

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 by 15-30% depending on plant size and H₂ purity. Current effort for development of this technology has focused on adsorbent scale-up and characterization, experimental process testing, process design development and evaluation, and construction of a fully cyclic experimental process test system.

A preferred CO₂ adsorbent, K₂CO₃ promoted hydrotalcite, has been shown to satisfy all of the initial H₂-SER performance targets and has been scaled up (in the lab) to produce a 50 lb batch for process testing. Recent experiments show that the adsorbent is stable at up to 550C, the CO₂ capacity is high even in the presence of steam, the mass transfer rate is fast (sharp breakthrough curves), and the adsorbent can be used in a pressure swing adsorption cycle. A new method of promoting the adsorbent with carbonate (spray impregnation) has been developed and demonstrated. Plans for scale-up of the promoted adsorbent to >1000 lb range are being discussed with multiple vendors of the hydrotalcite support. Synthesis procedures for a promising second class of adsorbents have been improved to produce higher yields of material with better thermal stability than previous samples.

The process cycle for the H₂-SER process has been simplified by using a mixture of 5-10% H₂ in steam as a purge and pressurization fluid. Single-step process experiments (not cyclic) have been carried out to show that the presence of steam in the reactor does not negatively impact the performance of the

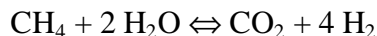
subsequent sorption-reaction step. Methane conversion in the H₂-SER reactor is much higher than for a conventional catalyst-only reactor operated at similar temperature and pressure. At 450C and 55 psig, the reactor effluent gas consists of 95+%H₂, balance CH₄, with only trace levels (<50 ppm) of carbon oxides.

A process design for a H₂-SER unit utilizing an alternative method for providing heat to the SER reactors, via indirect gas heating, has been developed. Higher reaction temperatures (400-500C) can be achieved with this approach. The economics of this design are as favorable as previous designs based on heat transfer with a vaporized heat transfer fluid. The H₂-SER approach retains its economic advantage over conventional reforming even at higher production rates of 10 MM SCFD H₂.

A second experimental process test unit has been constructed which will permit demonstration and characterization of the performance of the fully cyclic H₂-SER process in FY99.

Introduction

The goal of this work is to develop a novel, more cost-effective steam-methane reforming (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 400-500°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 (95-98+%) is produced during this step. The primary impurity is methane with traces of carbon oxides. Once the adsorbent is saturated with CO₂, it is regenerated in situ by using the principles of pressure swing adsorption (PSA) at the reaction temperature.

The key benefits of producing H₂ by the SERP concept are:

- (i) reforming at a significantly lower temperature (400-500°C) than a 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 (50-400 psig) and at relatively high purity directly from the reactor (95% H₂, 5% CH₄, trace CO/CO₂)
- (iv) significant reduction or even elimination of downstream hydrogen purification steps
- (v) reduction of CO in the SER reactor effluent to ppm levels - elimination of shift reactors
- (vi) minimization of side reactions, e.g., coking
- (vii) reduction of the excess steam used in conventional SMR.

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

- (1) Characterize the performance of H₂-SER process steps with respect to process variables.
- (2) Develop new H₂-SER designs for economic analysis, as appropriate.
- (3) Complete construction of a cyclic SER process test unit.
- (4) Identify and demonstrate improved CO₂ adsorbents for the H₂-SER process.

Experimental Systems

Experimental equipment used to characterize the performance of various CO₂ adsorbents and for investigating the H₂-SER process steps have been described by Hufton et al. (1997; 1998) and Mayorga et al. (1997). Adsorbent screening is performed with a thermal gravimetric adsorption unit (for measurement of dry CO₂ working capacity), a binary desorption unit (to determine CO₂ capacity in steam environments), and a hydrothermal stability unit (to assess physical and chemical stability of adsorbents in steam/CO₂ mixtures at elevated temperatures). Procedures and equipment have also been developed for the production of pelletized forms of the synthesized adsorbents. Process and adsorption

breakthrough 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

H₂-SER Process Experiments

The H₂-SER process cycle was simplified and improved during the past year. The previous cycle included a sequence of 1) sorption-reaction, 2) countercurrent depressurization, 3) countercurrent purge with CH₄, 4) countercurrent product purge with pure H₂, and 5) countercurrent pressurization with H₂ (Hufton et al., 1998). The process performance and economics can be improved by replacing the CH₄ purge / H₂ purge / H₂ pressurization steps with a purge / pressurization sequence using a steam / H₂ mixture. Steam is cheaper than CH₄ on a volume basis and can be tolerated in the sorption-reaction step product since it is easily removed by condensation. Ideally, pure steam would be used to purge and pressurize the reactors, but this would also partially oxidize the Ni-based catalyst. A small amount of H₂ (5-10%) is included with the steam to maintain reducing conditions. A summary of the new process steps is listed in Table 1.

Table 1. Modified H₂-SER Process Steps.

