

Comparison of several pre-combustion decarbonisation routes for hydrogen production from methane

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Abstract

The efficiencies, expressed as a function of CH₄ to electricity conversion, of four sorption-enhanced (SE) techniques for pre-combustion decarbonisation are compared for three different sorbents. The spread in efficiencies after some optimisation of design layout for SE-SMR (steam reforming of methane) and SE-ATR (autothermal reforming) was from 51.6 to 52.6% depending on the sorbent chosen. This is rather surprising when considering the differing operational requirements of these sorbents. The total amount of steam used in the cycle (both for the steam reforming and regeneration) was the most critical parameter in determining overall efficiency. As the total steam requirement is increased efficiency drops slowly. At a certain point, the efficiency starts to drop much more rapidly. At this point the amount of steam in the steam cycle is not enough, and extra steam has to be created. Operation in a regime where this extra generation can be avoided is highly desirable.

Keywords: CO₂, efficiency, pre-combustion decarbonisation

Introduction

Even though fossil fuels will remain the most important energy source for at least the first half of this century, there is a growing awareness that energy must be produced with lower greenhouse gas emissions. This has led to new technologies to reduce the emission of the CO₂ produced while using fossil fuels. One possibility is to use pre-combustion decarbonisation [1-5]. Here, the CO₂ produced is captured prior to combustion, while transferring the energy content of the fuel to hydrogen. Various pre-combustion routes for electricity production are being investigated including sorption enhancement of the reaction equilibrium during hydrogen production by CO₂ capture. One important question to be answered is where the sorption enhancement should take place, for example during methane steam reforming (SMR) [2-4], or only during a water-gas shift (WGS) [1,5] and how this affects the efficiency of the chosen systems. Additionally, many different CO₂ sorbents have been proposed, but they have very different properties with regards to regeneration (pressure swing or temperature swing) and operating window during adsorption. Rarely, have different sorbent/system combinations been compared. This paper attempts to address some of these issues. A comparison of four differing system concepts together with three very different sorbent materials is made. This is done in the context of production of electricity, and the concept-material combinations are compared in turn to the relevant base cases. Not all combinations have been compared (see Table 1), but the trends can be clearly seen. The goal is to find a sorbent-concept combination that has only half the efficiency penalty that is suffered when using a post-combustion technique.

Concept-Sorbent Combinations

Two base cases have been chosen in the study. A gas turbine combined cycle without CO₂-capture based on a Siemens V94.3A with a combined cycle power output of 380 MW_e, and an efficiency of 57.1%. The second system is the same with an additional post-combustion amine adsorption system. The four systems chosen to be compared with these two base cases are described below:

ATR(Air)-SE-WGS: This system is a combination of an air-driven autothermal reformer followed by a

shift section and then a sorption-enhanced shift reactor as known from the work of Air Products [5]. Essentially the majority of the feedstock has already been converted into H₂, CO and CO₂ before entering the sorption enhanced reactor.

ATR(O₂)-SE-WGS: This system is very similar to ATR(Air)-SE-WGS except that an Air Separation Unit (ASU) is included, which will significantly reduce the size of the ATR reactor.

SE-SMR: This system combines a pre-reformer with a sorption enhanced methane steam reformer that can be underfired by either product (H₂) or fuel (CH₄).

SE-ATR: This system is very similar to SE-SMR except sorption enhancement takes place in an autothermal reformer instead of a methane steam reformer. This has an advantage in that it reduces the amount of external heat is needed to drive the conversion of CH₄ to H₂.

Table 1 Concept-Sorbent combinations checked

Sorbent	System Air-ATR	O ₂ -ATR	SE-SMR	SE-ATR
	SE-WGS	SE-WGS		
HTC	X	X	X	
Li ₄ SiO ₄			X	X
CaO			X	X

The emphasis in this study was to look at the efficiency of the complete power generation system as opposed to the individual units. The sorption-enhanced reactors are modelled as black boxes and continuous processes although this is not necessarily the expected mode of operation in a final system.

Three main type of sorbent can be considered, all with distinguishing properties, and which are listed in Table 2. Hydrotalcites are considered because they are effectively the only high temperature pressure swing material available. CaO is chosen, because this represents the extreme of chemical reaction, with a very large temperature rise needed to regenerate the material. Also, very many groups around the world are concentrating on CaO, not least because it is a very abundant mineral, and could be very useful in situation were separation of CO₂ is needed from impurity rich carbon sources such as coal. Even deactivation of CaO, for example by sulphur components inducing CaSO₄ formation can be dealt with when the feed stock adsorbent is very cheap. Although is should not be overlooked that the catalyst used would also need to be robust against impurities. The third material type to be chosen was a complex metal oxide. Of the many possibilities Lithium Orthosilicate (Li₄SiO₄), as bought to the attention by Toshiba, was chosen. This offers somewhat of a halfway house between the constant temperature regeneration for HTC, and the very large temperature swing needed for CaO.

