Feasibility Study of Vacuum Pressure Swing Adsorption for CO$_2$ Capture From an SMR Hydrogen Plant: Comparison Between Synthesis Gas Capture and Tail Gas Capture

Yan Chen and Hyungwoong Ahn

In this paper, a feasibility study was carried out to evaluate cyclic adsorption processes for capturing CO$_2$ from either shifted synthesis gas or H$_2$ PSA tail gas of an industrial-scale SMR-based hydrogen plant. It is expected that hydrogen is to be widely used in place of natural gas in various industrial sectors where electrification would be rather challenging. A SMR-based hydrogen plant is currently dominant in the market, as it can produce hydrogen at scale in the most economical way. Its CO$_2$ emission must be curtailed significantly by its integration with CCUS. Two Vacuum Pressure Swing Adsorption (VPSA) systems including a rinse step were designed to capture CO$_2$ from an industrial-scale SMR-based hydrogen plant: one for the shifted synthesis gas and the other for the H$_2$ PSA tail gas. Given the shapes of adsorption isotherms, zeolite 13X and activated carbon were selected for tail gas and syngas capture options, respectively. A simple Equilibrium Theory model developed for the limiting case of complete regeneration was taken to analyse the VPSA systems in this feasibility study. The process performances were compared to each other with respect to product recovery, bed productivity and power consumption. It was found that CO$_2$ could be captured more cost-effectively from the syngas than the tail gas, unless the desorption pressure was too low. The energy consumption of the VPSA was comparable to those of the conventional MDEA processes.

Keywords: CO$_2$ capture, equilibrium theory, hydrogen plant, pressure swing adsorption, synthesis gas, PSA tail gas, energy consumption, MDEA process

INTRODUCTION

UK has set a legally binding target to achieve net zero GHG emission by 2050 by revising the Climate Change Act 2008 in 2019. Similarly, Scottish Government has published its Hydrogen Policy Statement in which it is aimed to achieve net zero greenhouse gas emissions by 2045 and a 75% reduction by 2030 against the 1990 baseline (Scottish Government, 2020a). There is no doubts that both low-carbon hydrogen and renewable energy will play a pivotal role in the net zero GHG emission economy. Hydrogen will be taken as a fuel in the sectors where full electrification is challenging, such as furnace, long haul transport, etc. Also, hydrogen is considered as a good energy carrier, as it can be generated by electrolysis using the extra renewable electricity that would otherwise be wasted. For a net zero GHG emission, it is crucial capturing CO$_2$ from the air, in other
words, negative emission. The biomass-derived hydrogen integrated with CCUS (Carbon Capture, Utilisation and Storage) as well as direct air capture are identified as promising negative emission routes.

Accordingly, each country has announced a roadmap to expand drastically the hydrogen supply capacity for the next 30 years. UK plans to install 5 GW of green and blue H$_2$ production by 2030 and estimates the H$_2$ demand in 2050 will reach 250 – 460 TWh, equivalent to 20 – 35% of UK energy consumption (UK BEIS, 2021).

Up to now, hydrogen is produced at scale by reforming fossil fuels, mainly natural gas and coal. However, a chemical process producing grey hydrogen by reforming a natural gas using steam involves enormous CO$_2$ emission at a rate of 10 ton CO$_2$ per 1 ton H$_2$.

In principle, such an enormous CO$_2$ emission involved in grey H$_2$ production can be reduced greatly by its integration with CCUS. The hydrogen that is produced by reforming reactions of fossil fuels with its CO$_2$ emission curtailed by CCUS is referred to as blue hydrogen.

Green hydrogen is defined as the hydrogen produced by splitting water (H$_2$O) in an electrolyser powered by electricity. The electricity that an electrolyser consumes must not involve CO$_2$ emission over the process of its production to claim its “green” credit. Green hydrogen is obviously more promising than blue hydrogen in terms of sustainability, but the hydrogen demand that is expected to grow rapidly for achieving the net zero GHG emission target can be met only by producing both green and blue hydrogens. As pointed out by the latest Hydrogen Assessment report (Scottish Government, 2020b), green hydrogen is currently economically unfeasible, as its production cost is almost three times that of blue hydrogen. According to the study, it is not until 2050 that green hydrogen’s levelised cost will be reduced to an extent that it becomes comparable to the blue hydrogen’s levelised cost. Constructing an infrastructure for supplying a huge amount of renewable electricity to electrolysis plants must take precedence in order to produce green hydrogen at scale.

