Sorption-enhanced hydrogen production for pre-combustion CO_2 capture

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Abstract

Sorption-enhanced steam reforming of methane is a process, in which steam reforming reaction is carried out in the presence of a CO2 sorbent. The removal of CO2 from the reaction zone shifts the equilibrium to the product side and makes it possible to perform the reaction at much lower temperatures. In an experiment using potassium carbonate promoted hydrotalcite as CO2 adsorbent in combination with a steam reforming catalyst, it was shown that the average methane conversion over a adsorption cycle was more than 95%. Subsequently, the sorbent was regenerated with steam and this was repeated for 500 cycles without deterioration of the performance. Systems analysis shows that efficiency penalties can be as low as 5.5 percent point, provided that steam used in the regeneration step is kept low.

Keywords: CO_2 capture, pre-combustion, hydrotalcite, sorption

Introduction

In pre-combustion decarbonisation, the CO_2 produced is captured prior to combustion, while transferring the energy content of the fuel to hydrogen. Sorption-enhanced reforming is a special type of pre-combustion decarbonisation, in which the capture of CO_2 actually enhances the reaction rate.

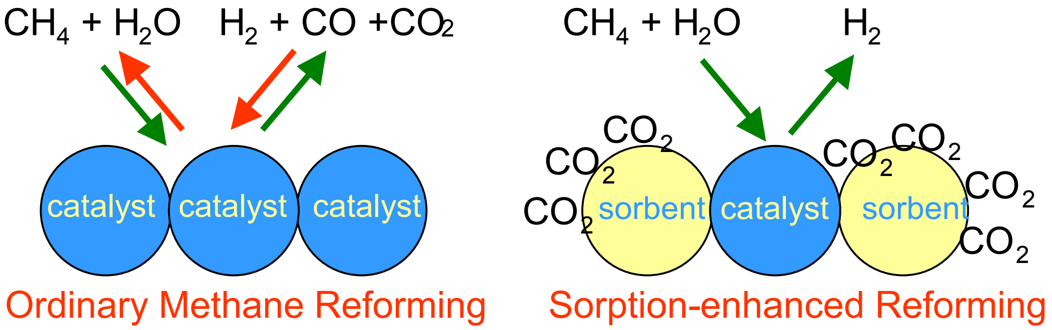

Figure 1. Inside the reactor of an ordinary and a sorption-enhanced steam methane reformer.

In an ordinary reformer hydrogen is produced using two equilibrium reactions, Steam Methane Reforming (SMR) and the Water Gas Shift Reaction (WGS). Figure 1 illustrates the overall reaction: methane and steam react to form hydrogen, carbon monoxide and carbon dioxide. However, at lower temperatures, the reverse reaction also occurs and an equilibrium is established. In a Sorption-enhanced reactor, CO_2 is captured by a sorbent and the reverse reaction cannot take place. So the equilibrium is shifted to the product (hydrogen) side. This makes it possible to run the steam reforming reaction at much lower temperature (400 - 500°C instead of 800 - 900°C). This principle can be applied to the shift section only (sorption-enhanced water gas shift: SEWGS) or to the entire reformer (sorption-enhanced steam methane reforming: SESMR)

In an electricity production system based on SESMR, the hydrogen is used in a combined cycle. At least two reactors are necessary: In the first reactor hydrogen is produced and the CO_2 stays in the reactor. The second reactor is in regeneration mode: the CO_2-saturated bed is regenerated using steam, which yields a pure CO_2 stream, ready for compression and storage (Figure 2). Air Products designed a system for Sorption-Enhanced Water Gas Shift (SEWGS), which used seven parallel reactors filled with catalyst and sorbent for continuous hydrogen production [1].