Table 2 Main properties of sorbent considered in system study

Sorbent Type	Adsorption T	Desorption T	Regeneration Mode
Promoted-Hydrotalcites	400-500	400-500	Pressure Swing
Complex Metal Oxides (Li ₄ SiO ₄ , Li ₂ ZrO ₃ etc..)	550-650	600-750	Temperature Swing
CaO (and CaO-based)	600-700	800-1000	Temperature Swing

The emphasis in this study is to look at the efficiency of the complete power generation system as opposed to the individual units. The sorption-enhanced reactors are modelled as black boxes and

continuous processes although this is not necessarily the expected mode of operation in a final system. IEA gas was assumed to be the fuel for the system, and the CO₂ was delivered at a final pressure of 110 bar, sufficient for sequestration. Several simplifications were also used: the steam system was assumed to operate at only one pressure, isentropic efficiencies were assumed constant and possible pressure drops in the reactors were ignored. The gas turbine inlet temperature and the gas turbine compressor inlet flow were kept the same, which results in slightly different fuel usage and electricity production of the systems analysed.

Results

Table 3 shows the efficiencies of some of the concepts using HTC as an adsorbent. It is clear that there is a significant decrease in efficiency compared to the base case, although all sorption-enhanced concepts perform better than the post-combustion amine adsorption concept. Several interesting remarks can be made at this point. Underfiring with product (H₂) is necessary to reach 85% CO₂ capture in the SE-SMR case. Also although the air driven ATR concept is more efficient than the O₂-driven variant, the decrease in size of the latter might still make the system more economically viable.

Table 3 Comparison of the efficiencies of several concepts using hydrotalcites as sorbent material

Concept	Efficiency (%)
ATR(O ₂)-SE-WGS	48.5
ATR(Air)-SE-WGS	50.4
SE-SMR	51.6
BASE (no capture)	57.1
Post-Combustion Capture (Amine)	48.0

Table 4 Comparison of the efficiencies of several adsorbent materials together with the SE-SMR concept

Selected Efficiencies	Base Case	Non-pressurised underfiring	No desorption turbine
<i>SE-SMR</i>			
HTC	51.6	49.3	51.4
Li ₄ SiO ₄	52.2	47.7	51.0
CaO	52.6	45.7	50.8

Table 4 shows a comparison of the efficiencies of the SE-SMR concept using different materials. HTCs perform the best in this comparison, but they still do not perform to the required efficiency goal of 52.6%, i.e. half way between the two base cases one with no capture, and the other with amine capture. Also two variations on these base cases are shown. In the first, the underfiring of the reformer is not done under pressure, and in the second a desorption-turbine is used to recover some of the energy in the purge stream. These modifications are shown in Figure 1. It is clear that non-pressurised underfiring is very detrimental to the efficiency of the system, causing a loss of even 6.9% to the efficiency of the CaO SE-SMR system. The HTC SE-SMR system is less sensitive to atmospheric underfiring, but still loses 2.3% efficiency points.

In the same way, the CaO SE-SMR system is also more sensitive to using a desorption turbine than the HTC SE-SMR system. The range of efficiencies for all the reforming based systems with all the sorbent falls in the rather narrow range of 51.6% to 52.6%. Unfortunately, this is insufficient to be able to pick a system configuration that will in practice outperform others.

