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SEWGS process cycle optimization

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Abstract

Sorption-enhanced water-gas shift (SEWGS) is a technology for pre-combustion CO_2 capture, which can be integrated in an IGCC plant. A computer model is used to simulate the SEWGS unit, using a counter-current steam rinse cycle with one equalization step. The sensitivity of the CO_2 recovery and the purity of the CO_2 stream with respect to the feed flow rate, rinse flow rate, purge flow rate and cycle time has been investigated at an initial operating point. One at a time variations show that the CO_2 recovery increases with increasing purge flow rate and decreases with increasing feed flow rate, cycle time and rinse flow, in order of decreasing sensitivity. The CO_2 purity is much less sensitive to changes of these conditions, unless either the rinse flow rate or the cycle time drop below certain values, which are determined by the ratio of the pressures at the end of the rinse and equalization steps. The optimum rinse flow, purge flow and cycle time have been determined with respect to the efficiency penalty due to the rinse and purge steam requirements, with a CO_2 recovery of 90% and a dry CO_2 purity of 98% as constraints, for a given feed flow rate, feed flow composition, operating pressure, reactor sizing and configuration. Minimum steam-to-carbon ratios are 0.55 for the rinse and 1.3 for the purge gas.

Keywords: sorption enhanced reaction; carbon capture; optimization; IGCC

1. Introduction

Sorption-enhanced water-gas shift (SEWGS) is a technology for pre-combustion CO_2 capture that combines water-gas shift with CO_2 adsorption in a single vessel. At typically 400 °C, a K_2CO_3 promoted hydrotalcite-based sorbent can adsorb CO_2 and catalyses the water-gas shift reaction [1], leading to a 100% CO conversion and a high CO_2 recovery. SEWGS uses a pressure swing cycle to regenerate the sorbent.

The integration of SEWGS in a Natural Gas Combined Cycle (NGCC) plant has been studied by others [2]. In this earlier work, the process design and operating conditions were optimized with respect to the lowest CO_2 avoidance costs. In the current study, the scope of SEWGS technology is broadened to integration into an IGCC power plant. As can be seen in Figure 1, H_2S could be removed downstream of the SEWGS unit. The composition of the gas stream to the SEWGS unit, as well as the pressures at the feed and purge steps, and the temperature are taken from a system simulation and are shown in Table 1. Compared to the NGCC case, the carbon fraction is 68% larger in the IGCC case. This results in a higher CO_2 partial pressure and consequently a higher breakthrough capacity.

A test installation consisting of 6 reactors of 6 m length has been built at ECN to investigate the SEWGS process [3]. The adsorbent is a promoted hydrotalcite-based material, which has been demonstrated to be a suitable adsorbent for

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thousands of process cycles for an NGCC application. It has also been shown that the adsorbent has sufficient water-gas shift activity, and it has good stability under syngas containing 200 ppm H_2S [1].
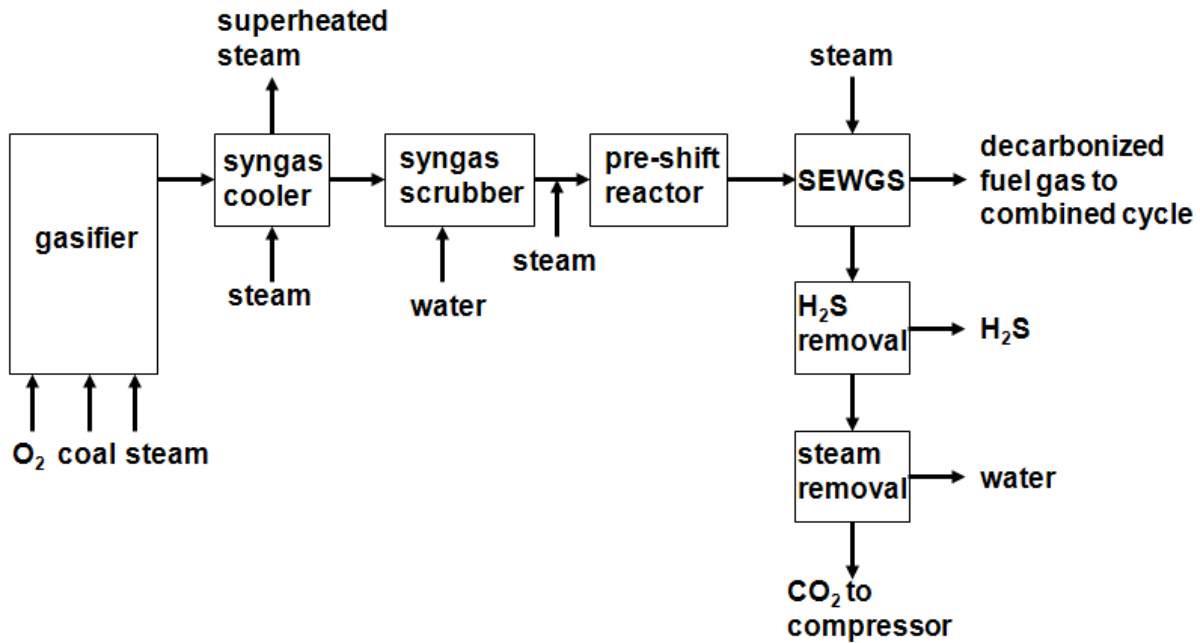