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| <ol style="list-style-type: none">Sorption-Reaction Step: The reactor is initially presaturated with a mixture of steam and H₂ at the desired reaction temperature and pressure. Steam and methane at a prescribed ratio (e.g., 3:1) are fed to the reactor and an enriched H₂ product (>95% purity) is collected as the reactor effluent. The reaction step is continued up to the point when the H₂ purity in the product decreases to a preset level. The feed is then diverted to a second identical reactor.Depressurization Step: The reactor is countercurrently depressurized. The effluent gas can be recycled as feed to another reactor or used as fuel.Purge Step: The reactor is countercurrently purged with a mixture of 5-10% H₂ in steam to desorb the CO₂. The desorption pressure may range between 0.2 and 1.1 atmospheres. The desorbed gas consists of CH₄, CO₂, H₂ and H₂O and is used as fuel after removing H₂O via condensation.Pressurization: The reactor is countercurrently pressurized to the reaction pressure with the steam / H₂ mixture. At this point, the regeneration of the reactor is complete and it is ready to undergo a new cycle. |
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Process experiments with a fixed bed reactor (1.5" ID, 60" long) were carried out to determine if initial pressurization with a mixture of steam/H₂ would be detrimental to the ensuing sorption-reaction step. A reactor containing 1:1 HTC adsorbent:catalyst at 450°C was initially pressurized to 55 psig with a mixture of 20% H₂ / 80% steam, and then fed a feed gas of 14% methane in steam. The average effluent gas composition during the sorption-reaction step plotted versus the net amount of hydrogen produced from

the reactor is illustrated in Figure 1. The reactor produces 0.8 mmole of H₂ product per g of solid in the reactor, at an average purity of 96% H₂, 4% CH₄, and less than 50 ppm CO + CO₂. The methane conversion to H₂ product reaches 82%. The conversion and product purity are substantially higher than the thermodynamic limits for a catalyst-only reactor operated at these same conditions (28% conversion, 53% H₂, 34% CH₄, 13% CO/CO₂). The effect of steam in the pressurization gas has no negative impact on the sorption-reaction step performance.

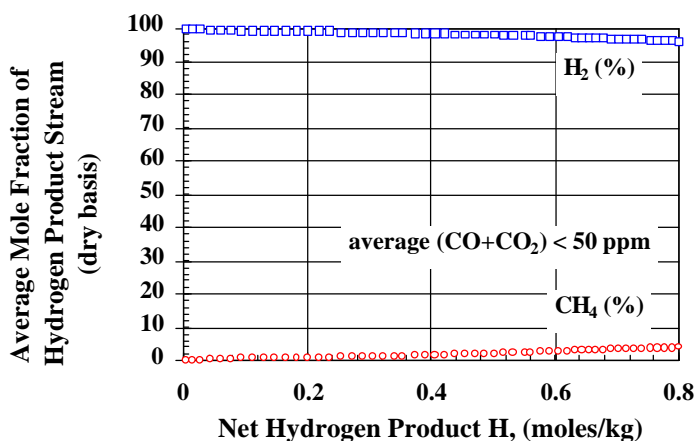


Figure 1. Average Product Gas Composition during a Sorption-Reaction Step with Initial H₂/Steam Pressurization as Measured on Lab-Scale SER#1 Unit; 6:1 steam/carbon feed, 1:1 adsorbent (HTC)/catalyst, 55 psig, 450C.

The development of a novel K₂CO₃/hydrotalcite (HTC) CO₂ adsorbent for the H₂-SER process has been described previously (Mayorga et al., 1997; Hufton et al., 1998). The adsorption properties of this unique material were characterized during the past year.

Cyclic adsorption/desorption experiments were carried out with HTC in the Binary Desorption Unit (BDU) to determine the working capacity and stability of the adsorbent at temperatures greater than 400°C (the upper limit of previous cyclic tests). Adsorbent sample at 550°C was repetitively exposed to two hours of 0.3 atm CO₂ / 9.7 atm steam and two hours of 1 atm N₂. The effective working capacity of the adsorbent is illustrated in Figure 2. The CO₂ capacity initially declines but then stabilizes after 10 cycles at ~ 0.5 mmole/g solid. Similar trends were observed at a temperature of 450C. A separate batch of adsorbent was continuously exposed for 16 days to a static environment of 0.3 atm CO₂ and 18 atm of steam at 450 and 550°C. The CO₂ capacity of the exposed material was found to be essentially the same as the fresh material. These tests indicate that the adsorbent is stable and has a high CO₂ working adsorption capacity in steam environments at temperatures between 450 and 550°C.

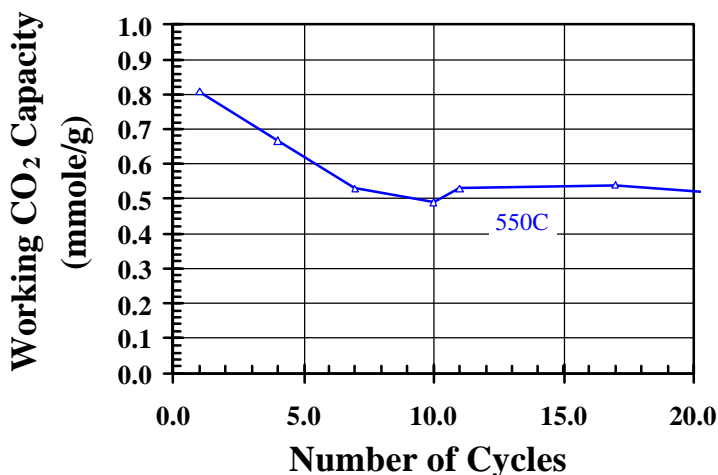


Figure 2. CO₂ Working Capacity on K₂CO₃/HTC at 450 and 550C Measured on the BDU.

