Sorption-enhanced steam-methane reforming: CaO-CaCO$_3$ Capture technology

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Abstract

Calcium oxide (CaO) has been investigated in the context of CO$_2$ capture. In its application for the sorption-enhanced steam-methane reforming process (SE-SMR), CO$_2$ is captured in a sorption mode through the formation of CaCO$_3$, at which stage, the conversion of CH$_4$ to H$_2$ is also enhanced. Subsequently, the CO$_2$ is released in a separate desorption mode where the CaCO$_3$ is calcined to CaO. In a combined system modeling and experimental approach a sweet-spot in operational conditions has been determined in terms of adsorption-reaction and desorption temperature and pressure. Additionally the required performance in terms of cyclic capacity has been determined in relation to system efficiency. Long term cyclic capacity under sweet-spot conditions has been demonstrated in a lab-scale experiment in excess of 200 loading cycles, with stabilization of cyclic capacity occurred after 100 cycles, and above the required minimum of 15% of the thermodynamic capacity. Increasing the adsorption temperature above 600°C reactivated the CaO-CaCO$_3$ sorbent system.

Keywords: Pre-combustion decarbonisation; CaO; CaCO$_3$ CO$_2$ sorbent; Cyclic capacity; Temperature swing

1. Introduction

Calcium oxide (CaO) is a material that is being widely investigated in the context of CO$_2$ capture, for both pre-combustion and post-combustion processes [1]. One such pre-combustion application is the sorption-enhanced steam-methane reforming process (SE-SMR), also known as sorption-enhanced reaction process (SERP) [2]. CO$_2$ is captured in a sorption-reaction mode through the formation of CaCO$_3$, at which stage, the conversion of CH$_4$ to H$_2$ is also enhanced. Subsequently, the CO$_2$ is released in a separate desorption mode where the CaCO$_3$ is calcined to CaO. System calculations have shown that the process can be quite efficient in terms of power generation if the steam consumption in the two stages of the cycle can be kept below a threshold value of 7 H$_2$O per carbon processed.

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and captured, bearing in mind an overall target of 90% CO₂ capture [3]. Furthermore, a sweet-spot in operational condition has been identified with respect to cyclic capacity, and operational temperatures and pressures [4]. Building on these finding, experimental reported here shows that the required cyclic capacities for long term operation can be achieved in lab-scale experiments.

There are many operational parameters that can influence the overall performance and efficiency of the SE-SMR reactor within the context of power production combined with CO₂ capture. Thermodynamic limitations on the formation and calcination of CaCO₃ drive the temperatures at which the sorption-reaction and desorption-calcination steps take place. They have a fundamental impact of the amount of steam needed for steam reforming on the sorption-reaction side, and the amount of steam used in the desorption-calcination reactor. The effect of tuning process operating conditions on system efficiency has been investigated by process simulations using Aspen Plus®. Possible system heat integration routes to reduce the efficiency penalty are proposed and the results of the process simulations are presented.

Many studies have shown that the capacity of CaO for CO₂ can be seriously impaired during cyclic operation. This study sets bounds on the allowable amount of sorbent performance degradation without significant loss in system efficiency. The sorbent must retain at least 15% of its thermodynamic capacity in cyclic operation to avoid a large drop in efficiency.

2. System Evaluation

The interaction of CO₂ with the CaO-CaCO₃ system is not one of adsorption, i.e. a surface interaction, but a bulk thermodynamic interaction, i.e. absorption. This means that at a given temperature, there will be an associated partial pressure of CO₂. In a sorption-reaction step the partial pressure of CO₂ in a system will never be lower than this equilibrium partial pressure, such that the possible conversion of CH₄ in an SE-SMR is essentially limited by the slip of CO₂. At low temperatures, CO₂ slip will be low, but the enhancement of CH₄ conversion would be high, such that a desired CO₂ capture target could be reached. However, the kinetics of CaCO₃ formation also starts to play a role, and the desired partial pressures of CO₂ cannot be reached. At higher temperatures the thermodynamics of the steam-methane conversion is improved, as is the kinetics of CaCO₃ formation but the amount of slip of CO₂ is also increases. There is a trade-off in terms of temperature and pressure for the operation of such a system when a specific level of CO₂ capture is required.

