GHGT-9

Reduction in the cost of pre-combustion CO_2 capture through advancements in sorption-enhanced water-gas-shift

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Abstract

Sorption-enhanced water-gas-shift (SEWGS) is a pre-combustion decarbonisation technology combining adsorption of CO_2 with the water-gas-shift reaction. This process maximises the production of hydrogen from syngas whilst simultaneously capturing and separating CO_2.

Simulations have been completed to evaluate the use of SEWGS for power generation from natural gas with carbon capture. The modelling results show that using the SEWGS process could significantly reduce the cost of capturing CO_2 versus a reference design that uses amine absorption. Work has also been completed to show that using a counter-current steam-rinse step may be an improvement over a co-current CO_2-rinse cycle proposed previously. © 2008 Air Products and Chemicals, Inc. All rights reserved

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1. Introduction

Sorption-enhanced water-gas-shift (SEWGS) is a novel pre-combustion decarbonisation technology that has the potential to reduce CO_2 capture costs versus conventional removal processes such as amine scrubbing. The process combines CO_2 adsorption with the high-temperature water-gas-shift reaction (HTS).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{1}$$

HTS is employed industrially to modify the composition of a syngas stream and shift CO and H_2O into CO_2 and H_2. A packed bed of iron-chrome is used to catalyze the reaction with a typical feed temperature in the range of 370-400 °C (Twigg [1]).

In pre-combustion decarbonisation, the desire is to convert as much CO into H_2 as possible and then separate the CO_2 from the H_2. The H_2 can then be fed to a gas turbine to generate power, whilst the CO_2 is sequestered. Unfortunately, at the HTS operating temperature, conversion of CO is equilibrium limited. The current solution to

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this problem is to cool the gas down to around 200 °C and carry out a second low-temperature shift reaction (LTS) to achieve the required conversion of CO. Further cooling is then required to enable the capture of CO_2 by absorption with an amine solution. Finally the H_2-rich stream is reheated to around 400°C before it is combusted in a gas turbine.

Instead of cooling down the gases to achieve full conversion and separate out the CO_2, an alternative solution is the use of SEWGS. In this process, the partially shifted syngas from the HTS reaction is contacted with a packed bed containing shift catalyst and an adsorbent material to remove CO_2. By Le Chatelier's principle, the adsorption and removal of CO_2 from the syngas drives the reaction to the right-hand-side, thereby completely converting the CO and maximizing the production of H_2. The benefit of this approach is that no cooling of the gas is required so that the H_2-rich product can be fed directly to a gas turbine at around 400 °C. This removes the inefficiency of cooling down and heating up the H_2 that is an inherent part of the LTS/amine process. An additional benefit of the SEWGS technology is that the CO_2 can be regenerated from the adsorbent material at sufficient purity for direct sequestration.

An initial economic assessment by Allam et al. [2] showed that the SEWGS process using a pressure-swing-adsorption (PSA) cycle to regenerate the adsorbent can reduce the cost of CO_2 capture versus a traditional amine scrubbing system.