Figure 1 Schematic of an IGCC-SEWGS system.

Table 1 Fixed simulation conditions.

Feed gas composition [vol%]	32.6% H_2O
	34.6% H_2
	4.7% CO
	23.8% CO_2
Feed pressure [bar]	23.6
Purge pressure [bar]	2
Temperature [ºC]	400
Bed length [m]	9

2. SEWGS Process Cycle

A process cycle using counter-current steam rinse was patented by Ying et al. [6]. Such a cycle with one equalization step is shown in Figure 2, requiring 6 parallel reactors.

During the feed step, syngas from the pre-shift reactor (Figure 1) is fed to the reactor while H_2 is produced. The feed step is followed by a rinse step by feeding counter-currently medium-pressure steam into the reactor. The rinse product, mainly syngas, is mixed with the feed gas. During a subsequent pressure equalization step, the rinse gas expands throughout the reactor, thereby pushing the interstitial syngas to a receiving reactor at lower pressure. The CO_2 product is collected from the blowdown and purge steps. After removal of H_2S and H_2O the CO_2 is sufficiently pure for transport and sequestration. After repressurization of the reactor using part of the produced H_2, the reactor is ready for the feed step of the next cycle.
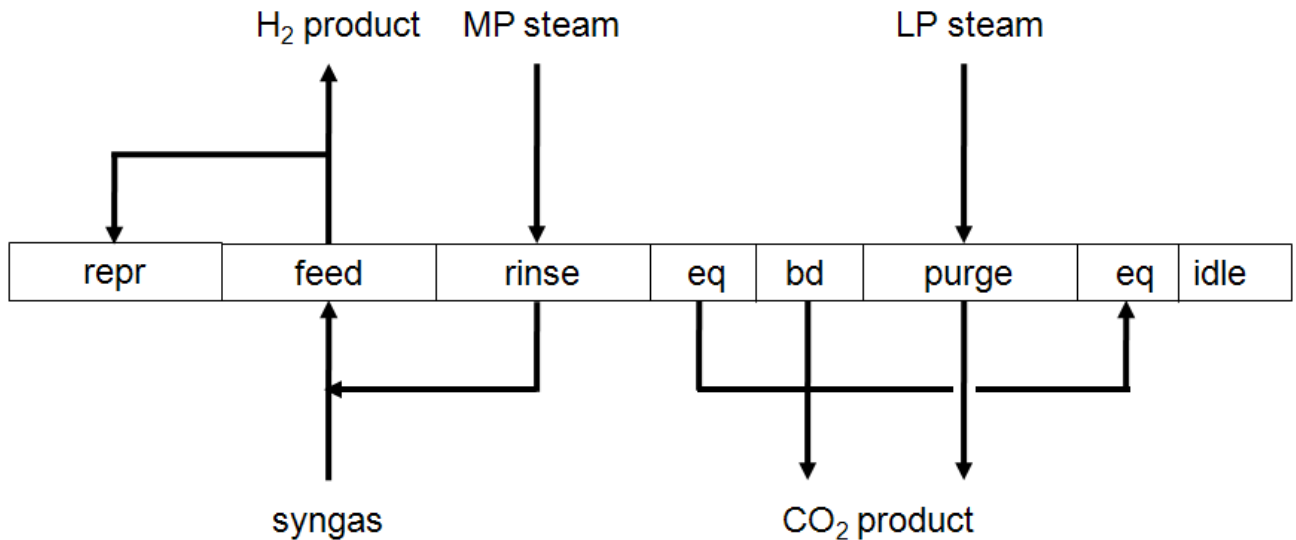
Figure 2 Simulated cycle with one equalization step (eq) (bd = blowdown, repr = repressurisation).

