

Evaluation of Hydrogen Sorption Enhanced Reforming with CO₂ Capture

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Metal hydrides are evaluated as hydrogen sorbents in a hydrogen production process (HSER) which combines chemical reaction and hydrogen separation in a single step. Experimental tests results indicate that surface modifications could reduce undesirable interactions towards process gas.

A technical and economical evaluation of the HSER process including CO₂ capture has been carried out and compared to conventional steam methane reforming (SMR). The technical evaluation of the HSER process shows potential for an increased energy efficiency compared to conventional SMR (80 % vs. 73 %).

The estimated cost of the HSER process appears to be somewhat higher than the conventional SMR process at this stage. This cost disadvantage could be reduced by more favorable conditions for CO₂ capture, which has not been taken into account in the current study. However significant cost reductions for the HSER process would require novel reactor designs and/or improved hydrogen sorbent formulations with improved stability and capacity.

1. Introduction

Large scale hydrogen production is conventionally carried out at high temperatures. The steam methane reforming reaction ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3 \text{H}_2$) is highly endothermic, and the heat required for the reaction is obtained through external heating.

Hydrogen sorption enhanced reforming (HSER) is a novel process for hydrogen production which combines chemical reaction and hydrogen separation in a single step using a solid material as hydrogen sorbent. By absorbing one of the reaction products, hydrogen, and continuously removing it from the reaction mixture one may shift the equilibriums and obtain sufficient conversion at a lower temperature. Hydrogen can afterwards be released by lowering the pressure or increasing the temperature of the hydrogen absorbent. Such a solution can result in lower operation temperatures leading to higher efficiencies (Børresen 2008).

Hydrogen-absorbing materials should exhibit high reactivity only towards the hydrogen gas. In other words, other gases should not affect the ability of the alloys to absorb and desorb hydrogen. In the HSER reactor the sorbent materials will be exposed to a gaseous mixture of the remaining fuel; CH₄, with H₂O, CO₂ and CO which all are chemically reactive. CO is found to be the strongest contributor to the deactivation of metal alloys. It has been suggested that chemisorption on the hydride/alloy surfaces leads to blocking of the hydrogen-active sites, thus decreasing the reactivity of the alloy towards hydrogen (Sakaguchi 1995).

Hydrogen storage metals and alloys like Mg, Mg₂Ni and LaNi₅ have been found to be resistant to O₂ at the PPM level; however, at high concentrations of oxygen the oxidation of the alloys takes place (Bouaricha 2002). Gases as CH₄, H₂O and CO₂ have also been found to be detrimental to intermetallic hydrides, including those based on LaNi₅, Mg₂Ni and TiFe intermetallic, due a chemical interaction leading to the formation of carbonates, metal oxides, hydroxides etc. (Selvam 1991).

Titanium and vanadium form hydrides at temperatures suitable for the HSER process. Ti-V alloys have been studied as related to their potential application for selective hydrogen absorption in gases containing CO and steam. In this work high temperature Ti-V metal hydrides were tested in cycle experiments in realistic process gas mixtures. A technical and economical evaluation has been carried out for the HSER process compared to conventional SMR. CO₂ capture has been included in both processes.

1. Experimental results and discussion

Various Ti-V alloys with noble metal surface coatings have been evaluated at relevant temperatures, pressures and gas atmospheres. Several experimental cycle tests of metal hydrides with surface coating have been performed. In Figure 1 experimental results of the metal hydride Ti90V10Hx with surface coating of Pd and Pt is shown. Small amounts of CO and/or steam were subsequently added to the gas during the course of temperature programmed absorption cycles. Desorption was performed by heating the sample in Ar gas. More details of the materials and methods can be found elsewhere (Suwarno 2012).