2. CACHET (EU Sixth Framework Programme)

Within CACHET (a project under the EU's Sixth Framework Programme) further study and optimisation of the SEWGS process is underway. Longer term testing of the SEWGS cycle in a single column has been completed by van Selow et al. [3] and work has begun to validate this process in a multi-column pilot plant unit. In a parallel effort described here, alternative cycle options have been modelled that could potentially improve the efficiency of the overall power generation process.
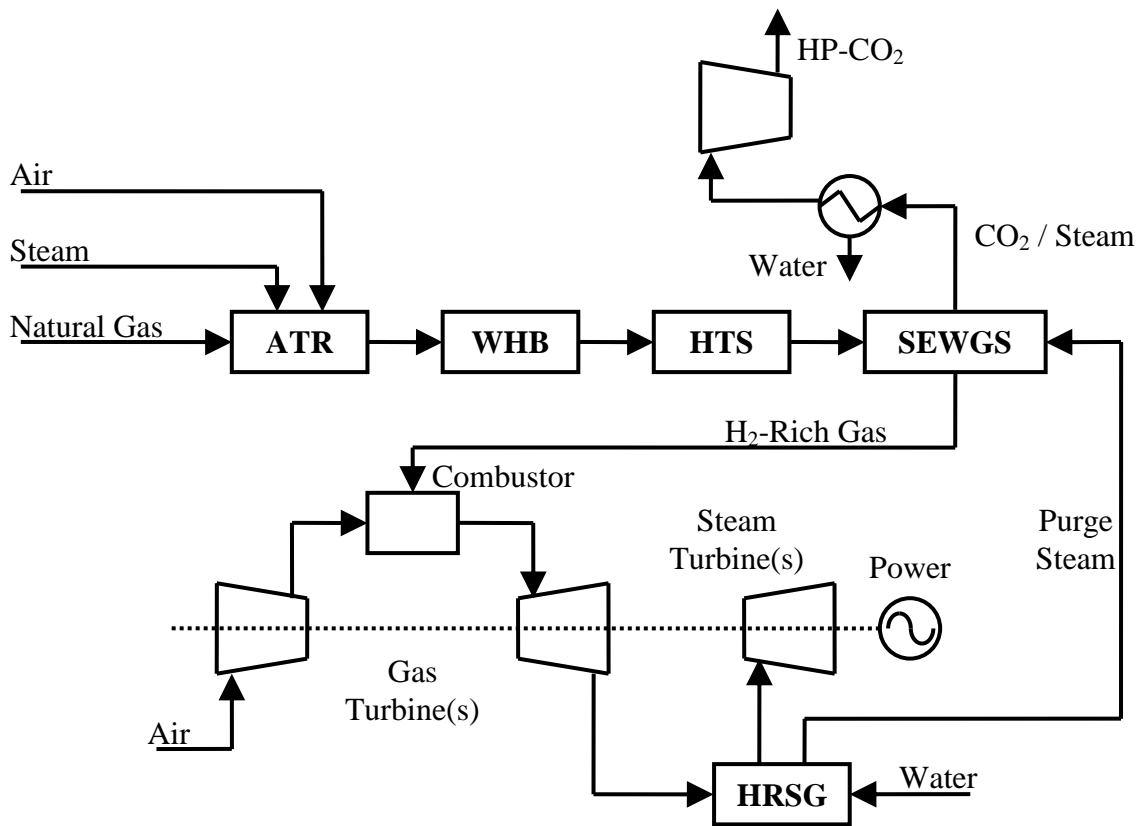

Fig 1. Flowsheet for CACHET including the SEWGS technology.

The goal of the CACHET project is to research new and novel technologies that could significantly reduce the cost of capturing CO_2 from the pre-combustion of natural gas. The reference case for this project uses an amine system for capturing the CO_2. However, this flowsheet can be easily modified to incorporate the SEWGS unit operation (as shown in Fig. 1). In the updated design, a syngas stream is generated in an air-blown autothermal reformer (ATR) using a mixture of natural gas and steam. The syngas exits the reformer and is cooled down using a waste heat boiler (WHB) to generate steam. This syngas is then passed through a HTS reactor to convert as much CO as possible.

Depending upon the feed conditions and outlet temperature, the gas stream exiting the HTS can contain 2–6% CO. In the reference case, this gas is cooled down and reacted in a LTS to produce greater quantities of H_2 and then cooled again to facilitate CO_2 capture. However, as shown in Fig. 1, the product can also be fed directly from the HTS into a SEWGS process at a temperature around 350-450 °C. The SEWGS unit then simultaneously drives the WGS reaction to completion whilst separating the CO_2 from the H_2-rich fuel gas.

Regeneration of the adsorbent inside the SEWGS vessels is achieved through reducing the pressure and purging the material with steam. By cooling this low-pressure product and condensing out the steam, a stream of relatively pure CO_2 is obtained which can be compressed without further treatment before sequestration.

The H_2-rich fuel gas produced at high pressure and temperature can be combusted directly in a gas turbine to generate power. The resulting excess heat is used to generate steam via the HRSG (heat recovery steam generator). Some of this steam is used to provide purge for the SEWGS unit, with the bulk used to generate extra power in a steam turbine.