Similarly in the desorption step a trade-off is present. At low temperatures, the maximum partial pressure of CO₂ that can be recovered from the sorbent is limited by the same thermodynamic properties that enhance reaction at lower temperatures. Therefore, the temperature of the desorption step will always be higher that that of the adsorption step, as this will increase the partial pressure of CO₂ in the stripping gas. Similarly, the desorption must be carried out at as lower total pressure as possible, to increase the proportion of the exhaust that is CO₂. In the case where steam is used as a carrier gas for the CO₂, which is a good choice because it can be easily condensed out of the CO₂ stream before being prepared for sequestration, minimizing the steam usage can be achieved in this manner. This will be beneficial to the overall system performance [3]. Essentially calcination at an extremely high temperature would lead to a high partial pressure CO₂ stream, but then the problem become on of CaO-CaCO₃ performance and realistic possibilities for reactor materials and design.

The model used to describe the SE-SMR simulations using Aspen Plus® have been described elsewhere [3]. In terms of operational parameter, the thermodynamic dictate that efficient power production from SE-SMR requires; production of high partial pressure of hydrogen; minimization of steam use; low CO₂ slip; and a temperature swing operational mode. Figure 1, shows the required temperature swing in a system that operate in the sorption-reaction mode at 17 bar, 600°C and a Steam-to-Carbon (S/C) ration of 4.2. These are parameters that allow a carbon capture ration of 85% provided the sorbent can be fully regenerated [4]. The temperature swing is set out as a function of the S/CO₂ ratio desired in the desorption mode. Operation of the desorption mode at the same pressure as the sorption-reaction mode means that the required temperature swing is in excess of 350°C even in a large excess of steam, i.e. at an operational temperature above 950°C and approaching 1080°C at low steam usage. Both the absolute temperature and size of the swing required will represent a large engineering investment in terms of both the material to be used (vessels and sorbent), and how to physically introduce so much heat into the system. At a desorption pressure of 1 bar, the needed temperature swing is ~200°C lower under all S/CO₂ ratios. This represents a more probably scenario in terms of sorbent capabilities and physically heating the sorbent to the desired
temperature, but introduces the engineering problem of how to circulate a solid between two reactor systems at different pressures. No solution is offered here, although a temperature swing even in excess of 300°C would seem to be very difficult to achieve, meaning that any viable solution would also require a pressure swing cycle.

![Diagram showing variation of required temperature swing for the desorption step as a function of the S/CO₂ purge ratio for a system operated in adsorption mode at 600°C, S/CH₄ = 4.2 with a carbon capture ratio of 85%.

The variation in system efficiency as a function of the S/CO₂ purge required is shown in figure 2. The system is most efficient at the lowest S/CO₂ ratios, as would be expected [3], but as can be seen in figure 1; the size of the temperature swing would become prohibitive. The sweet-spot in operations can be determined from the performance criteria in figures 1 and 2, combined with knowledge of sorbent properties and engineering aspects. Operation in a temperature-and-pressure swing-mode with sorption-reaction at 600°C, S/CH₄ = 4.2 and desorption at 820°C and S/CO₂ = 1.8, will offer a carbon capture ratio of 85% and a system efficiency for power generation with production of sequestration ready CO₂ of 51% [4].

![Diagram showing variation in system efficiency as function of S/CO₂ purge ratio required for two different desorption pressures; sorption-reaction conditions are the same as in figure 1.

This also satisfies the criteria of reducing the Steam to total carbon processed and captured ratio below 7 as has been previously demonstrated as a minimum requirement [3]. Of course, should the size of the temperature swing be increased, a further improvement of 1.5 %pt could be achieved for ~500°C. This however does not seem currently
feasible. The calculations performed took into account a perfect sorbent, with full thermodynamic capacity, however many studies have shown that CaO-CaCO₃ looping cycles suffer from rapid degradation of cyclic capacity. A study was performed to determine the effect of cyclic capacity on system efficiency, shown in figure 3, and described elsewhere in detail [4].