3. Reactor model

The process has been simulated with a pseudo-homogeneous reactor model, by solving the material, energy and momentum equations with the appropriate initial and boundary conditions per step, incorporating kinetics for adsorption and water-gas shift reaction [4]. The model calculates time-varying axial profiles of the mole fractions of the gas components, superficial gas velocity, CO_2 loading, temperature and pressure. The fixed bed tubular reactors are assumed to be adiabatic. The reactor model is 1-dimensional. An axially dispersed plug flow is assumed (Peclet number > 5000). A Freundlich isotherm and a linear driving force equation are used to describe the CO_2 adsorption and desorption process. The parameters of the isotherm have been derived from CO_2 breakthrough experiments, and the mass transfer coefficient for adsorption and desorption from cyclic experiments. The mass transfer coefficient takes limitations into account arising from gas phase transport from the bulk gas phase to the adsorption sites inside the particle, and also limitations due to transition from the gas phase to the adsorbed phase.

4. Simulation and optimization procedure

The equations are discretized in space and integrated in time using the ode15 solver from the Matlab^{TM} software package [4]. Only one reactor is simulated, and produced gases are stored in simulated storage tanks (uni-bed approach). Typically ten cycles are simulated before a cyclic steady state is obtained.

The main energy penalty for the SEWGS process arises from the steam requirement for the rinse and purge steps. These steam flows must be taken from the steam cycle. For optimization of the selected process cycle with respect to the lowest efficiency penalty, an efficiency penalty function (EPF) is evaluated, defined as:

$$EPF = \frac{w_1 \, S_{rinse} + w_2 \, S_{purge}}{C * CCR} \qquad (1)$$

with

$$w_1 = 0.58 \; and \; w_2 = 1 - w_1 \qquad (2)$$

where S is the required steam amount for the purge or rinse step in one cycle, and C the total amount of carbon fed as CO or CO_2 during one cycle, CR is the carbon recovery. The weight factors w_1 and w_2 reflect the higher energy penalty of MP rinse steam compared with LP purge steam, on the basis of the relative exergy content of the steams. The rinse and purge flow rates and the cycle time have been varied to optimize the selected SEWGS process cycle when used in an Integrated Gasifier Combined Cycle (IGCC) power plant, with respect to the energy penalty, obeying certain constraints:

- the carbon recovery (fraction of total carbon fed to the system which is captured as CO_2) > 90%
- the purity of the CO_2 product on dry basis > 98%.

A following optimization procedure has been applied. The feed flow has been kept constant, while the rinse flow, purge flow and cycle time were allowed to vary. The procedure makes use of the trends for the CO_2 recovery and CO_2 purity with these variables, and of interpolation to determine the conditions resulting in the minimum required recovery and purity of CO_2. The result is a set of combinations of rinse flow, purge flow and cycle time obeying the constraints. The values obtained by interpolation were verified by running simulations at these conditions afterwards.

5. Results

Figures 3 and 4 show the sensitivity of the CO_2 recovery and the CO_2 purity, respectively, when the independent variables are varied, one at a time The common point of the various curves corresponds with the set of starting conditions giving a CO_2 recovery of 90.4% and a CO_2 purity of 99.0%. In Figure 3 the CO_2 recovery decreases with increasing feed flow, cycle time and rinse flow. Increasing feed flow and cycle time directly results in more CO_2 being fed to the bed per cycle, that cannot be completely adsorbed and ends up in the H_2 product. Even though steam is used, an increasing rinse flow also means an increased reactor loading with CO_2 since the removed void gas during the rinse is mixed with feed gas and thus increases the CO and CO_2 flows to the reactor. Note that the curves for variation of feed flow and cycle time do not coincide. Increasing the feed flow by a certain factor has not the same effect as decreasing the cycle time by the same factor due to the kinetics of the water-gas shift reaction and the adsorption kinetics. Increasing the purge flow improves the CO_2 recovery since more CO_2 is stripped from the sorbent.