Hence, blue hydrogen production is essential for propping up the hydrogen economy for the next decades to come before green hydrogen technologies mature. In this respect, we must endeavour to develop the most cost-effective way of capturing CO$_2$ from a reforming-based H$_2$ plant.

Currently, a majority of hydrogen production plants are based on steam methane reforming (SMR) of hydrocarbon gases. The SMR H$_2$ plant mainly comprises reforming reactors followed by a hydrogen purification Pressure Swing Adsorption (PSA) as shown in Figure 1. In principle, the highly endothermic SMR reaction is favoured by low pressure and high temperature conditions, whilst the subsequent PSA unit needs a feed at high pressure and low temperature conditions for a decent working capacity of adsorbents. It is not advisable compressing the synthesis gas between the reforming and purification sections, as it would incur a huge energy penalty. A SMR H$_2$ plant is normally designed to operate at around 20 bara, to reconcile the conflicting desired operating conditions of the two main units.

As shown in Figure 1, CO$_2$ can be captured from shifted synthesis gas (syngas), H$_2$ PSA tail gas (tail gas) or flue gas (Soltani et al., 2014; Voss, 2014). To identify the stream conditions of the three process streams, a 6.8 ton H$_2$/hr-scale H$_2$ production plant was simulated using Honeywell UniSim. Table 1 shows stream conditions of the synthesis gas and the PSA tail gas that were estimated in the H$_2$ plant UniSim simulation. A typical SMR H$_2$ plant exhibits the following performances: 1) CH$_4$ feed consumption (2.5–3.5 Gcal/1,000 Nm$^3$ H$_2$), 2) CH$_4$ fuel consumption (0.5–1.5 Gcal/1,000 Nm$^3$ H$_2$), 3) Steam export (0.3–0.8 Gcal/1,000 Nm$^3$ H$_2$), and 4) CO$_2$ emission rate (around 800 kg CO$_2$/1,000 Nm$^3$ H$_2$). The extra steam available in a SMR H$_2$ plant is so useful as it can be utilised to run a carbon capture plant that often requires heat or electricity for sorbent regeneration.

Among the three stream candidates, the flue gas has been ruled out on the grounds that its CO$_2$ partial pressure is the lowest of three. Both syngas and tail gas are worth investigation as each of...
two has some distinctive features that make the gas favourable for CO₂ capture. The syngas has the highest CO₂ partial pressure of around 3 bara and the lowest actual gas volumetric flowrate. In contrast, the tail gas has the highest CO₂ mole fraction of 0.57 and the lowest molar flowrate. It should be noted that the overall CO₂ capture rate could increase from 59% to 90+% in case of the syngas capture case, as the decarbonised syngas can also be used as fuel in place of natural gas fuel (Ieaghg, 2017).

Several blue hydrogen projects have been commercialised successfully. The most eminent ones are Air Products’ Port Arthur project and Shell’s Quest CCS project, both of which capture CO₂ from syngas. The Port Arthur project has captured 7 million tonnes of CO₂ with a Vacuum Swing Adsorption process and used the CO₂ for EOR since 2013. Quest CCS Project has captured over 5 million tonnes of CO₂ with an amine process using ADIP-X solvent, a mixture of MDEA and piperazine, since 2015. CO₂ capture from tail gas has also been developed at scales close to commercialisation. Japan’s Tomakomai project features a MDEA process with a capacity of 0.1 Mt CO₂ per year. Air Liquide’s Port Jerome Project has developed a hybrid process comprising a cold box for CO₂ liquefaction and a membrane unit for H₂ recovery.