A series of breakthrough experiments were carried out with the SER#1 process test unit to generate the CO₂ adsorption isotherm at 450C, characterize the adsorption mass transfer process, and demonstrate cyclic performance of the HTC adsorbent. The first two tasks were completed with both dry CO₂/N₂ feed streams and with steam-containing feed gas streams.

A series of breakthrough experiments were carried out at 250 psig, 450C, with a column packed with 1:2 K₂CO₃/HTC adsorbent:catalyst mixture and a feed gas of 2% CO₂ in N₂ (CO₂ partial pressure of 0.38 atm). This CO₂ concentration is consistent with the equilibrium amount of CO₂ formed from the SMR reaction at these pressure / temperature conditions (3:1 S/C feed). The column was thoroughly regenerated overnight with 2-4 lpm N₂ at 1 atm and 450C between breakthrough experiments. These experiments yield a stable CO₂ capacity (~0.48 mmole/g adsorbent) after the first adsorption/desorption cycle. Regeneration of the packed column by N₂ purge yields the same amount of CO₂ in the effluent gas as was adsorbed during breakthrough (within ± 10%), indicating that the adsorption during the latter cycles is completely reversible.

A breakthrough curve obtained at a G-rate of 1.8lbmole/hr-ft² is plotted in Figure 3 (squares). The initial portion of the CO₂ concentration profile is very steep, indicating that the adsorption mass transfer process is fast. A more disperse concentration profile is observed as the effluent mole fraction approaches the inlet value of 2.0%, which is likely due to heat transfer effects.

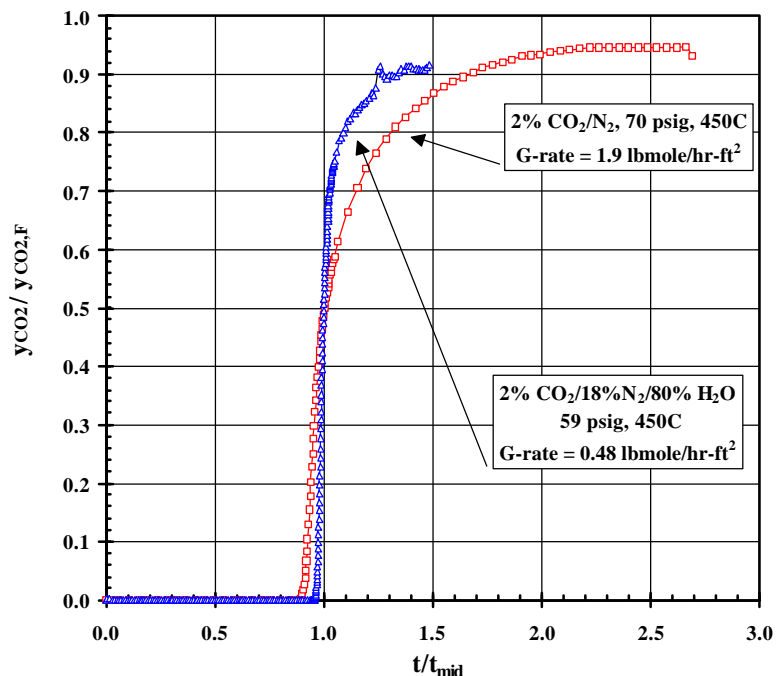


Figure 3: CO₂ Breakthrough Curves on K₂CO₃/HTC Adsorbent at 450°C.

The same experimental system was used to determine the effect of feed flow rate on the length of the adsorption mass transfer zone (LMTZ). The LMTZ provides a quantitative indication of effect of the rate of mass transfer on the adsorption step. Fast mass transfer processes are characterized by small LMTZ's. For a feed rate of 0.23 lbmole.hr-ft², the experimental LMTZ was only 4.2 inches based on breakthrough at y_{CO₂}=0.01%. Increasing the G-rate increased the LMTZ as illustrated in Figure 4. Extrapolation of these data to a feed G-rate of 100 lbmole/hr-ft² (a high industrial rate) yields a LMTZ of 35 in. The overall effect of this LMTZ on process performance will be small since 35 inches is only a small fraction of the total industrial reactor length (e.g. 20ft).

An isotherm for dry CO₂ on the K₂CO₃/HTC adsorbent generated from breakthrough experiments (0 to 250 psig, 450C, 1:2 K₂CO₃/HTC adsorbent:catalyst, 0.1 to 10% CO₂ in N₂) is illustrated as solid blue squares in Figure 5. These data were obtained after the adsorbent had been subjected to a number of CO₂ adsorption/desorption cycles, so the data correspond to the reversible CO₂ adsorption component and exclude the irreversible component. Also included in this plot are data obtained from a TGA and a volumetric uptake unit. The data from different analysis units are in reasonable agreement. The isotherm is Type I shape with relatively steep initial slope (Henry's law region). The final stable CO₂ capacity of the adsorbent at CO₂ partial pressures consistent with H₂-SER (P_{CO₂}>0.3 atm) are greater than the target value of 0.3 mmole/g adsorbent.