The CO_2 purity constraint is fulfilled in most cases, unless the rinse flow or the cycle time drop below their starting values. In these cases, the purity rapidly decreases. The minimum rinse flow and cycle time directly result from calculating the required rinse gas volume that just fills the whole bed during expansion in the subsequent equalization step. Here, the CO_2 desorbed during the rinse has been neglected and the CO_2 recovery is 98%, not 100% as assumed above. These effects will reduce the calculated minimum rinse flow slightly when taken into account. A smaller amount of rinse gas due to a lower flow or shorter cycle time, will result in insufficient removal of the H_2 product from the bed before blowdown starts. As a consequence, the amount of impurities – mainly H_2 – inthe CO_2 product increases rapidly.
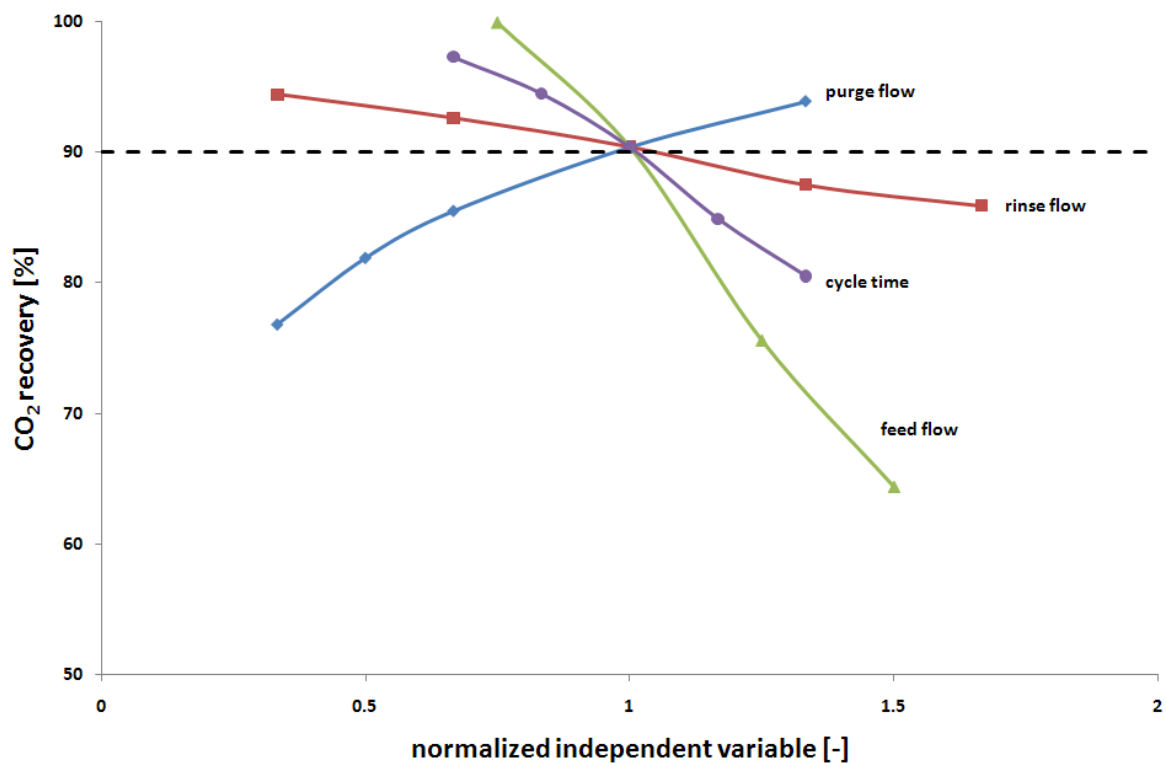

