Production of Hydrogen by Cyclic Sorption Enhanced Reaction Process

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The Sorption Enhanced Reaction Process (SERP) is a novel concept for hydrogen production by steam-methane reforming (SMR). It uses a fixed-bed reactor packed with an admixture of a SMR catalyst and a chemisorbent for selective removal of carbon dioxide (one of the reaction products) from the reaction zone (Hufton et al., 1999; Sircar et al., 2000). The unique steps of the SERP concept allow direct production of $\sim 90+$ mol. % hydrogen from the reactor at the reaction pressure. The impurities in the hydrogen product consist primarily of methane (<10 mol. %) and trace quantities ($<$ 50 ppm level) of carbon oxides. The chemisorbent is periodically regenerated by using the principles of pressure swing adsorption (PSA). The reaction can be carried out at a moderate temperature range of 450−550°C, which is much less than that of a conventional SMR reactor (800−900°C) packed with reforming catalyst only. The purpose of this article is to describe the actual cyclic performance of the SERP concept for hydrogen production using a pilot-scale apparatus with a proprietary SMR catalyst (noble metal on alumina) and a proprietary CO_2 chemisorbent (pelletized potassium carbonate promoted hydrotalcite), which has been described earlier (Hufton et al., 1999).

SERP Steps for Hydrogen Production

The SERP consists of the following cyclic steps:

Step a: Sorption-Reaction. The reactants consisting of a mixture of steam and methane at pressure P_R and temperature T_R are passed through the feed end of a packed-bed reactor containing the admixture of the catalyst and the chemisorbent. The reactor is previously pressurized at temperature T_R with steam to a pressure level of P_R. A hydrogen-enriched product stream at pressure P_R is withdrawn through the product end of the reactor until the carbon oxide concentration levels in the effluent gas reach a preset level.

Step b: Depressurization. At the end of step (a), the reactor is depressurized to near ambient pressure by withdrawing desorbed and void gases through the feed end. The effluent gas is vented.

Step c: Evacuation with Steam Purge. The reactor is then countercurrently evacuated to a subatmospheric pressure level of P_D, while introducing ambient pressure steam at temperature T_R through the product end of the reactor. The effluent gas, consisting mostly of desorbed CO_2 and steam, is vented.

Step d: Pressurization. Finally, the reactor is countercurrently pressurized from P_D to P_R by introducing steam at temperature T_R through the product end while the feed end is kept closed. The reactor is now ready to repeat a new cycle starting from step a.

The reactor is externally heated in order to carry out all four steps of the process under nearly isothermal conditions. The heat is used to (i) supply the net endothermic heat of reaction [created by simultaneous endothermic steam methane reforming (SMR), exothermic water gas shift (WGS), and exothermic chemisorption of CO_2] during step (a) of the cycle and (ii) provide the heat of desorption of CO_2 during steps b and c of the cycle.

Description of Test Apparatus

A pilot-scale test apparatus was constructed to evaluate the SERP cycle for hydrogen production. Figure 1 depicts the key parts of the apparatus. The reactor was made from schedule 40 stainless steel pipe, 1.0 in. (25.4 mm) ID and 240.0 in. (6.1 m) long. The inlet and the outlet ends of the reactor were fitted with several air-actuated, bellows sealed valves for transporting gas to and from the reactor. The feed end of the reactor was also connected to a laboratory-scale mechanical vacuum pump for evacuating the reactor. The reactor was heated externally using ten insulated, electrical heating blankets. The internal reactor temperature was monitored continuously and the data was fed back to control the heating element outputs in order to maintain a near constant reactor temperature during the cycle. All reactor temperatures and pressures were monitored using type K thermocouples and electronic pressure transducers.