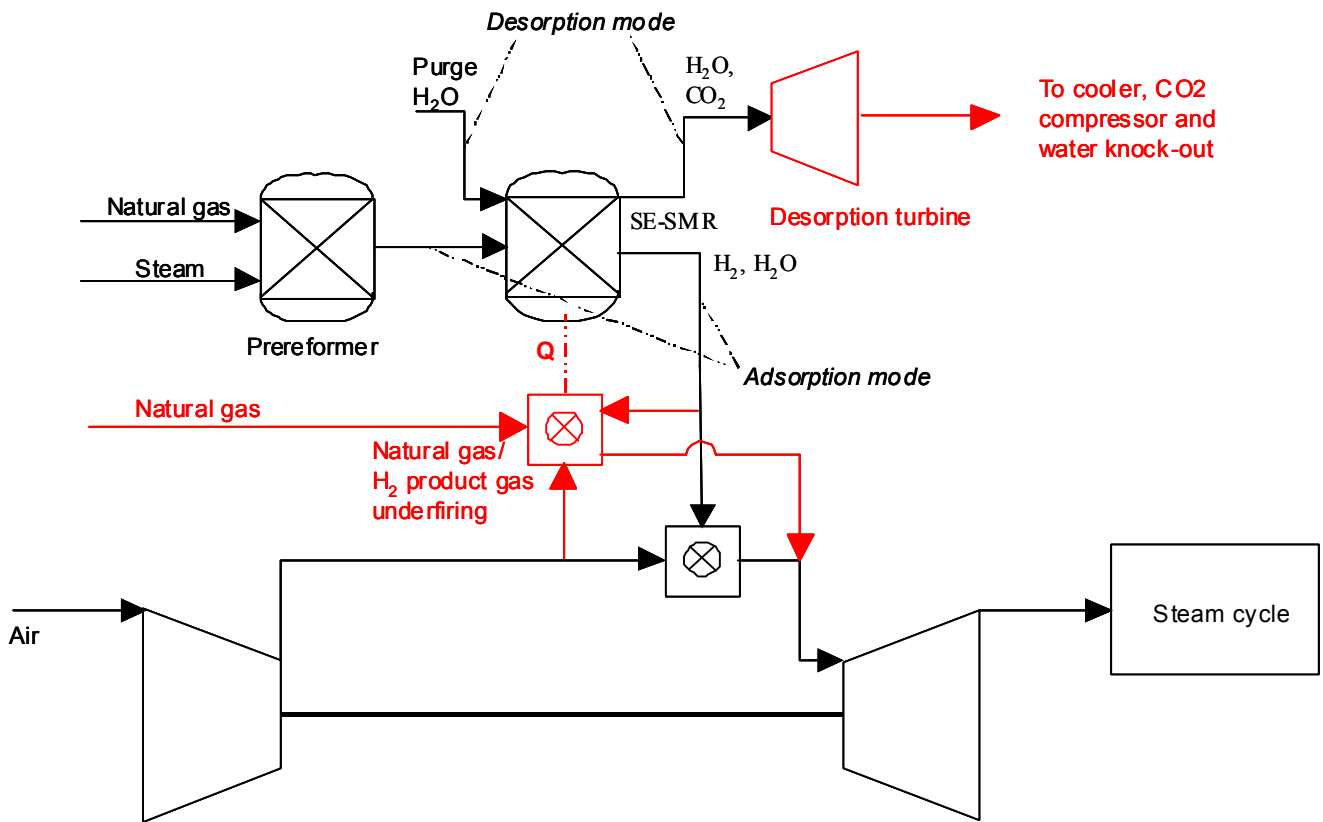


Figure 1 Representation of SE-SMR system, with changes that induce efficiency improvements shown in red; pressurised underfiring and a desorption turbine.

This systems analysis can however be used to highlight how the steam/ CO_2 ratio during regeneration and the S/C ratio in the steam reforming reaction have a synergetic effect on the efficiency. This is shown in Figure 2. There are obviously two regimes present. At lower S/C ratios the efficiency drops slowly as the steam required is increased. This is until a point that the efficiency rapidly starts to drop. This point is also a function of the S/ CO_2 ratio. This behaviour is shown in Figure 3. Below the line shown, there is enough steam in the system to drive both the reforming and the desorption cycles, but above the line, extra fuel is used in producing this steam and the efficiency drop rapidly. As a simple rule of thumb it is possible to say that the total steam needed for both reforming and desorption should not be more than 7 mol/mol.