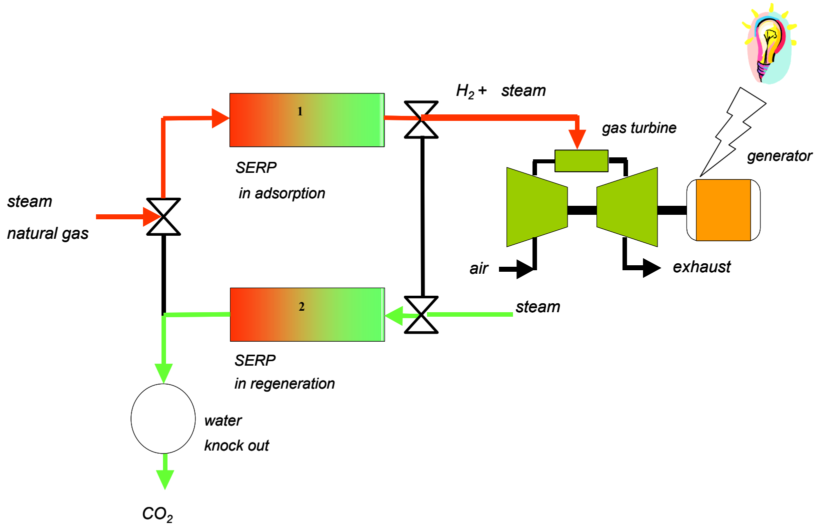

Figure 2 Electricity generation with CO_2 capture using Sorption-Enhanced reforming.

This paper describes the work at ECN on SESMR and SEWGS. We carried out:
- thermodynamic assessments of the complete SESMR system,
- kinetic modeling of CO_2 adsorption and the SESMR process,
- sorbent (promoted hydrotalcites) development and investigations of the CO_2 adsorption mechanism and lab-scale experiments on the cyclic SESMR process.

This paper focuses on the latter two subjects. The thermodynamic work on SESMR systems is summarized below and dealt with in more detail in another paper by ECN in this conference [2].

Systems analysis

A natural gas fired gas turbine combined cycle (NGCC), using a Siemens V94.3A turbine, was used as a reference system. Combined cycle power was approximately 380 MWe and efficiency 57.1% without CO_2 capture. In ASPEN+, a sorption-enhanced reforming (SESMR) system, fed by natural gas and steam was analysed, using promoted hydrotalcite as adsorbent in a pressure swing adsorption mode. The hydrogen produced by the SESMR system is combusted in the gas turbine and the CO_2 is compressed to 110 bar. A minimum CO_2 capture percentage of 85% was set as a boundary condition. In SESMR, underfiring of the reactor is necessary to run the endothermic reaction. When natural gas is used, less than 85% of the CO_2 is captured, so product hydrogen was used for underfiring in addition. The overall efficiency of this system was calculated to be 51.6%, which means that the efficiency penalty for CO_2 capture is 5.5 percent point. The most important parameter determining the system efficiency, was the amount of steam necessary to remove the CO_2 from the adsorbent. Calculations were performed using a molar ratio of steam to adsorbed CO_2 of 1.8. When amounts of steam higher than a steam to CO_2 ratio of about 5 are necessary, efficiency decreases sharply.

Kinetic modelling

A complete reactor model for sorption enhanced steam reforming of methane was made. It is now possible to solve a system of partial differential equations in two dimensions (axial coordinate and time) resulting in local values for 6 mole fractions (CH_4, H_2O, H_2, CO, CO_2, and N_2), the pellet-averaged amount of CO_2 adsorbed, gas velocity, pressure, and mean temperature. Adsorption kinetics is taken into account by the linear driving force model for an arbitrary isotherm (Langmuir, Freundlich, or

other) and reaction kinetics have been adopted from literature. The model is used to study adsorption and desorption of CO_2 and to design novel regeneration strategies.
Figure 3 illustrates the use of the model. It shows a model verification experiment, in which a CO_2 adsorption experiment on K_2CO_3-promoted hydrotalcite in ECN's lab scale reactor is simulated. The picture on the left shows that the model describes the experimental breakthrough curve well. On the right-hand side the CO_2 concentration inside the adsorbent bed of 3 cm length is shown. In the lower curves, that represent the situation early in the adsorption experiment (time between zero and 5 minutes), no CO_2 is observed in the outlet of the reactor (0.030 m on the horizontal axis). When the bed fills up, the CO_2 concentration at the exit of the bed increases. The model will be used to describe the much more complex situation when, next to CO_2 adsorption, also the steam reforming reaction is taking place. In that case, also profiles of the methane, CO and hydrogen concentrations will be calculated.

