the H<sub>2</sub>-SER processes are due to substantial capital cost reductions (H<sub>2</sub>-SER capital 50 to 60% less costly than conventional SMR).

## Development of the Cyclic Process Unit

The APCI technical and management teams have decided that demonstration of the cyclic H<sub>2</sub>-SER process using a continuous process test unit (SER#2) is needed before the technical and financial risk of a full-scale process development unit are undertaken. This will allow for more reliable development of a process design and definition of cost advantages. Significant effort has been directed towards the design of this experimental unit. It will consist of two reactors in parallel, each 20 ft long and 1 inch in diameter. Both the heat transfer fluid and indirect gas heating schemes will be tested. Valve operations will be completely automated, and the unit will be capable of regenerating the reactors under atmospheric or subatmospheric conditions. Reaction step flow rates will be similar to those envisioned for the industrial-scale process. A detailed process and instrumentation diagram has been developed, along with an initial cost estimate.

The addition of this equipment to the program will require a change in the project schedule. A no-cost extension of the Phase II efforts to the end of October 98 has been accepted by DOE. Completion of the SER#2 unit design and construction of the unit are planned during this time. Phase III efforts will also be adjusted so that the first year will be used for evaluation of the SER#2 unit, while the last two years will be identical to the original project plan (PDU design and operation). This approach will add one year to the overall project lifetime (extending it to six years), but the total cost to the DOE will remain the same.

## Future Work

The laboratory data, process design, and economic analysis described above indicate that the H<sub>2</sub>-SER process offers very high potential for developing a more cost-effective SMR process for the production of hydrogen. The next phase of effort will largely be directed towards the operation of the cyclic SER#2 unit so that a more refined design of this new process can be developed. The unit will be used to characterize the effects of various operating parameters (e.g., reaction pressure, temperature, regeneration conditions, purge to feed gas ratio, adsorbent/catalyst ratio, type of reactor heating system, etc.) on the cyclic steady-state performance of the SER process. In particular, evaluation of the average hydrogen product purity, methane conversion, and reactor productivity at cyclic steady-state will be assessed.

Concurrent process testing efforts will continue with the present laboratory-scale unit (SER#1) to further investigate the effect of various process parameters on the reactor performance, and to characterize the performance of current and next-generation CO<sub>2</sub> adsorbents. The data obtained from this unit will also help define the range of parameters to be investigated with the SER#2 unit.

The process data generated by these two units will be implemented into revised process designs on a continuous basis, and the economics of H<sub>2</sub> production will be assessed. This will then allow us to develop a commercialization strategy with the APCI Hydrogen business group.

Materials research efforts will be focused on the scale up of production of  $K_2CO_3$ /HTC for use in SER#2 (50-100 lbs). Plans for adsorbent scale-up to the PDU level (10001bs) will also be considered, and commercial adsorbent vendors will be included in these discussions. The development of an improved second-generation adsorbent will also be pursued, initially by continuing efforts to improve the steam stability of the 'H' material by modifying the synthesis and/or the treatment processes.