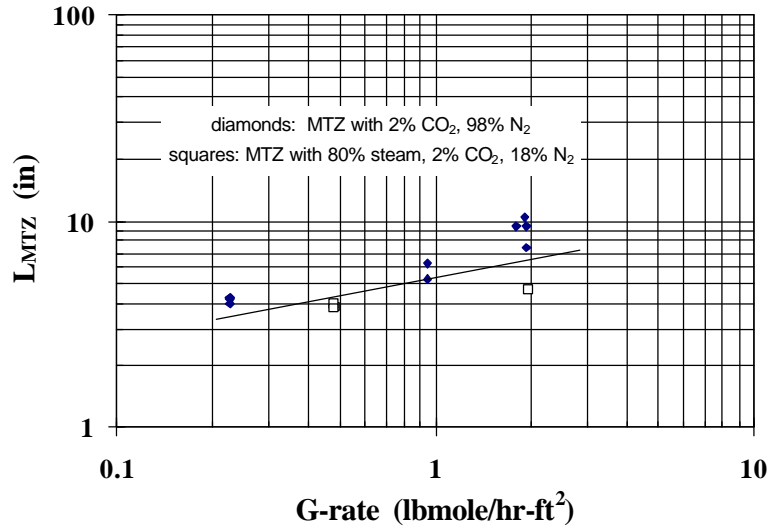


Figure 4: Effect of Feed Gas Velocity on Adsorption-Step Mass Transfer Zone; 450°C; 60 psig, 2% CO₂ with 98% N₂ or 80% steam/ 18% N₂, 450C, 1:2 ads/cat.

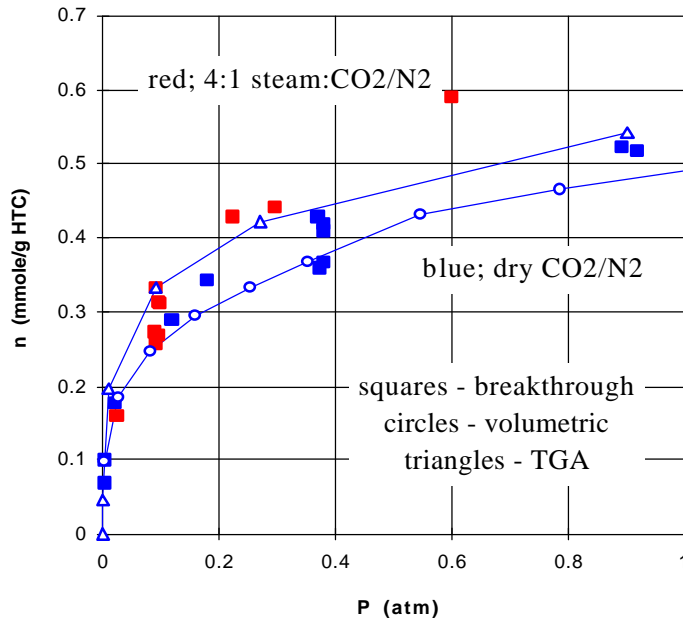


Figure 5: CO₂ Adsorption Isotherm on K₂CO₃/HTC Adsorbent at 450°C.

Desorption characteristics of CO₂ in dry N₂ were also evaluated from the above breakthrough experiments by countercurrently depressurizing the saturated column to 1 atm and purging at 450C with a given flow rate of N₂. This approach is capable of removing all of the CO₂ adsorbed during the

breakthrough step (excluding the ‘irreversible’ adsorption associated with the first exposure to CO₂). The amount of CO₂ desorbed during depressurization is typically 5% of the total.

Adsorption breakthrough experiments were also carried out in the presence of steam (adsorption of 2% CO₂, 18% N₂, 80% steam at 450C, 50-250 psig, purge at 1 atm with 60% N₂, 40% steam). The CO₂ adsorption capacity in the presence of steam is essentially the same as under dry conditions, as indicated in the isotherm at 450C (Figure 5). The mass transfer zone sharpened with addition of steam (Figure 3) yielding smaller LMTZ’s at a given feed flow rate (Figure 4). The presence of water vapor in the purge gas had no significant effect on the desorption characteristics of CO₂ from HTC.

Repetitive cycles of adsorption (2.1% CO₂/N₂, 450C, 1.86 lbmole/hr-ft²) / countercurrent depressurization / countercurrent N₂ purge (1 atm, N₂, 0.27 lbmole/hr-ft²) / countercurrent N₂ pressurization were carried out with 1:2 K₂C₃/HTC : catalyst to investigate the cyclic behavior of the adsorbent. The volumetric ratio of purge to feed gas (P/F ratio) was held at 2.0, which is relatively high for a conventional separative PSA, but is much lower than the effective value of ~18 used in the first pass H₂-SER designs. The effluent profiles for cycles 7-10 (Figure 6) match well, indicating that cyclic steady-state performance can be achieved with this system. This set of conditions would be capable of producing CO₂-free product if the column length was extended. The residual CO₂ left on the adsorbent between regeneration and adsorption steps decreased the effective CO₂ capacity and increased the LMTZ for this experiment compared to clean-column experiments. Higher effective CO₂ capacity and lower LMTZ can be achieved for higher P/F ratio. These results demonstrate that the adsorbent can be utilized effectively in a PSA-based process.