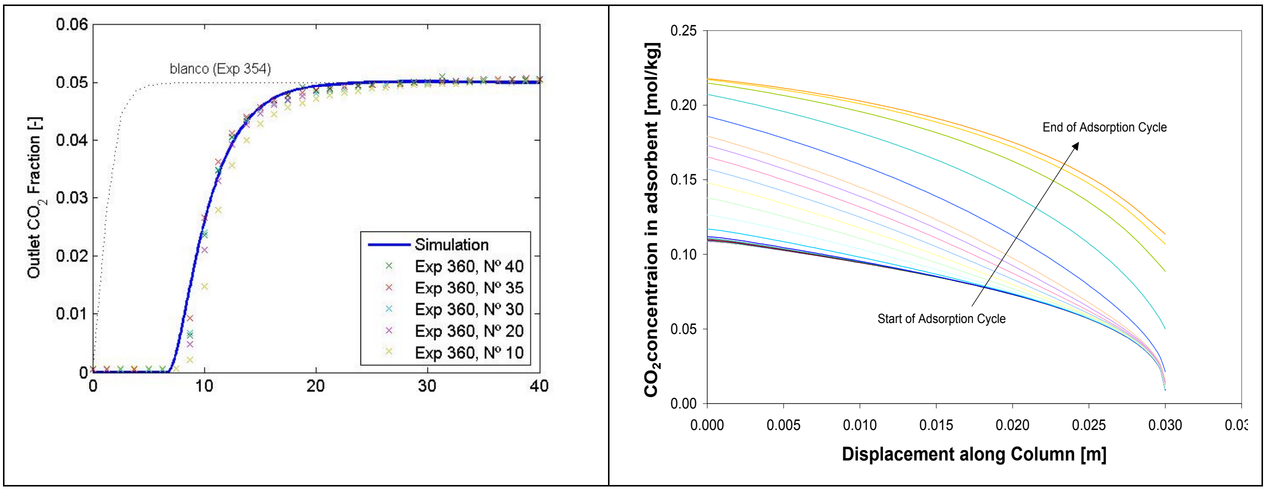

Figure 3 Results of modeling and experiment with CO_2 adsortion on K_2CO_3-promoted hydrotalcite at 400°C and atmospheric pressure.

Sorbent development

The work at ECN has mainly been based on hydrotalcites. Hydrotalcites (HTC), also called layered double hydroxides or Feitknecht compounds, belong to the family of anionic clays. The most common HTC is:

$$(Mg)_{1-x}(Al)_x(OH)_2(CO_3)_{x/2}.mH_2O$$

Experimental details have been described before [3]. The HTC was promoted by K_2CO_3, and 22 wt% was found to be the optimal concentration [3]. The effects of temperature, duration of the desorption step and purge flow on the adsorption and desorption properties have been studied, as well as the preparation methods.

Figure 4 shows that the presence of steam in the feed during the adsorption of CO_2 has a positive effect on the capacity of CO_2 of the K_2CO_3-promoted hydrotalcite. At concentrations of higher than 15 vol.% steam, capacity does not increase anymore. The CO_2 adsorption capacity of promoted HTC decreases with temperature. Above 500°C HTC loses its CO_2 adsorption capacity altogether. Strictly speaking, above 400°C the sorbent material is not a hydrotalcite anymore, since XRD measurements show that the hydrotalcite structure is lost at temperatures between 350 and 400°C [4].

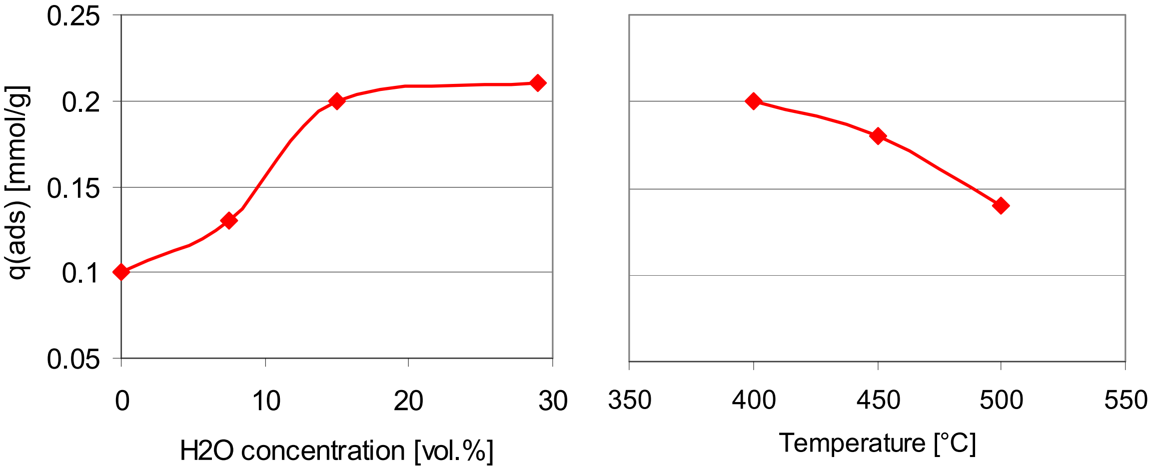

Figure 4 Amount of CO2 adsorbed vs. Left: H2O concentration (vol.% in nitrogen) and Right: vs. Temperature. Sorbent: 22 wt.% K_2CO_3 on Pural MG70.