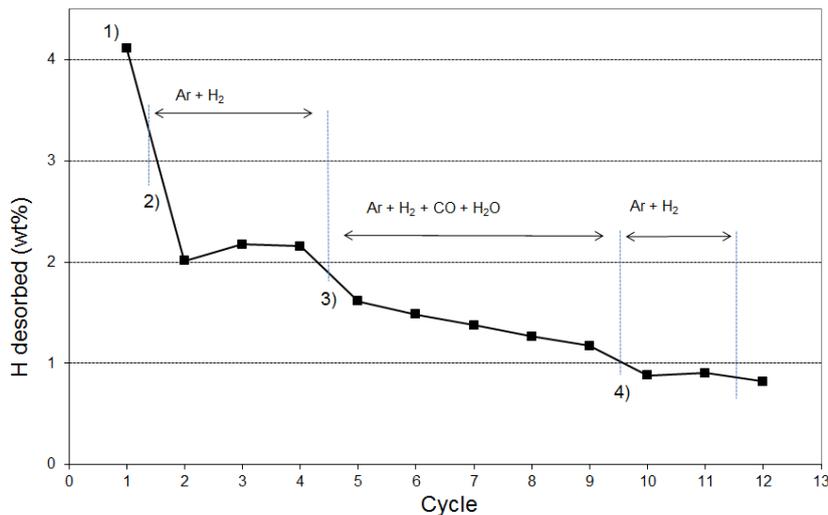


Figure 1: Cycle test showing effect of H₂O and CO on H desorbed from the hydrogenated Ti_{0.9}V_{0.1} + nano Pd/Pt sample. Gas flow rate was 100 ml/min and total pressure was 7 bar. Heating and cooling rates were 30 K/min. Absorption temperature window was 675-370 °C. Gas mixtures during the absorption were 1) Initial fully hydrogenated sample; 2) 2.6 bar Ar + 3.4 bar H₂; 3) 3 bar Ar + 3.6 bar H₂ + 0.25 bar CO + 0.01 bar H₂O; 4) 2.6 bar Ar + 3.4 bar H₂. Desorption in Ar gas was performed between 370-675 °C.

The results showed a distinct reduction in hydrogen absorption capacity for these materials when reforming gases were present as compared to the capacity under pure hydrogen atmosphere. This process was partially reversible and the existing results indicate a deactivation due to a surface effect. In fact, it has been observed presence of Ti-oxides at the surface of the alloys after cycling. These oxides may occupy active sites and make difficult the hydrogen absorption.

In addition to the instantly reduction when reforming gases were introduced, it has been observed a continuous decrease of hydrogen capacity for each cycle which could be related to accumulation of absorbed hydrogen during desorption periods (Suwarno 2012).

Understanding and improving this loss of absorption capacity will be necessary to find the cause to the pronounced decrease in capacity when gases such as CH_4 , H_2O and CO were added to hydrogen in the gas environment under absorption.

Further investigations should focus on the effect of other deposition metals to the properties of the hydride. Initial experimental results indicate that surface modifications might change hydrogenation behavior of the alloy in mixture of $\text{CO}+\text{H}_2$. Further improvement of the surface coating when it comes to deposition methods and choice of metal could reduce undesirable interactions towards process gas.

2. Technical and economic results and discussion

The technical evaluation, based on process simulations, indicates that HSER shows potential for an increased energy efficiency compared to conventional SMR. The difference in energy efficiency between HSER and SMR varies considerably with the operation conditions of HSER. Best case scenarios at auto thermal reactor conditions and a hydrogen plateau pressure of 2 bars indicate a net efficiency of HSER of 80 % (SMR 73 %).

Both two cases have been simulated including CO_2 capture with amine based technology, even though the partial pressure of CO_2 before capture is much higher in the HSER case than SMR. The CO_2 content in the process gas from the HSER reactor is almost 80 vol. % and for the SMR only 20 vol. %. Figure 2 shows a simplified flow diagram for hydrogen production via HSER and SMR.

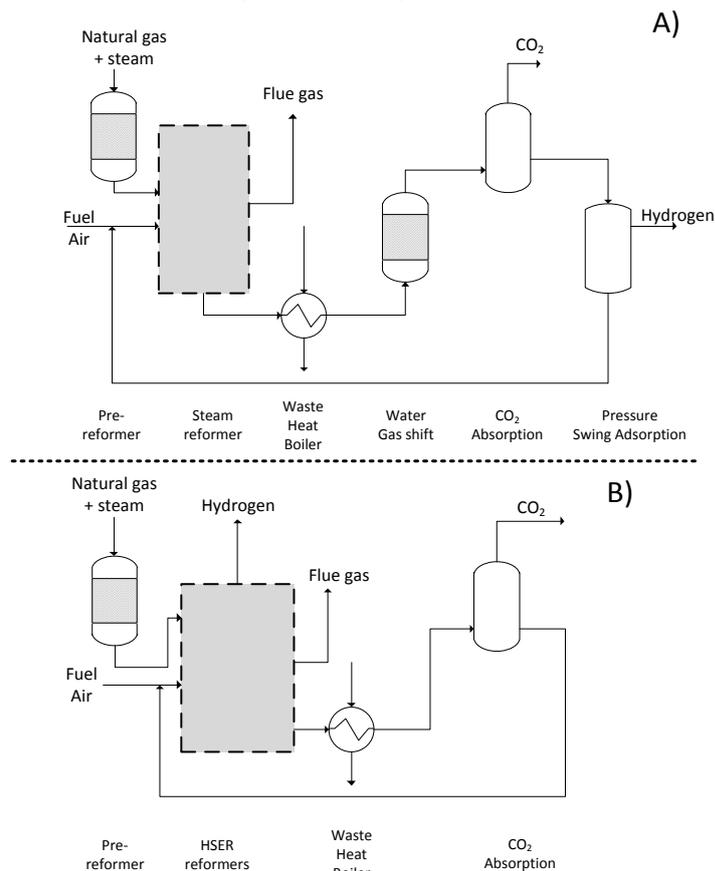


Figure 2: Simplified flow process diagram of SMR (A) and HSER (B). Details of the HSER reformer are shown in Figure 3.