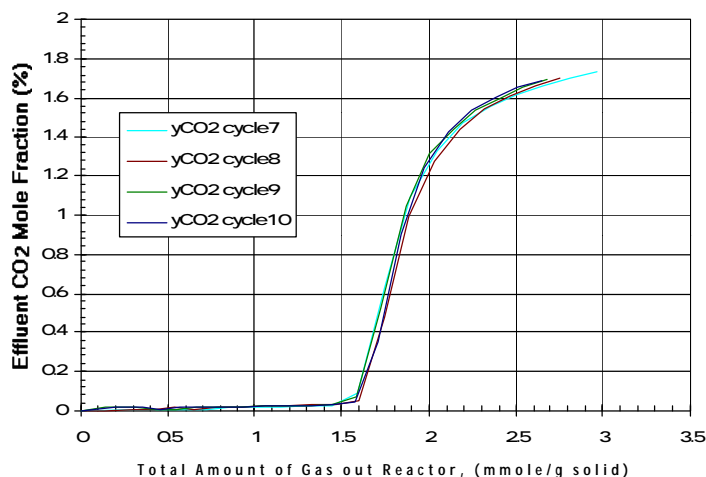


Figure 6: Effluent CO₂ Composition during Repetitive Feed/Depressurization/Purge/Pressurization Cycles; K₂CO₃/HTC adsorbent at 450°C.

The H₂-SER process utilizes a Ni-based prereforming catalyst to catalyze the reaction of steam and methane at 400-500°C. It is known that some prereforming catalysts can lose physical strength when exposed to high levels of steam and temperatures > 400°C. The stability of ten different commercial Ni-based catalysts (reforming, prereforming, and methanation catalysts) was evaluated by determining physical crush strength before and after exposure to 1-8 days of 18 atm of steam at 550C. Materials

which passed this test were then screened for SMR activity at 400-550°C. For many of the catalysts, the crush strength dropped by 50% or more after only a few days of steam exposure. A reforming and prereforming catalyst were identified with high crush strength and >95% CH₄ conversion at 400°C, 3:1 steam/CH₄, 18 atm, 24,000 hr⁻¹. The prereforming catalyst is an alternative formulation of the material we have used in previous SER experiments. We will test these two catalysts in the SER process via the lab-scale SER#1 unit and the new cyclic SER#2 unit (described later in this paper).

The heat of adsorption, i.e. the amount of energy released when CO₂ is adsorbed onto the K₂CO₃/HTC adsorbent, is an important design variable for the SER process. There has been some discrepancy between heats of adsorption measured from breakthrough experiments, TGA/BDU experiments, and expected values based on the mechanism of CO₂ adsorption. To resolve these differences, we have built an experimental unit based on a volumetric technique to determine heats of adsorption for the CO₂/HTC system.

Process Development Work

Two approaches have been developed for providing reaction energy to the SER reactors. Both are based on shell-and-tube reactor configurations with the catalyst/adsorbent mixture on the tube-side and a heat transfer medium on the shell-side. Use of vaporized heat transfer fluid, designated the HTF approach, as the shell-side fluid has been described in previous reports (Hufton et.al.,1998). This system is limited to temperatures of 400°C due to the characteristics of the organic heat transfer fluid.

A second approach, capable of reaching temperatures of 400-550°C, is based on transfer of sensible heat from hot flue gas (the indirect gas heating, or IGH, approach). Since the shell-side heat transfer coefficient is lower for this case, finned reactor tubes are used to achieve adequate heat transfer flux to the reaction gas. An axial temperature gradient is formed which decreases in the direction of flow of the flue gas. A patent application (Sircar, et. al., 1999) has been filed which describes how this gradient in temperature can be used to improve process performance.

A detailed H₂-SER process design was developed for the IGH approach. Like the HTF H₂-SER design, it utilizes conventional types of process equipment. The economics of both the HTF and IGH designs were evaluated for production of 99.9% H₂ at 2.5 and 10 MMSCFD production levels. The results show that the two approaches are both economically feasible, producing H₂ at 20-25% lower cost than standard reforming technology at 2.5 MMSCFD, and 10-20% lower at 10 MMSCFD H₂. Even greater savings (~30%) could be realized if a product of 95%H₂, 5%CH₄, and 100ppm CO+CO₂ is acceptable (e.g. fuel cell applications).