Among various CO₂ capture processes considered for blue hydrogen production, it appears that adsorptive capture processes are the most harmonious with a hydrogen production plant in a sense that they may be able to produce pure hydrogen as

**TABLE 1 |** Stream conditions of two VPSA feed gases in the SMR hydrogen plant at the production capacity of 6.8 ton H₂/hr.

| Process stream | Shifted synthesis gas | H₂ PSA tail gas |
|----------------|-----------------------|-----------------|
| Molar flowrate [kmol hr⁻¹] | 5,099 | 1,626 |
| Actual volumetric flowrate [m³ s⁻¹] | 1.73 | 7.59 |
| Gas composition of the actual feed gas [mol %] | 75% H₂, 18% CO₂, 4% CH₄, 2% CO, <1% H₂O | 24% H₂, 57% CO₂, 11% CH₄, 7% CO, 1% H₂O |
| Gas composition of the simulated feed approximated by binary mixture [mol %] | 82% H₂, 18% CO₂ | 43% H₂, 57% CO₂ |
| Temperature [K] | 308 | 308 |
| Feed pressure [bar] | 21 | 1.5 |
well as pure CO₂. Adsorption processes, once applied to syngas for CO₂ capture, can be configured so as to produce a high purity of hydrogen as well as a high purity of CO₂ (Sircar and Kratz, 1988; Streb and Mazzotti, 2020). Accordingly, a CO₂ capture adsorption unit may be able to replace the existing H₂ purification PSA in case of syngas capture, and it can also produce additional hydrogen product in case of tail gas capture as shown in Figure 2.

In this study it was aimed to carry out a feasibility study of cyclic adsorption processes for CO₂ capture from the syngas and the tail gas. For the sake of simplicity, the process streams were approximated by a binary mixture of H₂ and CO₂ in which the other gases were replaced by hydrogen. The CO₂ capture PSA design was based on a simple five-step VPSA cycle as shown in Figure 3. The CO₂ capture PSA was analysed by Equilibrium Theory method, the mathematical model of which is delineated in the reference (Ruthven et al., 1994) and presented in Equilibrium Theory Model for PSA Analysis Section. As depicted in Figure 3, the five-step PSA unit has four effluents: pure H₂, pure CO₂, rinse step effluent and mixed gas. Accordingly, Figure 3 shows clearly where the four outlet streams are directed to. The two capture systems are to be designed by Equilibrium Theory and evaluated in terms of various performance indices for comparison.

**MATHEMATICAL MODEL**

**Adsorption Isotherm**

In this study, activated carbon and zeolite 13X were chosen for selective adsorption of CO₂ from the syngas and the tail gas, respectively. In designing a hydrogen purification PSA system of a SMR hydrogen plant (see Figure 1), activated carbons are often taken for the bottom layer near the column end that the feed gas is admitted to. This is because activated carbons own excellent CO₂ adsorption capacities at the CO₂ partial pressure in the feed (Ahn et al., 1999; Lee et al., 1999; Ahn et al., 2001). In contrast, zeolite 13X is deemed a benchmark adsorbent for capturing CO₂ from a gas mixture around atmospheric pressure, for example, a flue gas composed mainly of N₂ and CO₂ (Krishnamurthy et al., 2014; Luberti et al., 2017; Ahn et al., 2020) and a synthesis gas generated by biomass gasification (Oreggioni et al., 2015). The CO₂ isotherms of the two adsorbents are compared in Figure 4A. The CO₂ isotherm on 13X is so close to an irreversible isotherm that it can capture large CO₂ even at a very low CO₂ partial pressure and the CO₂ consumption for the rinse step would be very low. However, the 13X column is hard to regenerate unless it is evacuated to a very low pressure. The CO₂ isotherm on the activated carbon is still favourable but way less irreversible than that on 13X, which imparts an excellent working capacity of CO₂ without having to reduce the pressure so low for desorption.

The dual-site Langmuir isotherm was taken to estimate the non-linear adsorption isotherm of CO₂ on the activated carbon.

\[ q_A = \frac{q_{A1}b_A P_A}{1 + b_A P_A} + \frac{q_{A2}b_A P_A}{1 + b_A P_A} \]  

(1)

in which \( q_{A1} = 6.611 \text{ mol kg}^{-1}, q_{A2} = 0.011 \text{ mol kg}^{-1}, b_{A1} = 4.762 \text{ bar}^{-1}, b_{A2} = 3.492 \text{ bar}^{-1} \) at 308 K (Park et al., 2021).