3. Description of the SEWGS Process

The SEWGS process is based around a multi-bed PSA unit with each vessel filled with a mixture of iron-chrome catalyst and CO_2 adsorbent. When syngas is fed at high pressure and temperature (c. 30 bara, 400 °C), CO_2 is removed by the sorbent and the reaction equilibrium shifts to produce more H_2. At a predetermined level of CO_2 breakthrough from a vessel, the bed is taken off-line and regenerated. A pressure swing cycle is employed to regenerate the adsorbent and this produces a low-pressure stream rich in CO_2. By using multiple beds, a pseudo-continuous process can be realised.
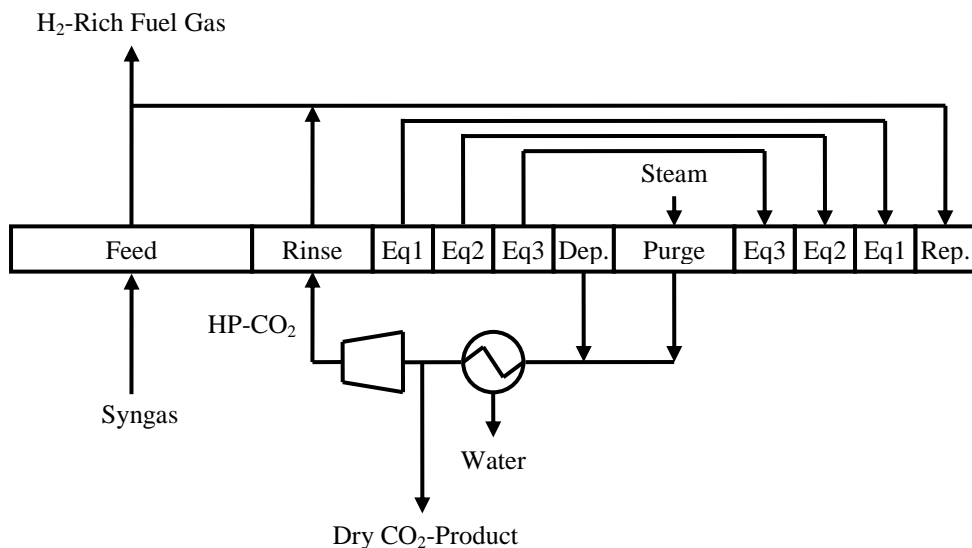

Fig 2. SEWGS cycle with CO_2-rinse step.

In the previous work of Allam et al. [2] a CO_2-rinse cycle was proposed for SEWGS and this is embodied in Fig 2. In this particular design, high purity CO_2 is added after the feed step to displace some of the gas within the voids of the adsorbent bed. Sufficient CO_2 must be added so that at the end of the last equalisation step, the majority of the H_2-rich gas is recovered. Without this step, a substantial quantity of fuel gas would end up in the CO_2 product, reducing its purity and also the amount of gas available for power production.

Following the CO_2-rinse step, the bed is equalised with other vessels to recover compression energy before finally being fully depressurised. After depressurisation, the adsorbent is regenerated by passing purge gas through the adsorbent to drive CO_2 from it. The chosen purge gas for the SEWGS process is steam from the steam turbine as this can be separated with relative ease from the CO_2-product stream. The purged CO_2 is cooled to condense out water and then either sequestrated, or compressed to the feed pressure and supplied for the rinse step. After regenerating a required portion of the CO_2 from the bed, the vessel is repressurised back to the syngas feed pressure and the cycle started again.

The benefit of adding a rinse step is that it minimises the loss of fuel gas, but using CO_2 is costly as it comes from compressing part of the low-pressure product stream. A secondary problem with using CO_2 is that the adsorbent is specifically chosen to have a high capacity for CO_2. Therefore, to fill the voids of the bed, extra CO_2 must be supplied to compensate for the gas that is adsorbed during this process. The use of an alternative, inert component for rinsing would therefore have substantial benefit over CO_2, but care must be taken as this species will ultimately end up contaminating the CO_2-product.

With this in mind, Ying et al. [4] proposed a cycle that uses counter-current steam for rinsing rather than co-current CO_2 (Fig. 3). Steam is already present in the CO_2 product due to the purge step, and it is relatively easy to separate these two components by cooling and condensing out water. Steam is supplied to the H_2-product end of the bed rather than co-currently in order to maintain a high CO_2 concentration at the feed end and thereby maximise its rate of desorption during the purge step.
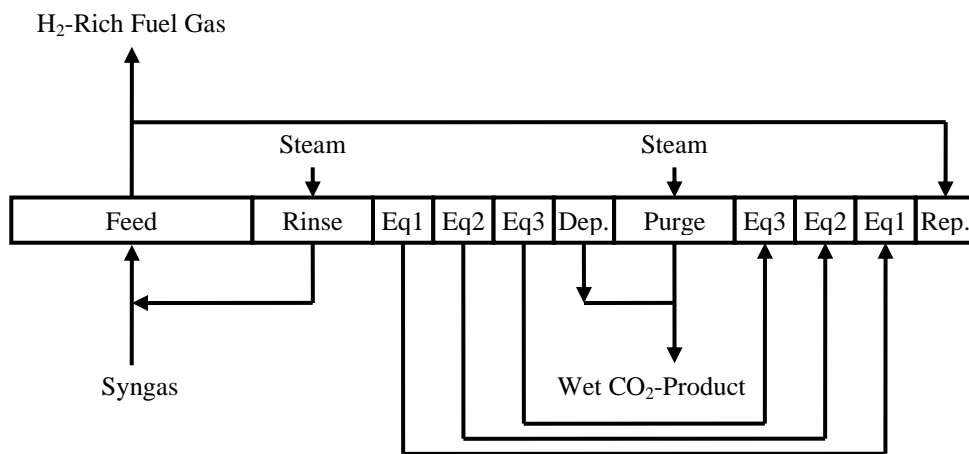