A major advantage of the H₂-SER process is that it can produce relatively high purity H₂ with only 5-10% CH₄ and very low (ppm) levels of carbon oxides. A conventional reformer and shift reactor, on the other hand, typically yields product gas containing 75% H₂, 5% CH₄, 16% CO₂ and 4% CO. A Pressure Swing Adsorption (PSA) unit, used to separate H₂ from this feed gas, must contain a large amount of adsorbent to remove the carbon oxides. In principle, the absence of carbon oxides in the SER product gas can lead to a smaller and cheaper PSA unit. Simulations were carried out with the APCI adsorption process simulator to confirm these ideas. The results showed that for the production of high purity H₂,

higher H₂ recovery (1-2 points) can be achieved with 40% smaller adsorption beds when the SER product gas is used as feed.

Construction of the SER#2 Process Test Unit

A great deal of current year effort was directed towards the development of a cyclic process test unit, referred to as SER#2. Unlike the current lab unit, the SER-2 system will permit study of the full sequence of SER process steps, performed in repetitive fashion, in a pair of industrial-scale tubular reactors at relatively high feed/purge flow rates (feed G-rate = 10 lbmole/hr-ft²). The unit will be used to demonstrate the cyclic steady-state performance of the SER system, and will allow us to directly characterize parameters such as CH₄ conversion, H₂ product purity, and H₂ productivity with respect to important process variables. These include reactor temperature, purge pressure and quantity, feed pressure, feed steam/methane ratio, axial temperature gradient, feed rate, and alternative pressure equalization steps.

A simple schematic and photograph of the SER#2 process unit is illustrated in Figures 7 and 8. The unit consists of two tubular reactors, each 1 in ID and 20 ft long. It includes a feed/purge gas manifold (CH₄, natural gas, H₂, N₂), steam generation systems for both the feed and purge gas, various high temperature switching valves, a vacuum system for carrying out sub-atmospheric regeneration steps, and analytical equipment needed to continually quantify the process flow rates (wet tests meters) and compositions (process mass spectrometer (MS)). Data acquisition is through the programmable logic controller (PLC) and process MS and includes quantification of

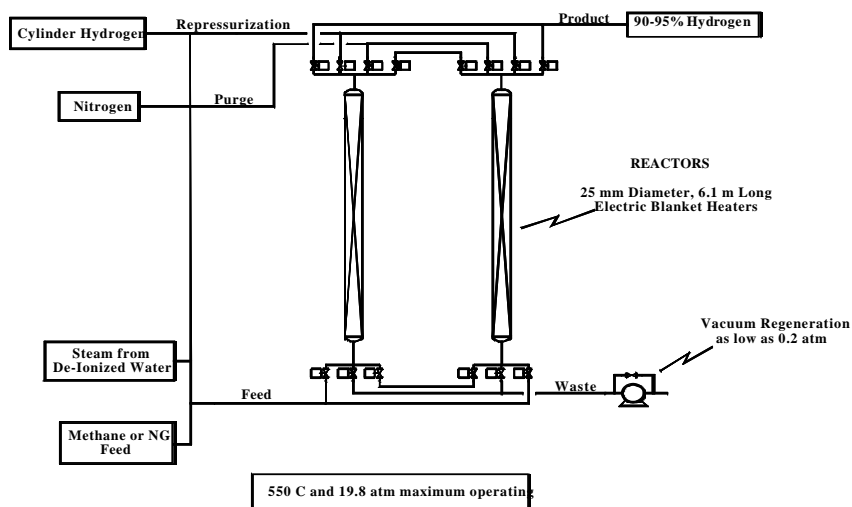


Figure 7: Schematic of SER#2 test unit

inlet and outlet flow rates, effluent gas compositions, and reactor temperatures (axially through the bed) and pressure (inlet and outlet). Valve sequencing is automated through the dedicated PLC system. The unit will be capable of testing various process sequences including vacuum purge, pressure equalization, feed or product repressurization, etc. Initial experiments will use external electrical resistance heaters for supply of reaction energy. Provisions have also been made for implementing HTF and /or IGH heating

modes. Extensive HAZOP safety analysis have been carried out to insure that the unit can be operated safely.