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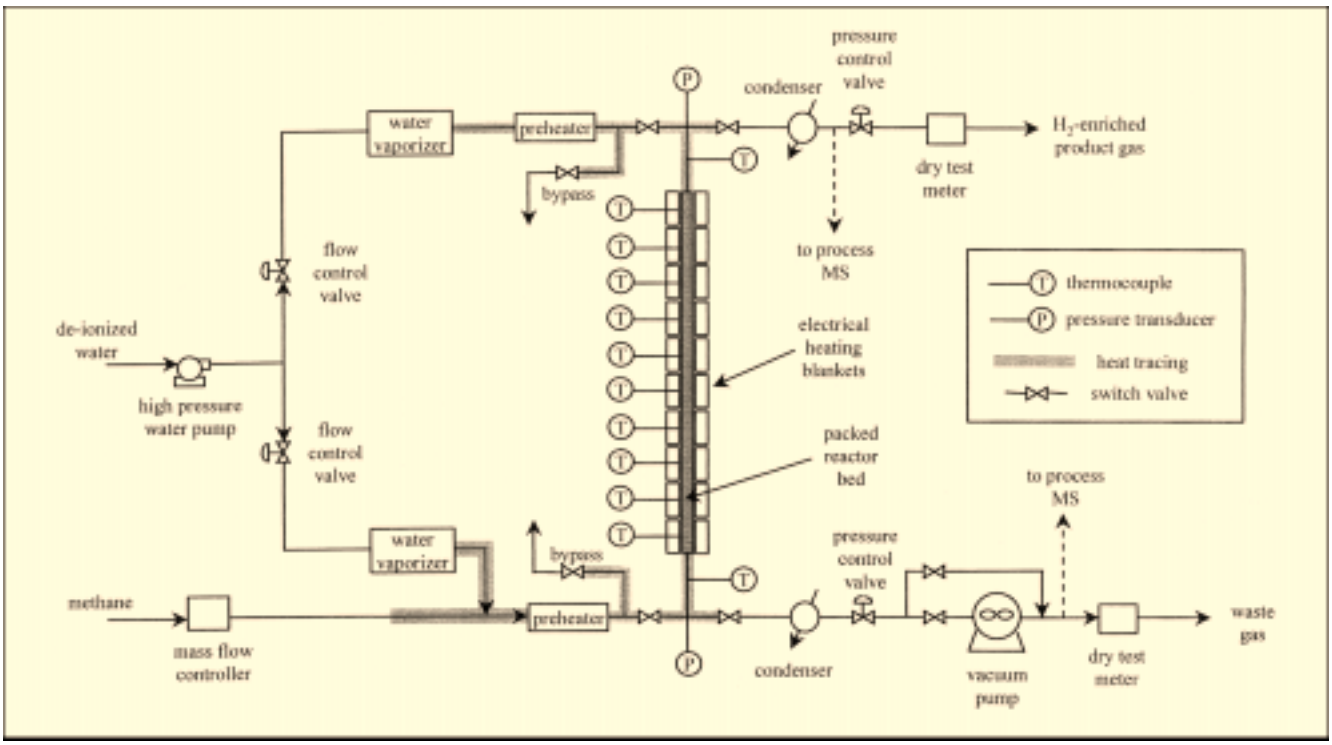

Figure 1. SERP test apparatus.

The feed methane was supplied from a bank of gas cylinders and its flow rate was controlled by a mass-flow controller. Steam for the sorption-reaction, purge, and pressurization steps was produced by pumping deionized water through a high-pressure liquid pump and two separate electrically heated water vaporizers. The flow rate of water was controlled using metering valves. Electric preheaters were used to raise the temperature of all gas streams to the reactor temperature before entering the reactor. Effluent gas streams were cooled down to near ambient temperature with a chiller-condenser system, and condensed water was removed. The effluent gas flow rates and molar compositions were measured using dry test meters and a process mass spectrometer.

The process data were collected by using an Allen-Bradley programmable logic control (PLC) system. All process and safety controls were directed by the same system. The key safety systems included an ultraviolet fire detection unit, high-temperature process alarms, high-pressure relief valves, and oxygen analyzers in the vacuum lines. The entire system was placed outdoors.

Cyclic Test Results

The column was packed with an admixture of the SMR catalyst ($\sim$ 2.0 lb, $\sim$ 0.9 kg) and the CO_2 chemisorbent ($\sim$ 4.0 lb, $\sim$ 1.8 kg). It was heated to a temperature of 490°C ($= T_R$). A mixture of steam and methane in the mol ratio of 6:1 was fed to the reactor at pressure P_R ($\sim$ 26 and 66 psia, $\sim$ 179 and 455 kPa). The feed gas flow rate was $\sim$ 7.7 lb mol/h/ft^2 (37.9 kg mol/h/m^2) (based on the empty cross-sectional area of the reactor). The reactor pressure was reduced to $\sim$ 15 psia ($\sim$ 103 kPa) during step b of the cycle. During the vacuum purge step (step c), the reactor pressures at the product and the feed ends of the reactor were, respectively, 10 ± 1 and 5 ± 1 psia. The inlet steam flow rate during step (c) varied between 7.5–9.2 lb mol/h/ft^2 (36.6–44.9 kg mol/h/ft^2). The individual cycle times for each step of the process were varied to alter the amounts of feed reactant and purge steam introduced into the reactor per cycle. The total cycle times for all steps were between 630 and 1,130 s.

The average hydrogen mol fraction in the product stream from step (a) of the process was maintained at $\geq$ 87.0 mol % (dry basis) for all runs, and the concentration of CO_2 impurity in the product gas was less than 130 ppm. The concentration of CO in the product gas was not detectable ($<$ 30 ppm). Steady state was typically achieved after $\sim$ 30 cycles of operation.

Table 1 summarizes the cyclic steady-state test results. It demonstrates that the SERP concept can be used to directly produce an essentially carbon oxide-free, hydrogen-rich gas stream by reacting methane and steam at a relatively low temperature of $\sim$ 500°C. The primary impurity in the product hydrogen is methane. The purity of hydrogen (mol % in dry basis) in the product gas and its specific productivity (lb mol of product/1b of solid in reactor/cycle) can be altered by changing the specific amounts of feed reactants and purge steam (lb mol/lb of solid/cycle) used in the process. For the same specific amount of steam purge, decreasing the specific amount of feed increases the purity of hydrogen in the product gas, but its productivity is decreased. For the same specific amount of feed gas, increasing the specific quantity of steam purge increases both the hydrogen purity in the product gas and its productivity.