Fig 3. SEWGS cycle with steam-rinse step. Before sequestering, the wet CO_2-product is dried by condensing out water.

The rinse steam is obtained from the steam turbine, taken off at a higher pressure than the purge steam. There is therefore a power penalty in using steam for rinsing, but it is unclear whether this is offset by the power saving in removing the need for the SEWGS CO_2-product compressor. Therefore a goal of the CACHET project is to investigate the steam-rinse cycle as an alternative to the CO_2-rinse.

4. Simulation of the SEWGS Process

The SEWGS process was modeled using an adsorption-process simulator based on that of Kumar et al. [5]. The tool was modified to account for the WGS reaction and used to solve the coupled equations describing the material,

momentum and energy balances over the entire SEWGS cycle. These balances were first converted into a set of ordinary differential equations (ODE) using a finite volume technique, before integrating with respect to time using a stiff-ODE solver.

The HTS catalyst was modeled using commercial performance data (Raise [6]) and the adsorbent chosen was K_2CO_3-promoted hydrotalcite. It is recognised that the performance of hydrotalcite under the SEWGS operating conditions is difficult to model and still requires significant investigation to fully understand the sorption process. However, this material has shown promise as a high temperature CO_2 adsorbent and is currently being studied experimentally for application in SEWGS. A simplified model of the hydrotalcite was therefore created based on Langmuirian equilibrium and linear driving force kinetics. Appropriate CO_2 equilibrium and mass transfer parameters were adopted after comparing the model with experimental breakthrough and cyclic data (van Selow et al. [3]). It was assumed in the simulations that steam does not adsorb appreciably on hydrotalcite, but this needs further validation.

5. Results and Discussion

The goal of this work was to model the CO_2-rinse and steam-rinse SEWGS cycles and provide an initial estimate of how the optimum designs compare economically against the CACHET reference case. However, optimisation of the SEWGS process is not a trivial task as there are a large number of variables that can be modified when designing such a unit and the computational time required to evaluate each option is significant. Therefore, as a first pass the decision was taken to specify the number of trains and vessel configuration, details of which are provided in Table 1. The vessels' diameter was chosen so that they would be easily shippable and the number of trains derives from fluidisation concerns. Eight vessels per train are required to use either the cycle shown in Fig. 2 or in Fig. 3.

Table 1. SEWGS train and vessel designs assumed for a 330 MW power plant.

Number of trains (-)	4
Number of vessels per train (-)	8
Number of vessels concurrently on feed per train (-)	2
Vessel length (mm)	7377
Vessel diameter (mm)	3658
Mass of adsorbent per vessel (kg)	44465
Mass of catalyst per vessel (kg)	12927

Simulations were run on the SEWGS unit using a feed gas flow and composition determined from an air-ATR design with an exit temperature of 913 °C. All streams entering the bed were at 400 °C and a feed pressure of 28 bara was used. The purge step was undertaken at 1.1 bara. Cases were run for the CO_2-rinse and steam-rinse options over various feed times, rinse flow rates, and purge flow rates. The CO_2-product purity and carbon recovery were then determined at cyclic steady state for each chosen condition. Interpolating these results, a cost minimisation was performed to obtain optimum operating conditions for both cycle types.

Table 2 shows the rinse and purge flows for the cost optimised designs with a constraint of at least 90% carbon capture and 98% purity of the CO_2-product. In the calculation of carbon capture only CO and CO_2 in the feed were considered, trace hydrocarbons such as CH_4 in the inert stream were ignored.

Table 2. Rinse and purge flows for the optimum designs.