The main process conditions and performance for the 8 t/h hydrogen plant based on SMR and HSER are compared in Table 1.

Table 1: Process conditions and performance of a hydrogen production plant; SMR and HSER case

	SMR	HSER
Total NG feed [kmole/h]	1524	1402
Hydrogen production [kmole/h]	3925	3925
Power import [MW]	3.3	4.0
Fired duty [MW]	79	55
Plant net efficiency [%] ¹	73	80

$$Net\ efficiency\ \% = \frac{Thermal\ output\ H_2 + Power\ output}{Thermal\ input\ NG - Steam\ Export\ (NGeq) + Power\ (NGeq)} \cdot 100$$

Steam export is calculated to natural gas (NG) equivalents assuming a NG boiler with 90% efficiency.

The power import is calculated to NG equivalent assuming a combined cycle NG power plant with 55% efficiency.

The desorption kinetics of the absorbent are identified as the rate limiting step in the process. An important assumption is that the present hydrogen acceptor also has a catalytic effect, which eliminates the need for separate reformer catalyst. The simplified reactor calculations are based on experimental performance data of existing metal hydrides obtained during idealised conditions. The experimental measured desorption rate have been used to size the required minimum reactor volume. Suggested reactor design parameters are shown in Table 2. The reactor switch time, defined as the time where each reactor are in the different modes, are determined from the absorption capacity and the desorption kinetics.

Table 2: Reactor design for SMR case and HSER case

	SMR	HSER
Catalyst volume [m ³]	27	---
Absorbent volume [m ³]	---	59
Absorption capacity [wt.%]	---	2
Desorption rate [kg H ₂ /kg acceptor, h.]	---	0.14
Number of reactors	1	3
Reactor switch time [min]	---	9
Number of tubes per reactor	254	253
Internal diameter tubes [in] ¹	4	6
Length [m]	13	13
Area of tubes per reactor [m ²]	1057	1575
Max temperature [°C]	870	750

¹ HSER has a higher diameter since the heat transfer is not so critical due to large volume of reactor

The proposed design and operation of the HSER reformer includes 3 identical reactors, which are operated at 3 different modes. During the reaction/absorption mode, natural gas and steam from the pre-reformer are routed into the reactor and converted to a mixture of H₂, CO, H₂O and CO₂, where H₂ are adsorbed. The heat required for endothermic reaction is balanced by heat stored in the catalyst/absorption mass and by the heat of absorption for H₂. When reaching the absorption capacity of the materials, the reactor is switched into desorption mode, where the absorption mass is heated up to the required temperature that allow hydrogen to be released. The absorbent mass are assume to maintain its performance with time. The reactor then enters a transition mode before going into the reaction/absorption mode. The proposed gas routing for the different modes of operation is illustrated in Figure 3.