Sorption-enhanced reforming experiments

In the case of sorption-enhanced reforming, it should be possible to reduce the temperature at which complete conversion of CH_4 is reached. In a standard industrial environment, temperatures of above 800°C are needed to induce high conversion of CH_4, but as can be seen from Figure 5 this is achievable at 400°C.

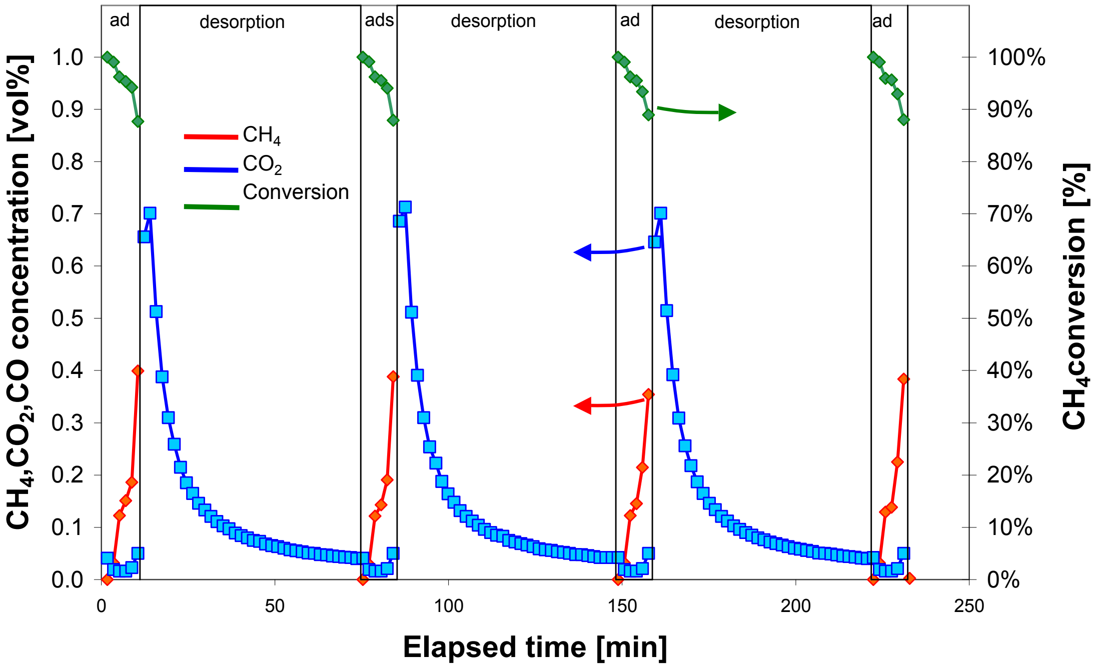

Figure 5 Three individual cycles of a 100-cycle sorption-enhanced steam reforming experiment. Sorbent: 22 wt.% K_2CO_3 on Pural MG70, catalyst: commercial pre-reforming catalyst. Sorbent:catalyst ratio 2:1. Gas composition: 2.9% CH_4, 17.5% H_2O, 79.5% N_2, Atmospheric pressure, Temperature = 400°C.

There are three main points that require attention from the proof-of-principle experiment:

- Firstly, the ratio of the time taken for desorption compared to adsorption-reaction is large. Although this has not been optimised in this experiment, it is clear that the adsorbent-catalyst bed must be purged at least to the extent that the amount of CO_2 expelled during desorption is the same as adsorbed during reaction, otherwise there will be CO_2 during adsorption. The capacity of the adsorbent used in this experiment is also much lower than the capacity measured during adsorption experiments.

- Secondly, there is breakthrough of CH_4 before CO_2. This could indicate that the kinetics of the reaction is too slow to effectuate complete conversion, or that the catalyst is less active in such an environment. Still, the average conversion during the adsorption-reaction side of the cycle is 95%. This is approximately a 40% improvement over the conversion expected at 400°C (55%).
- Thirdly, the process is stable for more than 100 cycles. In fact this sorbent sample was used in over 500 cycles without significant degradation.