The CO₂ adsorption on the 13X was estimated by single-site Langmuir isotherm.

\[ q_A = \frac{q_A b_A P_A}{1 + b_A P_A} \]  

(2)

in which \( q_A = 5.145 \text{ mol kg}^{-1}, b_A = 9.007 \text{ bar}^{-1} \) at 308 K (Park et al., 2016).

In stark contrast, the equilibrium isotherms of hydrogen on both adsorbents are so close to linearity as shown in Figure 4B (Park et al., 2016; Park et al., 2021). In this study, the two hydrogen isotherms were approximated by linear isotherms by regressing the data over the range of measurement. The slopes of the fitted linear isotherms are 0.0421 mol kg⁻¹ bar⁻¹ and 0.0175 mol kg⁻¹ bar⁻¹ for activated carbon and 13X, respectively.

**Equilibrium Theory Model for PSA Analysis**

The PSA system with a rinse step shown in Figure 3 is the simplest step sequence for producing the heavy component at a very high purity during the blowdown step and the 5-step PSA system was analysed by Equilibrium Theory. The performance of a 5-step PSA working to separate a binary gas mixture can be estimated by Eqs 3a–9 that are derived and presented in the reference (Ruthven et al., 1994). In the mathematical expression, the strongly adsorbing component A’s adsorption equilibrium is allowed to be nonlinear while the weakly adsorbing component B’s adsorption isotherm must be linear with pressure or concentration. In addition to the general assumptions...
required for Equilibrium Theory, it was also assumed that the two adsorption isotherms are uncoupled. This model was developed under the limiting condition that a column is fully regenerated during the purge step for the sake of simplicity.

In order to estimate the product recovery, bed productivity and power consumption, it is crucial to estimate the total number of moles of the influent and effluent during each step. The equations for the quantities were all derived using Equilibrium Theory and they are listed below. Subscript I and O indicate influent and effluent, respectively.

- **Feed step.**
  \[
  N_{FI} = \frac{P_{HI} \cdot L \cdot A_c}{\theta_A(P_{HI}, y_f, 0)RT} 
  \]
  \[
  N_{FO} = N_{FI} \left[ 1 + \left( \frac{\theta(P_{HI}, y_f, 0) - 1}{\theta(P_{HI}, 1, y_f)} \right) \right] 
  \]
- **Rinse step.**
  \[
  N_{RI} = N_{RO} \left[ 1 + \left( \frac{\theta(P_{HI}, 1, y_f) - 1}{\theta(P_{HI}, 1, y_f)} \right) \right] 
  \]
- **Blowdown step.**
  \[
  N_{BO} = \frac{P_{HI} \cdot L \cdot A_c}{\theta_A(P_{HI}, 1, 0)RT} - \frac{P_{LI} \cdot L \cdot A_c}{\theta_A(P_{LI}, 1, 0)RT} 
  \]
- **Purge step**
  \[
  N_{PI} = \frac{P_{LI} \cdot L \cdot A_c}{\theta_A(P_{LI}, 1, 0)RT} + \frac{P_{PI} \cdot L \cdot A_c}{\theta_A(P_{PI}, 1, 0)RT} 
  \]
- **Light Product Pressurisation.**
  \[
  N_{LI} = \frac{L \cdot A_c}{\theta_A(P_{HI}, 1, 0)RT} (P_H - P_L) 
  \]