Figure 3 CO_2 recovery vs. relative feed flow, rinse flow, purge flow and cycle time. The horizontal dashed line is the minimum required CO_2 recovery (90%).
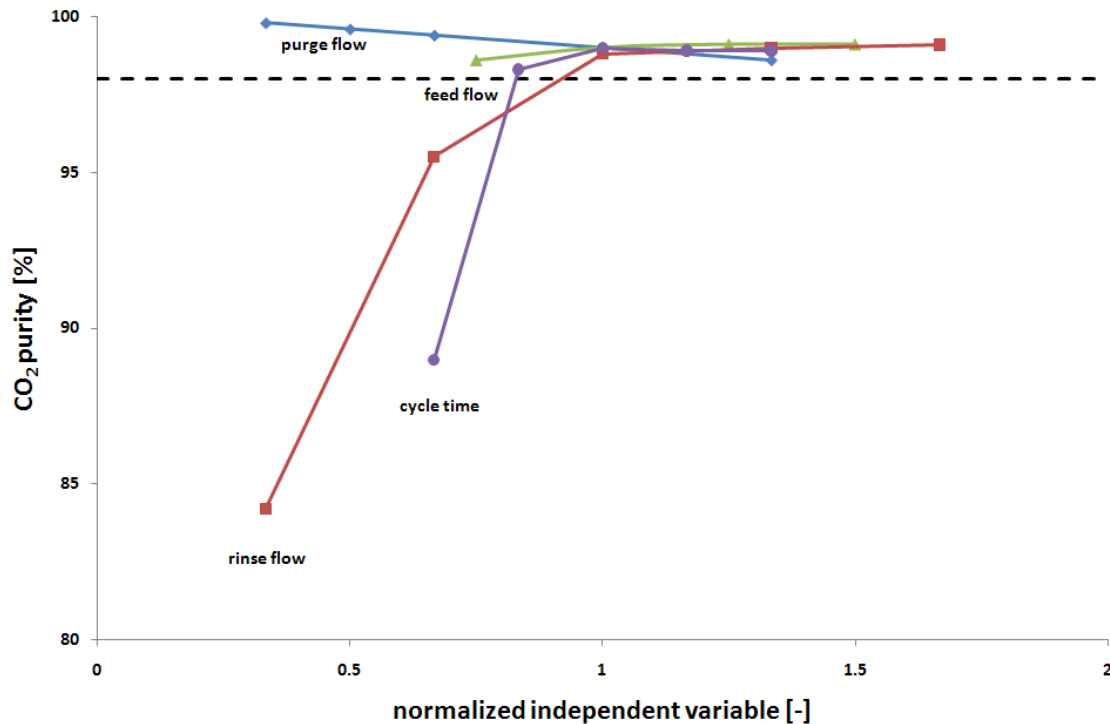
Figure 4 CO_2 purity vs. relative feed flow, rinse flow, purge flow and cycle time. The horizontal dashed line is the minimum required CO_2 purity (98%).

As can be seen in Figure 4, the purity slightly drops when the purge flow is increased from 0.3 to 1.3. A larger purge flow results in a cleaner bed at the beginning of the feed step. Thus, more CO_2 can be adsorbed per unit length of the bed and the CO_2 adsorption front moves slightly slower through the bed. This results in a few percent more H_2 gas in the bed at the beginning of the blowdown step, yielding a slightly lower purity of the CO_2 product.

The sensitivity study shows the trends and makes clear which variables have a major effect, and which have a minor effect on the recovery and purity of CO_2. The results can be used for process design and optimization. They have also been used in the optimization procedure. The results of the optimization are shown in Figure 5 as S/C ratio versus normalized cycle time for the purge and rinse flows separately. The S/C ratio of the rinse and purge flows show opposite trends as follows from Figure 5. At increasing cycle time, the amount of rinse steam decreases whereas the amount of purge steam increases. As discussed above, the amount of required rinse gas depends only on the ratio of the pressures at the rinse step and the end of the equalization step. As a consequence, the rinse flow is more or less inversely proportional to the cycle time. The reason it is not completely inversely proportional is that dispersion effects of the rinse gas flow become important at long cycle times, necessitating a larger rinse gas amount.

The cyclic capacity of the adsorbent is by definition proportional to the cycle time (Figure 6). This implies that at longer cycle time, not only more CO_2 must removed from the bed during purge, but that the bed should also be cleaned to lower CO_2 loading during the purge. According to the linear driving force equation, the rate of desorption is proportional with n_{act} - n_{eq} where n_{eq} is the CO_2 loading at equilibrium, and n_{act} is the actual CO_2 loading [4]. the desorption rate rapidly falls with decreasing n_{act}, so that a larger purge flow is required at lower CO_2 loading.