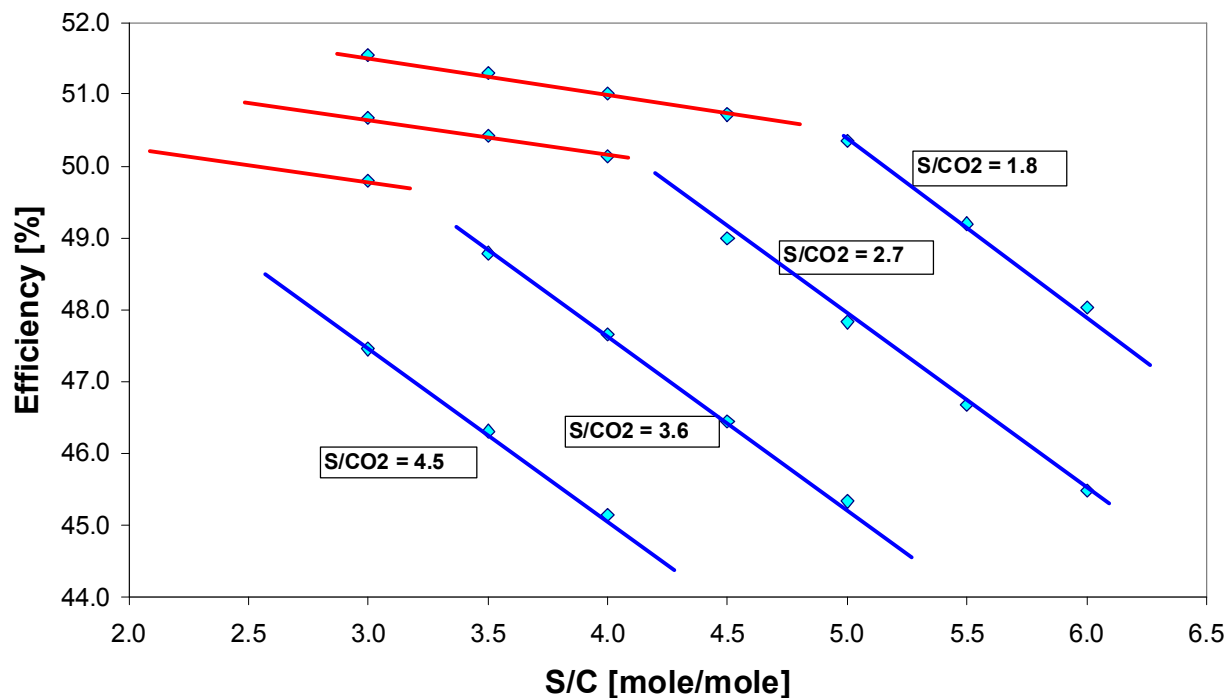


Figure 2 Effect of Steam/CO₂ ratio and S/C ratio during steam reforming of methane on the efficiency of the SE-SMR concept.

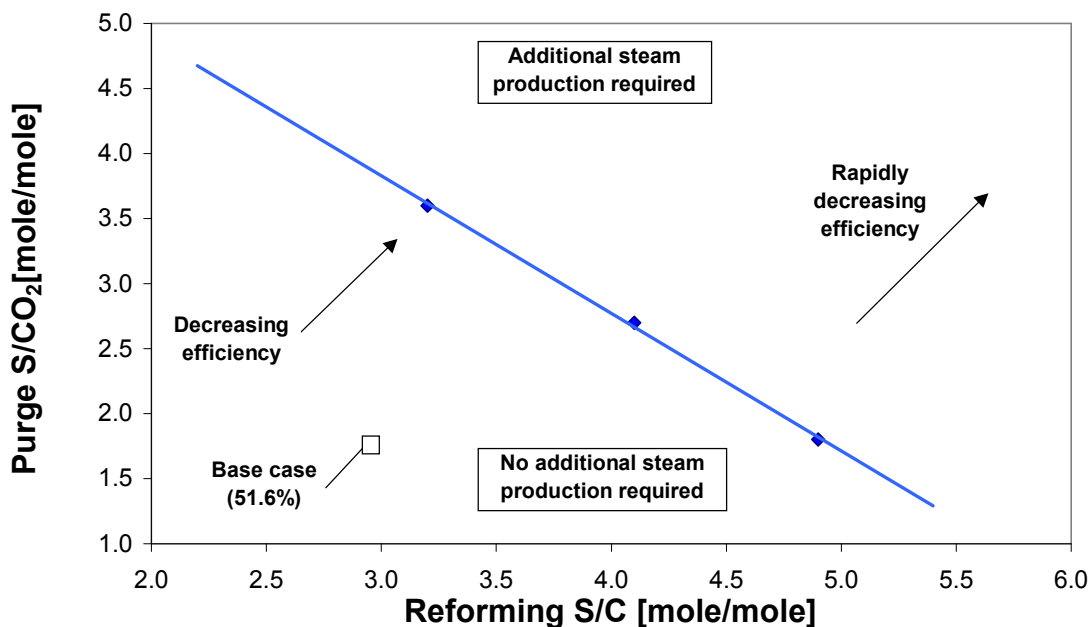


Figure 3 Relationship between S/C and S/CO₂

Conclusions

This study has begun the process of matching different pre-combustion decarbonisation system concepts with different types of adsorbents. The performance is still at or below the target 52.6%, i.e. halving the efficiency penalty as compared to a post-combustion amine adsorption configuration. It has, however been shown that the choice of concept and adsorbent cannot be taken independently of one another. New concepts and improved adsorbent properties will undoubtedly lead to more efficient pre-combustion options. Pressurised underfiring and a desorption turbine are necessary to attain higher

efficiencies. Surprising the choice of sorbent had little effect on the overall efficiency, even though the different sorbent act in different regimes of temperature and pressure. In all cases, the most important factor in determining efficiency was the steam required for methane reforming, and the steam required for desorption of CO₂ from the sorbent. Keeping the total steam requirement for both these processes beneath 7 mol/mol avoids moving into a regime where efficiency drops rapidly with increasing steam usage. This is related to the need above this threshold to make more steam than can be extracted from the steam cycle without extra methane combustion.

Acknowledgement

This research is part of the CATO programme, the Dutch national research programme on CO₂ Capture and Storage. CATO is financially supported by the Dutch Ministry of Economic Affairs (EZ) and the consortium partners. (www.co2-cato.nl).

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