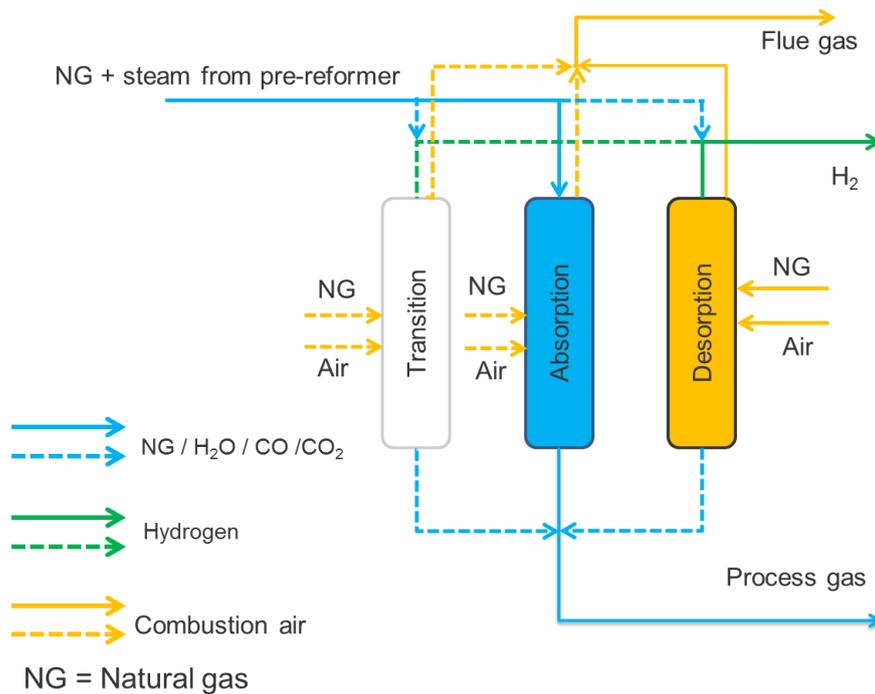


Figure 3: Principle for operation of the HSER system. Solid lines show the routing of feed and product gases for the reactors in operation for the given mode. Dotted lines show the routing of feed and product when the reactors have changed operation mode.

Typical cost distribution for a SMR reactor will be 50 % of the costs on the fire box and reactor tubes, and the remaining 50 % for the waste heat recovery section. As shown in Table 1 the SMR and HSER reactor contains the similar number of reactor tubes, but the tubes in the HSER have larger diameter to be able to contain the larger solid material volume. However, the HSER reactor operates at lower temperature and has a lower fired duty. The cost of the HSER fire box including reactor tubes is therefore assumed to be similar to the cost of the SMR firebox. The cost of the waste heat recovery section of the HSER will also be quite similar to the costs of the SMR heat recovery section. As the HSER reactor concept requires 3 reactor sections/fire boxes and one waste heat recovery section, the costs are estimated to be minimum 2 times the cost of the SMR, probably even higher due to complex design and advanced operation.

The total equipment costs of a hydrogen plant with a production rate of 8 t/h hydrogen, based on both SMR and HSER with CO₂ removal included have been estimated, assuming the HSER reactor cost to be 2 times the cost of the SMR reactor. The relative cost distribution for the main equipment parts are shown in Figure 4.

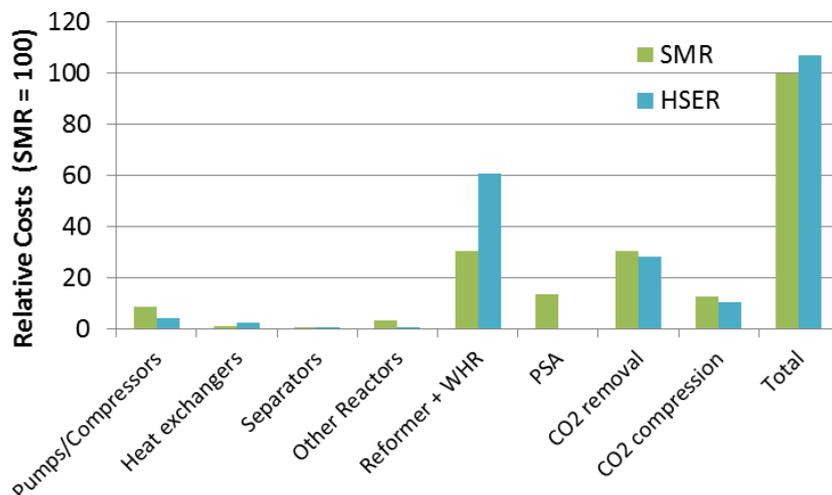


Figure 4: Relative major equipment costs for an 8 t/hour hydrogen plant based on an SMR reactor and a HSER reactor. HSER reactor costs = 2*SMR reactor costs. WHR = waste heat recovery, PSA = pressure swing absorption unit.

Even if the requirement for both shift reactors and PSA are eliminated in the HSER case, as well as a reduction in the costs of most other equipment, the total costs for the HSER equipment is slightly higher compared to the SMR equipment. This is due to the high costs of the HSER reactor system which accounts for over 50 % of the equipment costs.

3. Concluding remarks

Improvement of absorption capacity and stability of Ti-V hydrides when exposed to gases like CH₄, H₂O and CO is necessary. Experimental tests results indicate that surface modifications could reduce undesirable interactions towards process gas.

The technical evaluation of the HSER process shows potential for an increased energy efficiency compared to conventional SMR (80 % vs. 73 %) but at somewhat higher cost. The estimated cost of the HSER process appears to be somewhat higher than the conventional SMR process at this stage. This cost disadvantage could be reduced by more favorable conditions for CO₂ capture, which has not been taken into account in the current study. Significant cost reductions for the HSER process would require novel reactor designs and/or improved hydrogen sorbent formulations with improved stability and capacity.

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