In addition, the efficiency penalty function calculated from them using Equation (1) has been plotted in the same figure and shows a minimum at a relative cycle time of 0.90. At this minimum, the S/C ratios are 0.55 for rinse and 1.3 for the purge gas, respectively. The minimum is broad: efficiency penalties less than 10% higher than the minimum can be obtained for normalised cycle times between 0.79 and 1.03.
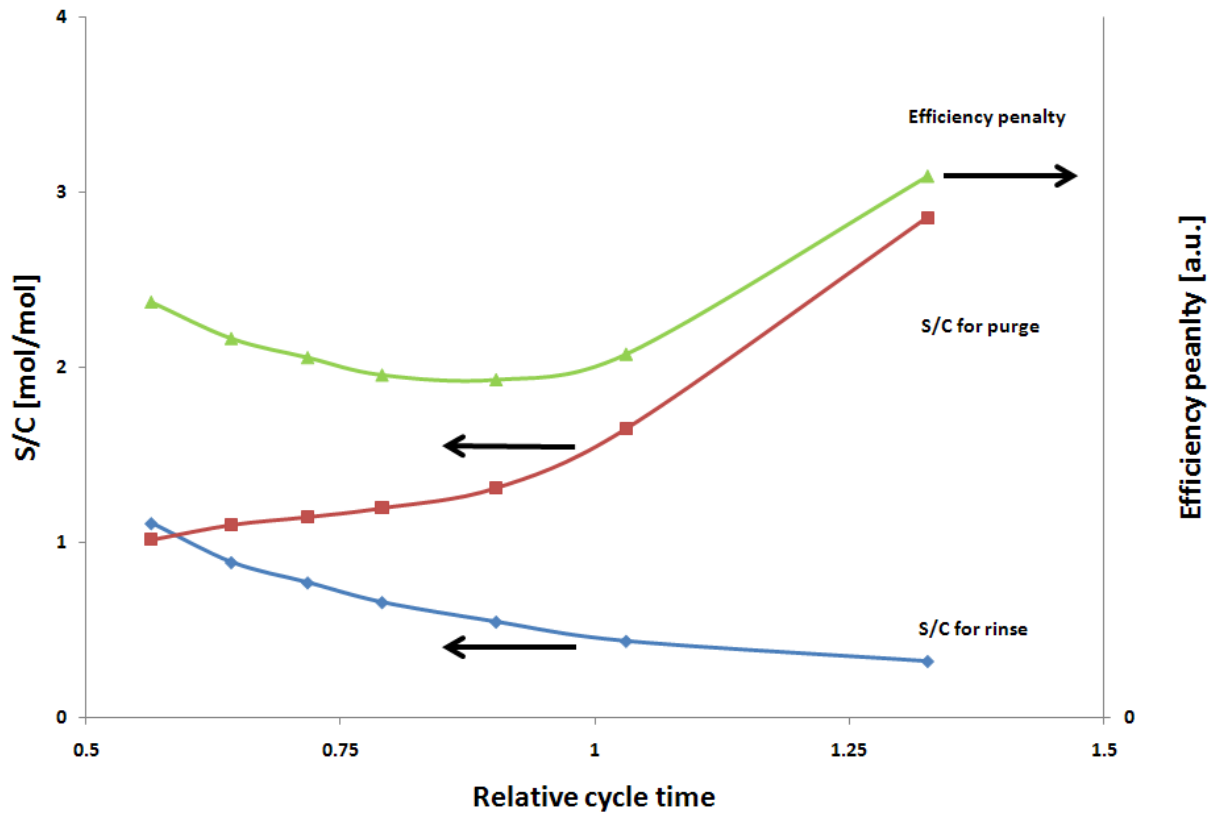
Figure 5 Required S/C ratios for purge and rinse steam (left axis) and resulting efficiency penalty (right axis) vs. relative cycle time at CO_2 recovery and CO_2 purity of 90% and 98%, respectively.
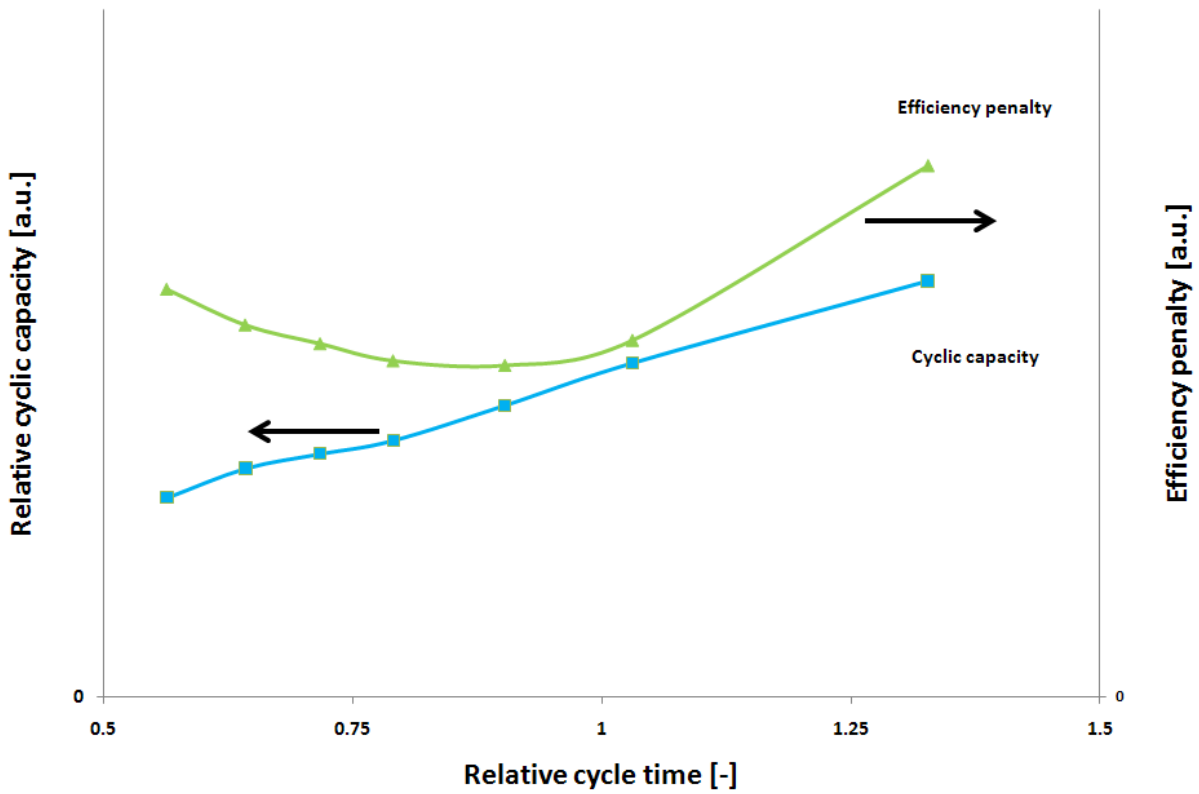