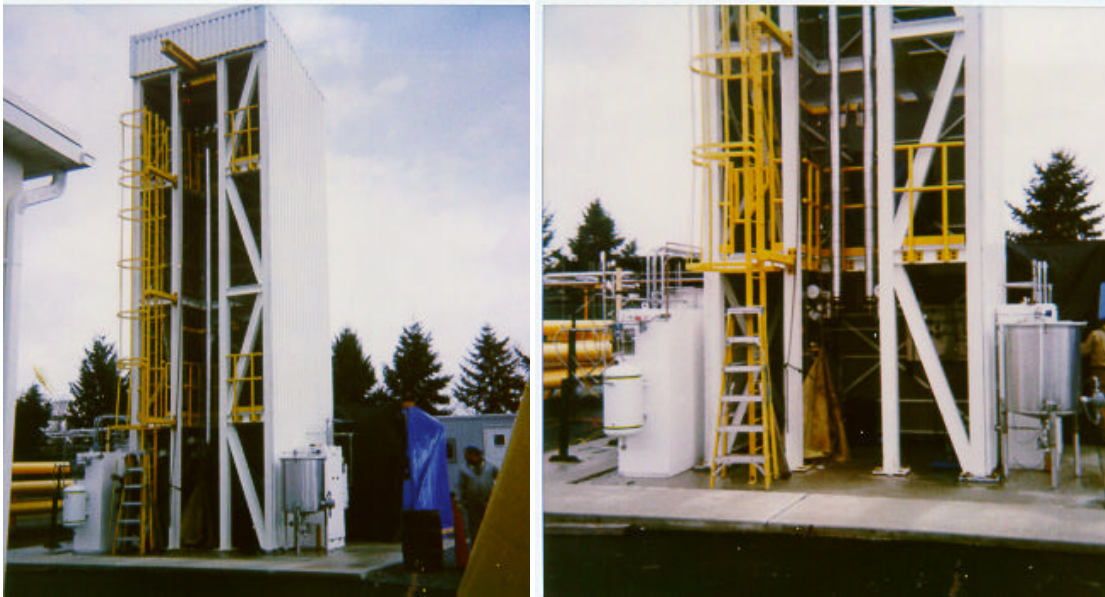


Figure 8: Photograph of SER#2 test unit

The unit was built and commissioned in Q1-3FY99, and will be operated through Q2FY00 to generate valuable process data. A detailed experimental plan has been drafted to guide this work.

CO₂ Adsorbent Development

Since laboratory testing of the potassium carbonate promoted HTC adsorbent has shown it to be attractive for use in the SER process, it was decided to proceed with the scale-up of this material. Sufficient quantities of adsorbent (~50 lbs) were prepared to sustain SER#1 and SER#2 process testing. After obtaining a batch of formed HTC from Alcoa, the material was promoted in the lab (via 2 lb batches) with K₂CO₃ using the incipient wetness method. TGA screening of the synthesized material showed that it had equivalent CO₂ capacity and desorption characteristics under dry gas conditions to the previous small-scale impregnation samples. This sample has been used in most of the SER#1 process experiments, and will be used in future SER#2 studies.

Long range supply of promoted K₂CO₃/HTC adsorbent for future PDU and commercial units relies on the manufacture of the activated adsorbent by an external vendor. Samples of formed HTC (the adsorbent 'support') from several different vendors have been evaluated in our lab. The as-received HTC was promoted with potassium carbonate and tested with the TGA unit. Each had acceptable CO₂ adsorption capacities at 450C that were 4-5 times greater than the non-promoted HTC. Analysis of these samples has also provided indications of relative properties between the various vendors such as adsorbent crush strength, pore volume, and potassium carbonate content, in addition to CO₂ capacity. Conversations with the vendors have identified their relative strengths and weaknesses (e.g. preferred impregnation techniques, interest in HTC business area, availability of personnel/equipment).

Aggressive supply timelines have been established with the adsorbent vendors that are based on the adsorbent requirements of the process units (SER#2, PDU commercial units). The first sample from the vendors is a proof-of-principle sample which will demonstrate that K_2CO_3 promoted HTC adsorbent with acceptable composition and adsorption performance can be made on a small scale using commercial techniques. The performance of this sample will be tested in the SER#2 cyclic unit. After this demonstration, a larger-scale HTC production campaign (e.g., >2000 lbs) will be conducted to demonstrate that a significant amount of adsorbent can be made that meets all product specifications (e.g. crush strength, CO_2 adsorption capacity, pore volume, and composition). This material will also be qualified in SER#2 and used to supply the future PDU in CY00. Thereafter, the promoted adsorbent will be produced via the industrial process to supply the first commercial units. The above timeline has been communicated and accepted by several vendors.

Impregnation of HTC extrudate with potassium carbonate is typically accomplished in the lab using incipient wetness techniques followed by activation at 300-500°C. During the current year, we investigated the use of spray impregnation routes to load the HTC with potassium carbonate. This process improves the control of loading potassium carbonate on the HTC, helps minimize the exotherm that occurs during incipient wetness, and decreases the amount of water removed during drying, i.e., lowers the cost of promoting the adsorbent. The loading of potassium carbonate can be optimized to prepare highly active HTC adsorbents at concentrations greater than 3.0 M K_2CO_3 . When 4 M K_2CO_3 is spray impregnated onto the HTC, the material has similar K_2CO_3 loading as the promoted HTC prepared in the lab using excess quantities of 2 M K_2CO_3 . Hence, these two materials exhibit similar CO_2 capacity and desorption characteristics. This allows for either spray impregnation or “dipping” techniques to be considered when preparing potassium carbonate promoted HTC in a commercial environment.

A second class of adsorbents, the H-family (H2, H3, H11) has been described in previous reports (Hufton, 1998). This year the effect of synthesis conditions (pH, water content, agitation, mixing and aging times) on the adsorption properties of the materials were investigated. Optimization of the synthesis procedure for material H3 yields higher yields of the adsorbents with ten times the CO_2 capacity and more efficient desorption characteristics than the K_2CO_3 /HTC adsorbents. With this new procedure, we have been able to produce several pounds of H11 adsorbent and form it via extrusion into 1/8” extrudates. This adsorbent has higher thermal stability than previous H-materials, and efforts are currently underway to evaluate its hydrothermal stability. Steam stability has been the major technical hurdle preventing utilization of these adsorbents in the SER process.