![Figure 3: System efficiency as a function of the fractional conversion of CaO to CaCO₃ achieved in the cycle. Sorption–reaction condition as in figure 1. Desorption conditions: S/CO₂ ratio: 1.8; temperature swing 220°C.](image)

Low cyclic capacities have a strong effect on the efficiency of the system when no system optimizations are performed. However, the following optimizations are introduced: using the sensible heat in the hot desorption solids to preheat both fuel and provide energy for the steam-reforming reaction, efficiency can be increased [4]. If the cyclic capacity of the sorbent can be maintained above ~15%, the system can operate at maximum efficiency under the selected sweet-spot conditions.

3. Experimental Results

Experiments have been carried out to verify the findings of the thermodynamic and system calculations. The experiments where performed in a small fixed bed reactor unit, with complete control of the gaseous environment, such that the sorbent could easily be exposed to variations in partial pressure of different component gases, including steam and CO₂, an operated for long periods of cyclic operation. Typical bed loading were of the order of 2-3 g CaO, with a typical desorption flow of 30ml/min and desorption flow of 100ml/min of which up to 30% is steam and up to 25% CO₂, as described elsewhere [3,5]. Cyclic capacities were determined by used of the mass balance of inlet and outlet conditions determine by a combination of gas chromatography and CO₂ analyzer.

The CaO used was a standard product from a commercial manufacturer. In a first set of experiments the, slip of CO₂ at the reactor outlet was measured as a function of the temperature. This was to confirm that the CO₂ concentration of an inlet gas will be reduced to the thermodynamic level during the loading of CaO for this reactor set-up. This indicates that there are no problems with the kinetic regime for this material in the reactor chosen under these reaction conditions. Figure 4 shows that the CO₂ slip was very close to the thermodynamic equilibrium partial pressure of CO₂. The cyclic capacity of the material was then determined with sorption at 600°C and desorption at 800°C, which corresponds to well to the temperature swing shown to be necessary for sweet-spot operations. This is illustrated in figure 5. Here the cyclic capacity at breakthrough, i.e. not the total available capacity, but the capacity
loading achieved when the CO₂ slip is significantly higher than the thermodynamic slip is shown as a function of cycle number. Note the full thermodynamic capacity of CaO is near 18 mmol CO₂ / g CaO. The stabilized value of 3.5 mmol CO₂ / g CaO achieved with this sorbent, i.e. ~20% of the full thermodynamic capacity is sufficient to justify further testing in a SE-SMR setup.

Figure 4: Measured slip from reactor as function of temperature compared to thermodynamic data.

Figure 5: Cyclic capacity of fresh CaO in CaO-CaCO₃ looping cycles as a function of cycle number with sorption conditions 15% CO₂, 600°C, and desorption conditions 800°C.
Deactivation of the sorbent is strongest at the lowest temperature. The minimum allowable capacity for avoiding efficiency losses is also shown. Here, after exposure to lower temperature sorption conditions, the sorbent does not reactivate to the minimum cyclic capacity required. In order to achieve this adsorption must be carried out at the higher temperature of 650°C. Of course, these experiments have been carried out at atmospheric pressure, whereas in a real SE-SMR environment, the pressure would need to be much higher to produce the high pressure hydrogen necessary for efficient electricity generation. The following step is to reproduce these sustainable capacities at higher partial pressures of CO₂, and eventually under SE-SMR conditions.

4. Conclusions

System evaluations have shown that there is a sweet spot in operational conditions for an SE-SMR system in terms of efficiency and acceptable process conditions. Operation of such a system under sorption-reaction conditions at 17 bar, 600°C and S/CH₄ ratio = 4.2 and desorption conditions 820°C and S/CO₂ ratio = 1.8, leads to an acceptable system efficiency for power production applications with 85% carbon capture ratio, if the cyclic sorbent capacity can be maintained above 15% of the thermodynamically available capacity. There is further scope for improving the efficiency of the system but this would require the ability to perform a much larger temperature swing to reduce the amount of steam required for regeneration. An experimental investigation has shown a commercially available CaO to be capable of maintaining this cyclic capacity under prolonged cyclic testing. Further testing at higher pressure for the sorption-reaction process and under steam-methane reforming conditions are now required.

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6. Literature