One of the requirements to achieve these results is that a relatively large amount of steam reforming catalyst is used, much more than is necessary to reach equilibrium methane conversion at 400°C. Increasing the temperature obviously improves kinetics of the steam reforming reaction. Indeed, Figure 6 shows that breakthrough of methane occurs later at 450°C than at 400°C. In line with the findings in Figure 4, the breakthrough of CO_2 is earlier at 450°C than at 400°C, because the capacity of the hydrotalcite decreases with increasing pressure. Interestingly, in the desorption step, the CO_2 seems to be released faster at 450°C than at 400°C.

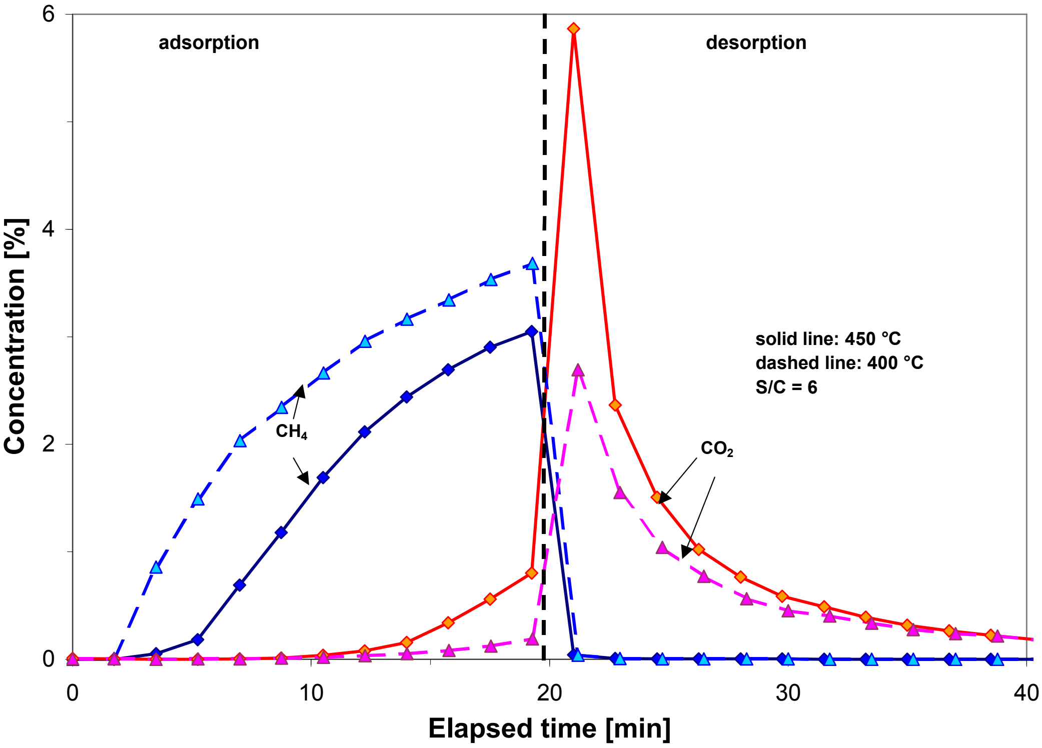

Figure 6 Effect on temperature on sorption-enhanced reforming. Sorbent: 22 wt.% K_2CO_3 on Pural MG70, catalyst: commercial pre-reforming catalyst. Sorbent:catalyst ratio 2:1. Gas composition: 2.9% CH_4, 17.5% H_2O, 79.5% N_2, Atmospheric pressure.

Conclusions

Thermodynamic analysis of an NGCC system with pre-combustion CO_2 capture via sorption-enhanced reforming, shows that efficiency penalties can be relatively low at 5.5 percent point. Potassium carbonate promoted hydrotalictes are used as sorbents for this process. Capacity for CO_2 adsorption increases with higher amounts of steam in the feed gas and decreases when temperature is increased. At 400°C, more than 95% methane conversion can be reached, much higher than equilibrium conversion under our experimental conditions, which is only 55%. The catalyst-sorbent system proved to be stable in an experiment of 500 adsorption-regeneration cycles. However, methane breakthrough occurs much earlier than methane and the time (and consequently steam input) required for regeneration of the adsorbent is still too high. Both points can be improved by carrying out the reaction at higher temperature.

Acknowledgment

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