Figure 6 Relative cyclic capacity (left axis) and efficiency penalty (right axis) vs. relative cycle time at CO_2 recovery and CO_2 purity of 90% and 98%, respectively.

5. Conclusions and future work

The effects of operating conditions of a SEWGS unit in an IGCC power plant on the performance have been investigated by modelling and simulations. A counter-current steam rinse cycle with one equalization step was assumed. The CO_2 recovery increases with purge flow, and decreases with feed flow, cycle time and rinse flow, in order of decreasing sensitivity. The CO_2 purity is much less sensitive to changes of these conditions, except when the rinse flow or cycle time drop below a certain value.

For given unit and cycle designs, the optimum cycle time and minimum steam requirements have been determined with respect to the lowest efficiency penalty , with a CO_2 recovery of 90% and a dry CO_2 purity of 98% as constraints. S/C ratios of 0.55 for the rinse and 1.3 for the purge gas result in the lowest efficiency penalty.

Future work will focus on an optimisation towards the lowest costs of CO_2 mitigation, taking into account capital costs in addition to operational costs. The optimization method will be automated, which allows a more accurate determination of the optimum condition(s). Variations of the currently studied process cycle, like using CO_2 for the rinse step, adding more pairs of equalization steps, will be included as well as adding more degrees of freedom (feed flow, feed pressure, purge pressure and bed length, amongst others).

Acknowledgement

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