### Acknowledgments

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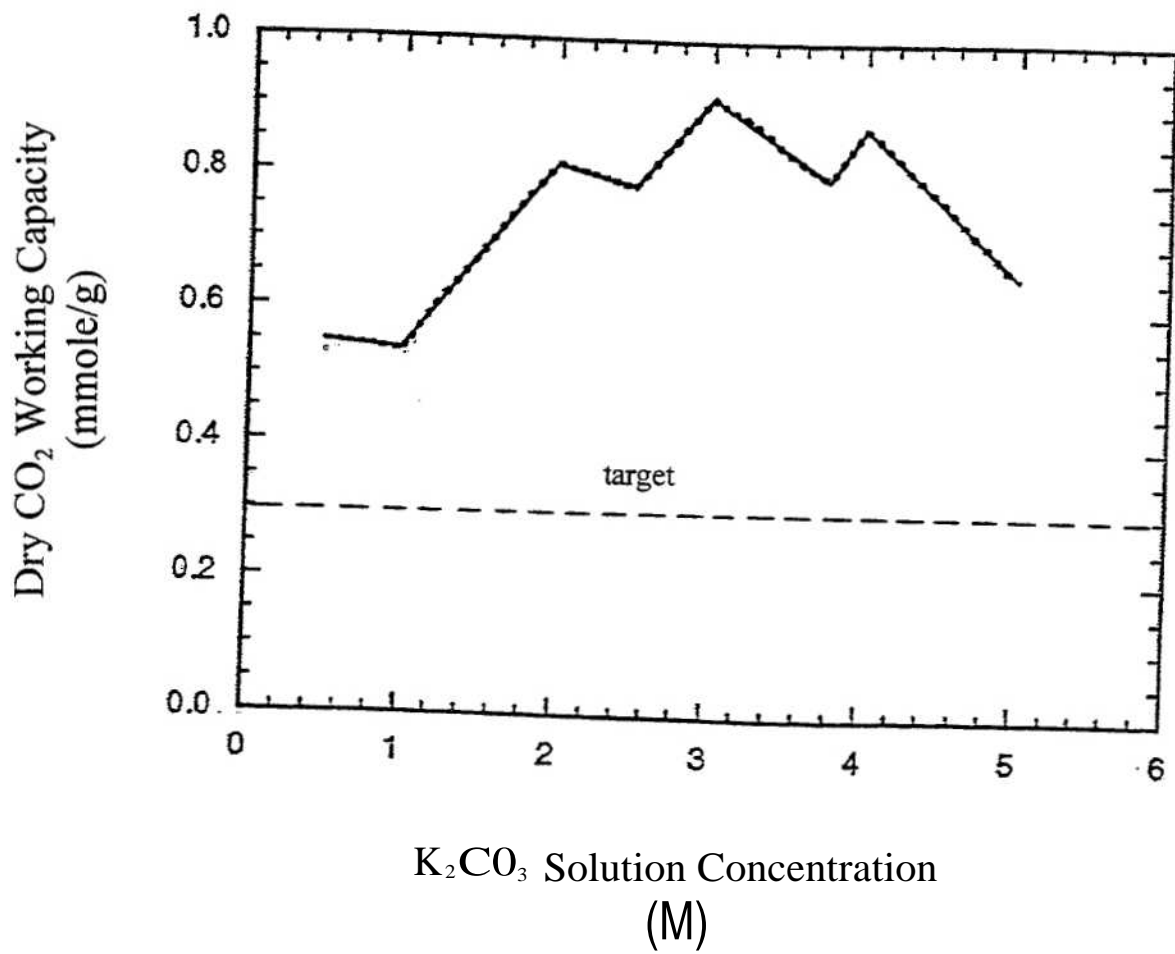
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Figures



**Figure 1.** The Effect of K<sub>2</sub>CO<sub>3</sub> Loading on CO<sub>2</sub> Adsorption Capacity for Promoted HTC at 400°C.