An additional experimental unit, the cyclic lifetime unit (CLU), has been built to help evaluate longer term (> 1 month) stability of the adsorbent and catalyst under dynamic hydrothermal process conditions. It will be capable of exposing four separate mixtures of catalyst and adsorbent to cycles of high pressure process gas (CH_4 , steam; 150-300 psig) and atmospheric pressure purge gas (N_2 , H_2 , steam) at temperatures up to 550°C. We will evaluate the performance and physical properties of the catalyst and adsorbent both before and after exposure to these conditions. The unit will also be used to determine the effect of common natural gas impurities (H_2S , heavy hydrocarbons) on adsorbent/catalyst performance and life.

Future Work

The next phase of effort will be directed towards the operation of the cyclic SER#2 unit so that more refined H₂-SER process designs can be developed. The unit will be used to first demonstrate the steady-state performance of the SER reactors, and then directly characterize the effects of various operating parameters (e.g., reaction pressure, temperature, regeneration conditions, purge to feed gas ratio, type of reactor heating system, etc.) on the steady-state process outputs (CH₄ conversion, H₂ purity, productivity).

Concurrent process testing efforts will continue with the laboratory-scale unit (SER#1) to investigate the effect of various process parameters (e.g., pressure) on the reactor performance, and to characterize the performance of current and next-generation CO₂ adsorbents (H-family) and catalysts (noble metals, reforming catalysts). Heat of adsorption data will be obtained for CO₂ on the K₂CO₃/HTC adsorbent with the recently built volumetric unit. Long term adsorbent and catalyst stability tests will also be carried out with the CLU and the K₂CO₃/HTC adsorbent.

The experimental data generated by the above efforts will be implemented into revised process designs on a continuous basis, and the economics of H₂ production by H₂-SER will be assessed. We will then be able to make a GO/no GO decision on construction of a 0.1MM SCFD H₂ demonstration unit (PDU) in Q2FY00. Design and construction of the PDU is planned for the latter part of FY00, with operation and demonstration in FY01. After the PDU decision, a commercialization strategy will be developed with the APCI Hydrogen business group.

Materials research efforts will be focused on addressing scale up of production of K₂CO₃/HTC to industrial levels (1000 lbs) for use in SER#2, PDU, and eventually commercial units. This will be accomplished by working directly with commercial adsorbent vendors. The development of an improved second-generation adsorbent will also be pursued.

Acknowledgments

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References / Publications / Patents

- Anand, M., J. Hufton, S. Mayorga, S. Nataraj, S. Sircar, T. Gaffney, "Sorption Enhanced Reaction Process (SERP) for Production of Hydrogen", *Proceedings of the 1996 U.S. DOE Hydrogen Program Review*, **1**, 537 (1996).
- Anand, M., Sircar, S., and Carvill, B.T., "Processes for Operating Equilibrium Controlled Reactions," 271PUS04904, U.S. Patent Pending (1995).
- Carvill, B.T., Hufton, J.R., Anand, M., and Sircar, S., "Sorption Enhanced Reaction Process," *AICHE J.*, **42**, 2765 (1996)
- Hufton, J.R., Mayorga, S.G., and Sircar, S., "Sorption Enhanced Reaction Process for Hydrogen Production," *AICHE J.*, **45**, 248 (1999).
- Hufton, J.R., S. Mayorga, T. Gaffney, S. Nataraj, and S. Sircar, 'Sorption Enhanced Reaction Process for Production of Hydrogen,' *Proceedings of the 1997 U.S. DOE Hydrogen Program Review*, 179 (1997).
- Hufton, J.R., S. Mayorga, T. Gaffney, S. Nataraj, M. Rao, and S. Sircar, 'Sorption Enhanced Reaction Process for Production of Hydrogen,' *Proceedings of the 1998 U.S. DOE Hydrogen Program Review*, 693 (1998).
- Mayorga, S. G., Golden, T. C., Gaffney, T. R, Brzozowski, J. R., and Taylor, F. W., " Carbon Dioxide Pressure Swing Adsorption Process Using Modified Alumina Adsorbents," U. S. Patent Pending (1996).
- Mayorga, S.G., J. R. Hufton, S. Sircar and T.R. Gaffney, 'Sorption Enhanced Reaction Process for Production of Hydrogen', Phase 1 Final Report, U.S. Department of Energy, July 1997.
- Nataraj, S.N., Carvill, B.T., Hufton, J.R., Mayorga, S.M., Gaffney, T.R., and Brzozowski, J.R., "Process for Operating Equilibrium Controlled Reactions," 271PUS05548, U.S. Patent Pending (1996).
- Sircar, S., Anand, M., Carvill, B.T., Hufton, J.R., Mayorga, S.G., and Miller, R.N., "Sorption Enhanced Reaction Process for Production of Hydrogen," *Proceedings of the 1995 U.S. DOE Hydrogen Program Review*, **1**, 815 (1995).
- Sircar, S., Hufton, J.R. and Nataraj, S., "Process and Apparatus for the Production of Hydrogen by Steam Reforming of Hydrocarbon", 271PUS05829, U.S. Patent Pending (1999).

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