	CO_2-Rinse	Steam-Rinse
CO_2-product required for rinsing (kmol/h)	6900	0
Steam required for rinsing (kmol/h)	0	3200
Steam required for purging (kmol/h)	9400	4800

A notable difference between these two cases is that around twice as much gas must be provided for rinsing the beds with CO_2 compared with steam. This is the result of CO_2 being adsorbed on to the hydrotalcite during the rinse

step, and therefore more gas must be added to compensate. A secondary benefit of using the steam-rinse is that it reduces the purge gas requirement. More purge gas is required for the CO_2-rinse case to help regenerate the adsorbent and increase its CO_2 capacity for the subsequent feed step. This allows the overall cycle time to be increased, reducing the frequency with which the bed needs to rinsed and thereby the amount of CO_2-rinse gas required.

Table 3. Feed and product flows for the optimum designs. The wet CO_2-product gas is the combined flow from the outlets of the SEWGS trains before any recycling of gas for rinsing. The dry CO_2-product is the gas stream that will eventually be sequestered.

Stream	Feed	H$_2$-Product		Wet CO$_2$-Product		Dry CO$_2$-Product	
Rinse Type	-	CO$_2$	Steam	CO$_2$	Steam	CO$_2$	Steam
Averaged flow rate (kmol/h)	25200	22200	23200	19300	10000	3300	3300
Averaged composition (mol%)							
CO	2.6	0.4	0.4	0.4	0.0	0.7	0.1
H$_2$O	15.2	15.9	19.5	47.4	67.1	-	-
CO$_2$	11.7	1.2	1.2	51.5	32.9	98.0	99.9
H$_2$	32.2	39.1	37.4	0.1	0.0	0.2	0.0
Inert	38.2	43.3	41.5	0.6	0.0	1.1	0.0

Table 3 contains the flows and compositions of the feed and product streams entering and leaving the bed. The H$_2$-product is diluted slightly by H_2O in the steam-rinse scenario versus the CO_2-rinse, although the actual quantity of H_2 recovered is approximately the same. It is also interesting to note that for the steam-rinse case that the CO_2-product purity is actually higher than the 98% constraint used in the optimisation. This is because the cost of added extra rinse steam is outweighed by the benefit of having a few extra H_2 molecules in the fuel gas..

Fig. 4 shows an in-bed comparison of the CO_2-rinse cycle and steam-rinse cycle at operating conditions close to the optimum. Profiles are presented of each component's partial pressure over the length of the bed after the feed step (top), the rinse step (middle) and the last equalisation step (bottom). At the end of the feed step, the compositions across the bed are similar for both cycles and the concentration of CO can be seen to decrease as CO_2 is adsorbed and further reaction occurs. After the feed step, rinse gas is then supplied at the feed pressure; CO_2 at the feed end and steam at the H$_2$-product end. As expected, when the bed pressure is subsequently decreased during equalisation, the rinse gas expands along the length of the bed, pushing H$_2$-rich gas out of the bed.

An economic summary of the two SEWGS cases versus the CACHET reference case (amine scrubbing) is shown in Table 4. The cost of producing power encapsulates both the operating cost and capital depreciation over 25 years. There is a slight difference in capital costs between the SEWGS cases due to an extra CO_2 compressor needed to produce the CO_2-rinse gas. However, both these capital costs are much lower than that for the reference case. The efficiency of the power generation process is also markedly improved by changing to a SEWGS system from amine scrubbing.

Table 4. Economic comparison of SEWGS versus the CACHET reference case. Calculations based on January 2006 prices.

	Reference Case	CO$_2$-Rinse	H$_2$O-Rinse
Fixed capital (million €)	462	409	375
Efficiency (%)	40.9	42.9	44.7
Cost of power (€/MWh)	87	83	77
Cost of CO$_2$ capture (€/ton CO$_2$)	82	79	72
Cost of CO$_2$ avoidance (€/ton CO$_2$)	118	109	96