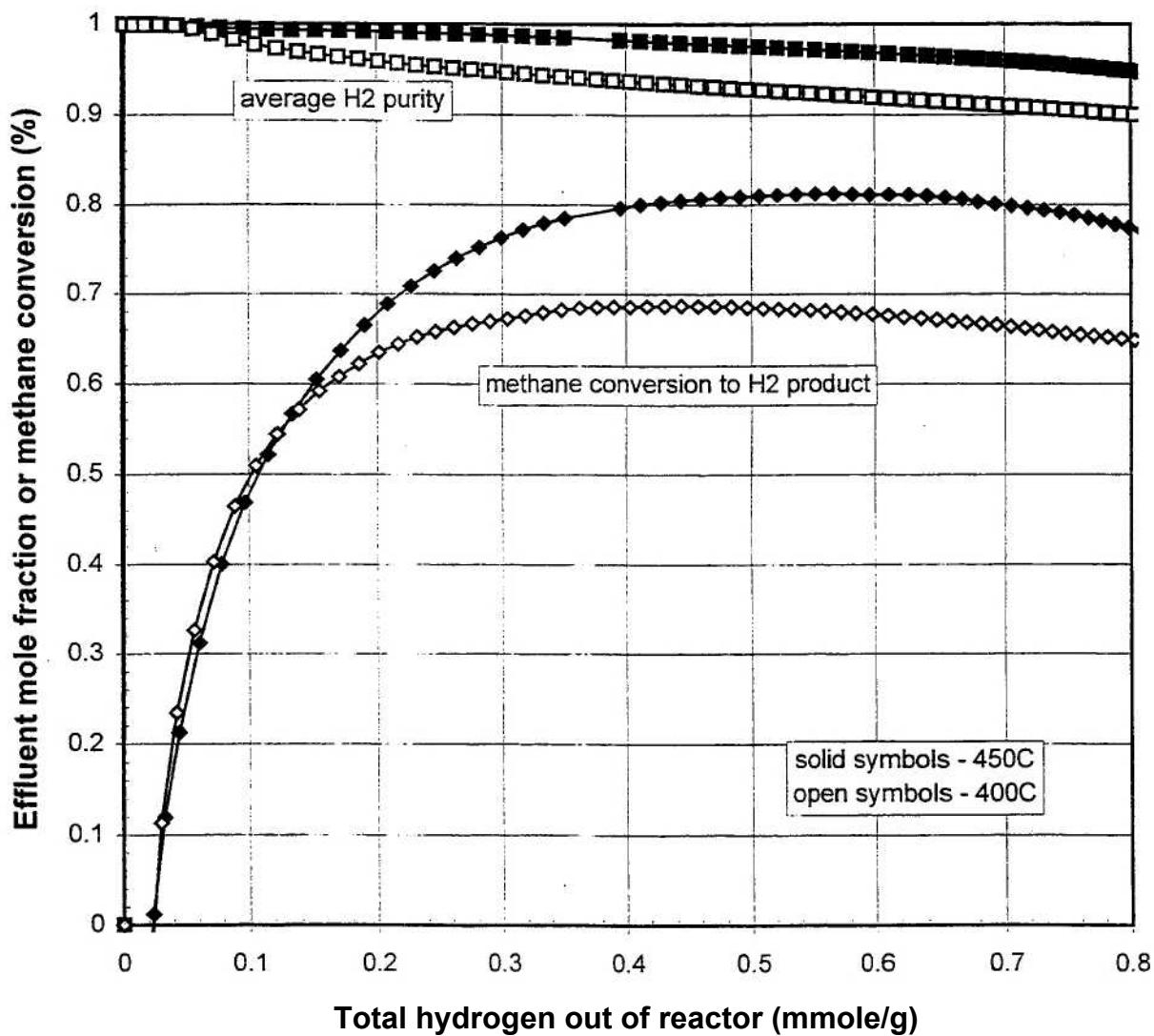


Figure 2. Average Hydrogen Purity and Methane Conversion to Product Hydrogen as Measured on Lab-Scale SER#1 Unit; 6:1 steam:carbon feed, 1:1 adsorbent (HTC)/catalyst, 55 psig.