Table 1. Cyclic SERP Tests for Hydrogen Production*

Feed Press. (psia)	Gas Quantities**			Hydrogen Product Purity (Dry)				Methane Conv. to Hydrogen (%)
	Feed	Purge Steam	Hydrogen Product	H_2 (%)	CH_4 (%)	CO_2 (ppm)	CO (ppm)	
26.1	0.60	0.75	0.20	88.6	11.4	60	ND	59
25.8	0.76	1.84	0.29	90.0	10.0	20	ND	66
26.2	0.60	1.88	0.25	94.4	5.6	40	ND	73
66.5	0.54	0.77	0.16	88.7	11.3	136	ND	54

*Feed Gas = 6:1 H_2O:CH_4, Reaction Temperature = 490°C.
**Gas quantities are in milli-lb mol/lb of solid in reactor/cycle.
ND = Not detectable.
SI unit: kPa = psia × 6.89.

Table 1 also reports the useful methane conversion to hydrogen by the SERP for the test runs. The useful conversion is defined by [mol of hydrogen in the product gas per cycle] / {4 [mol of methane in the feed gas per cycle]}. It should be noted that some hydrogen produced in the SERP reactor during step a is lost as void gas during the sorbent regeneration steps b and c of the cycle. The useful methane conversions from the SERP can be compared with the thermodynamic conversions of methane to hydrogen that would be obtained from a catalyst-only reactor operating at the test conditions of Table 1. They are reported in Table 2 along with the corresponding thermodynamic compositions of the hydrogen product gas (dry basis). The SERP concept (a) yields significantly higher methane conversion to hydrogen, and (b) provides a much purer product gas than the corresponding thermodynamically-controlled catalyst-only reactor operated under identical reaction conditions. This is because the removal of CO_2 from the reaction zone drives the reversible SMR and WGS reactions more towards the product side (Le Chatelier's Principle) and suppresses the formation of CO (Hufton et al., 1999).

It may be seen from Table 1 that increasing the reaction pressure in the SERP (for specific amounts of feed and purge steam) decreases the hydrogen productivity at a given hydrogen product purity. This suggests that the thermodynamics of the SMR reaction, which is adversely affected by increased pressure, controls the hydrogen productivity of the SERP despite the fact that higher pressure may increase the CO_2 capacity of the chemisorbent (Type I adsorption isotherm).

We calculated that the minimum thermodynamic reaction temperature to obtain a methane to hydrogen conversion of 73% by a catalyst-only reactor operating at a pressure of 26.0 psia (179 kPa) is 551°C. The corresponding product gas consists of 73.8% H_2, 7.0% CH_4, 16.4% CO_2, and 2.7% CO (dry basis). The third line of data in Table 1 shows that a much purer hydrogen stream (94.4% H_2, 5.6% CH_4, ~ 40 ppm CO_2 and < 30 ppm CO) can be directly produced by the SERP at a much lower temperature (490°C) with an identical methane to hydrogen conversion.

Table 2. Thermodynamic Limits of Reversible Steam-Methane Reforming and Water Gas Shift Reactions*

Press. (psia)	Equil Methane to Hydrogen Conv. (%)	Equil. Prod. Gas Compos. (Dry)			
		H_2 (%)	CH_4 (%)	CO_2 (%)	CO (%)
26.1	52	67.2	15.7	15.9	1.2
65.7	38	60.0	24.9	14.4	0.7

*Feed Gas = 6:1 H_2O:CH_4, Reaction Temperature = 490°C.
SI conversion: kPa = psia × 6.89.

Summary

The cyclic operation of the Sorption Enhanced Reaction Process (SERP) for direct production of a hydrogen enriched stream by reaction of steam and methane is demonstrated using a pilot-scale unit. An admixture of a proprietary steam methane reforming catalyst and a propriety chemisorbent for carbon dioxide is used as packing in the reactor. Steady-state performance data are reported for a reaction temperature of 490°C, reaction pressures of 26 and 66 psia (179 and 455 kPa), and a feed reactant composition of 6:1 steam/methane. The process is capable of directly producing 88–95% H_2 with methane as the primary impurity. The concentrations of CO_2 and CO in the product hydrogen can be kept below 40 ppm by controlling the operating conditions of the process. The conversion of methane to hydrogen can be much larger than that dictated by thermodynamics in a catalyst-alone reactor. The hydrogen product purity, which increases with decreasing hydrogen productivity, can also be manipulated by changing the operating conditions of the process. These characteristics of the SERP may be attractive for direct production of essentially CO free hydrogen in a fuel cell application.

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