These results show that the use of a counter-current steam-rinse improves the overall efficiency of the power generation process versus the previously proposed co-current CO_2-rinse option. This is therefore an option worth further simulation and experimental investigation. These results show that versus the amine scrubbing reference case used for CACHET, cost reductions around 19% may be achievable in both the capital expenditure and the CO_2 avoidance cost.
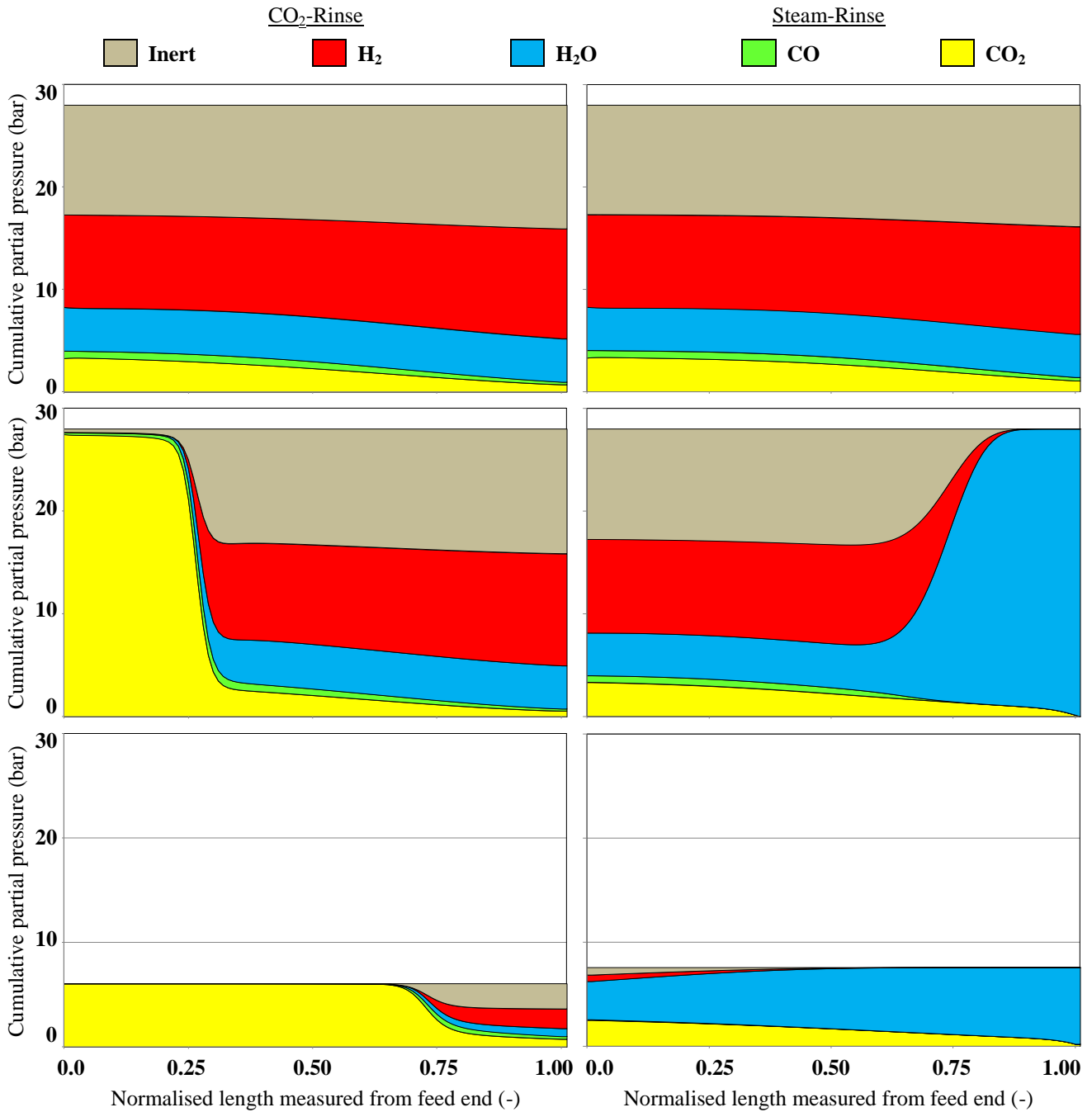
Fig 4. Component partial pressure profiles along the length of the bed after the feed (top), rinse (middle) and equalisation (bottom) steps.

6. Conclusions and Recommendations

The results from these simulations are useful in showing that the SEWGS process could be significantly better than using amine scrubbing for pre-combustion capture of CO_2 from natural gas. The new co-current steam-rinse option also appears to show an improvement over the CO_2-rinse design proposed previously and is worth further investigation.

Experimental work is currently underway in a pilot-plant to evaluate these different cycle options and show whether the simulated performance data can be obtained in practice. More information is needed to understand the performance of K_2CO_3-promoted hydrotalcite under the SEWGS conditions to improve modelling of this material. There is also scope to investigate alternative adsorption materials that could further improve performance of the SEWGS unit and reduce costs.

Due to the recent rapid rise in natural gas price versus other hydrocarbon feed-stocks, using pre-combustion capture of CO_2 appears to be a relatively expensive method of producing power. However, the SEWGS technology can equally be applied to syngas from other sources, such as the gasification of coal, and the learnings from this work can therefore be used on other applications.

7. Acknowledgements

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