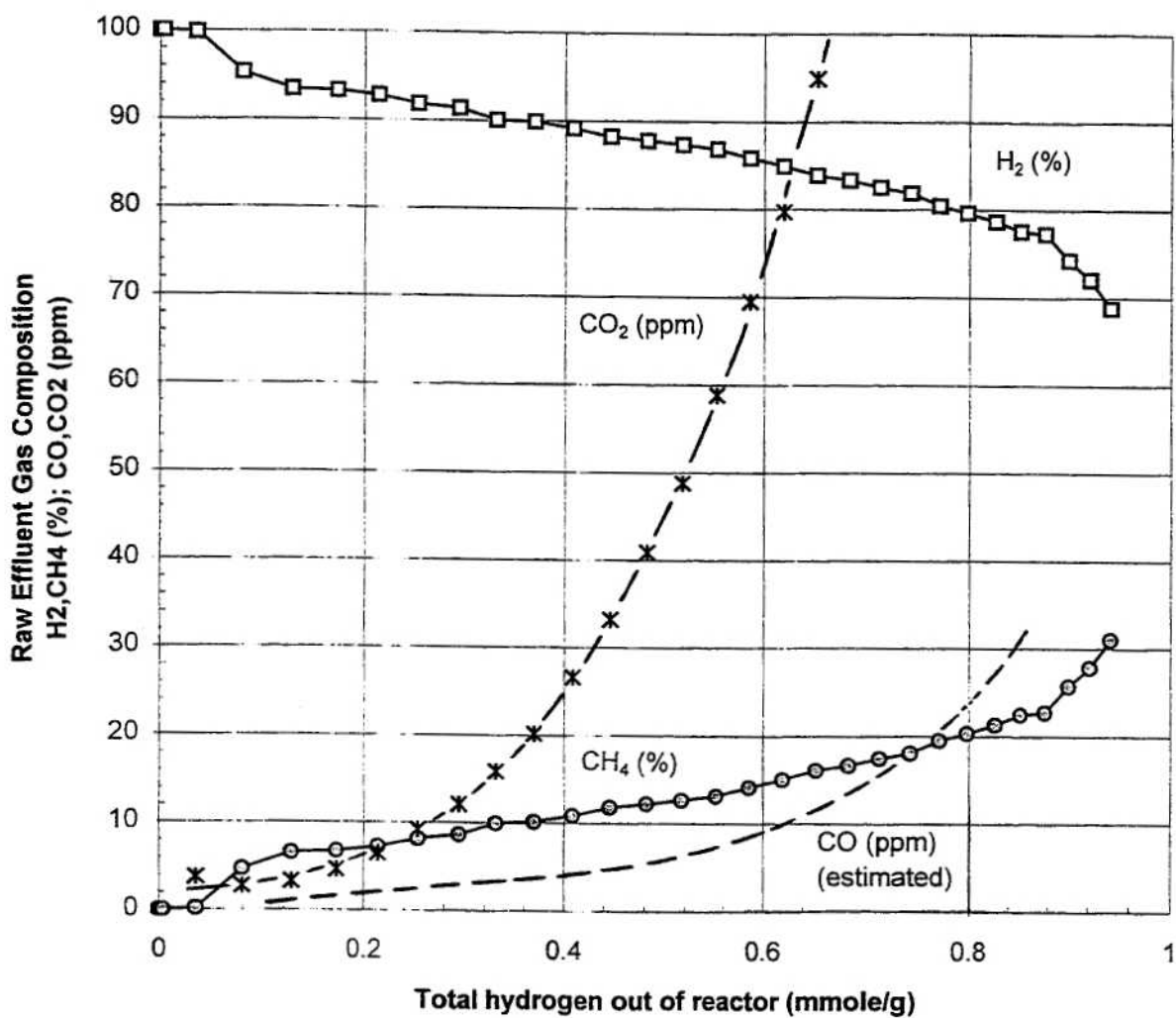


Figure 3. Reactor Effluent Gas Phase Compositions for Typical H<sub>2</sub>-SER Reaction Experiment; 6:1 steam/carbon feed, 1:1 adsorbent (HTC)/catalyst, 55 psig.

**Table 1.  $H_2$ -SER Process Steps.**

1. **Sorption-Reaction Step:** The reactor is initially presaturated with a portion of the product  $H_2$  at the desired reaction temperature and pressure. Steam and methane at a prescribed ratio (e.g., 2:1) are fed to the reactor and an essentially pure  $H_2$  product (>98% purity) is collected as the reactor effluent. The reaction step is continued up to the point when the  $H_2$  purity in the product decreases to a preset level. The feed is then diverted to a second identical reactor.
2. **Depressurization Step:** The reactor is countercurrently depressurized.. The effluent gas can be recycled as feed to another reactor or used as fuel.
3. **Purge Step:** The reactor is countercurrently purged with a weakly adsorbing gas such as methane to desorb the  $CO_2$ . The desorption pressure may range between 0.2 and 1.1 atmospheres. The desorbed gas consists of  $CH_4$ ,  $CO_2$ ,  $H_2$  and  $H_2O$  and is either separated for recycle of the  $CH_4$  purge gas or used as fuel.
4. **Product Purge Step:** The weakly adsorbing purge gas ( $CH_4$ ) is countercurrently displaced from the reactor with product  $H_2$ . The displaced  $CH_4$  is recycled as purge gas or used as fuel.
5. **Product Pressurization:** The reactor is countercurrently pressurized to the reaction pressure with pure  $H_2$ . At this point, the regeneration of the reactor is complete and it is ready to undergo a new cycle.

**Table 2. Experimental SER Performance Data; 55 psig,  
6:1 H<sub>2</sub>O/CH<sub>4</sub> feed, 1:1 adsorbent (HTC) I catalyst.**

	Effluent Product (dry basis)	Methane conversion (%)	Productivity (mmole H <sub>2</sub> /g)
SER @ 400°C	90% H <sub>2</sub> , 10% CH <sub>4</sub>	68	0.8
	95% H <sub>2</sub> , 5% CH <sub>4</sub>	-	0.4
No adsorbent, 400°C	42% H <sub>2</sub> , 47% CH <sub>4</sub> , 10% CO/CO <sub>2</sub>	18	
SER @ 450°C	96% H <sub>2</sub> , 4% CH <sub>4</sub>	82	0.8
	98% H <sub>2</sub> , 2% CH <sub>4</sub>		0.4
No adsorbent, 450°C	53% H <sub>2</sub> , 34% CH <sub>4</sub> , 13% CO/CO <sub>2</sub>	28	

**Table 3. Economic Performance of H<sub>2</sub>SER and Conventional SMR Processes;  
Relative Cost based on Conventional SMR,  
2.5 MMSCFD 99.9+% H<sub>2</sub>, \$2.5/MMBtu natural gas.**

	Conventional SMR	H <sub>2</sub> SER	H <sub>2</sub> SER with improved adsorbent	H <sub>2</sub> SER without H <sub>2</sub> PSA
capital cost	0.54	0.28	0.25	0.21
operating cost	0.46	0.47	0.44	0.48
H <sub>2</sub> product cost	1.0	0.75	0.69	<b>0.69</b>