The product recoveries of H₂ and CO₂ are estimated by simply taking the mass balance around the column as follows:

\[
R_B = \frac{N_{FO} - N_{PI} - N_{LI}}{(1 - y_f)(N_{FI} - N_{RO})} = 1 - \frac{\theta_A(p_{HI, y_f, a}) - \theta_A(p_{HI, y_f, 0})}{\psi(1 - y_f)[1 - \theta_A(p_{HI, y_f, 0})]}
\]

\[
R_A = \frac{N_{BO} - N_{RI}}{y_f(N_{FI} - N_{RO})}
\]

\[
= \frac{\psi \left( \frac{\theta_A(p_{HI, y_f, a})}{\theta_A(p_{HI, 1, 3.0})} + (1 - \theta_A(p_{HI, 1, y_f}))[y_f - 1] - \frac{\theta_A(p_{HI, 1, 3.0})}{\theta_A(p_{HI, 1, 0})} \right)}{\psi y_f \left[ \frac{\theta_A(p_{HI, y_f, a})}{\theta_A(p_{HI, y_f, a})} - \theta_A(p_{HI, 1, y_f}) \right]}
\]

The PSA system consumes power for evacuation of the column during the blowdown and purge steps and pressurisation of the rinse step’s effluent for its recycle to the feed. The power consumption for evacuation or compression was estimated by Eq. 10.

\[
W = \frac{F \cdot R \cdot T_1 \cdot y_f(y_f - 1) \cdot \left( \frac{P_2}{P_1} \right)^{(y_f - 1)/y_f} - 1}{\eta_{ad}} 
\]

where F is gas flowrate (mol/s), R is gas constant (J/mol/K), T₁ is inlet temperature (K), γ is volume exponent, P₁ and P₂ are inlet and outlet pressure of a vacuum pump or a compressor, and ηad is the adiabatic efficiency.

**RESULTS AND DISCUSSION**

**Process Design and Operation**

The column diameter and length were estimated based on the same actual interstitial velocity of the feed gas and feed step time, 1 m/s and 600 s, respectively. Accordingly, it was also assumed that the cycle times of the two adsorption systems would be identical. The column diameter was found so as to meet the gas velocity condition, given the sum of the fresh and recycled gas feed flowrates. The column length was determined as the distance that the shock wave travels along the column during the feed step time. The pressure drop along the column at the feed step was estimated by Ergun equation. The calculation results for the two cases are juxtaposed in Table 2. The required column volume of the syngas case was around 1.5 times larger than that of the tail gas case, but the difference was mainly down to the difference of the adsorbent densities. The masses of adsorbents in a column are very similar to each other. The ratios of the pressure drop to the feed inlet pressure are 8% and 7% for the syngas and tail gas cases, respectively.

**Figure 5** shows a z-t diagram to depict clearly how the simple and shock waves move around the column during each step of the 5-step VPSA, and this diagram is valid for both capture cases. As expected, the characteristic lines are straight during the constant-pressure steps while they are curved during the pressure-varying steps. During the feed and rinse steps, shock waves propagate along the column from one end to the other end of the column. The simple wave at y = 0 reaches the column end during the purge step for complete regeneration. The gas leaving the column during the purge step is initially a pure heavy component, and the gas mole fraction decreases gradually to zero in case of complete regeneration. The performance may be improved by regenerating the column incompletely so that some of the heavy components still remain in the column at the end of the purge step. In **Figure 5**, X indicates the extent of purging, e.g., X = 1 for complete regeneration (Chiang, 1996; Ahn and Lee, 2020).

**Comparison of the Syngas and Tail Gas Capture Cases**

**Product Recovery and Bed Productivity: Effect of Desorption Pressure**

It is desorption pressure that is the only operating variable considered in this study, with the other operating variables...
fixed at constant values. Figure 6 shows the effect of desorption pressure on the product recovery and bed productivity in the two capture cases. The H₂ product recovery varies linearly with desorption pressure in both cases as shown in Figure 6A. The H₂ recovery is estimated by Eq. 8 that is derived from the H₂ mass balance around the column in a cycle. Among the terms in Eq. 8, only the moles of light product consumed for purging and depressurisation, NDT and NDJ, are affected by desorption pressure. By rearranging Eq. 8, it turns out that only the pressure ratio, Ψ, is varied by changing the desorption pressure while the other terms’ values remain constant, which leads to the linear changes of H₂ recovery with desorption pressure as shown in Figure 6A. The H₂ recovery of the tail gas case is way too low, as the gas consumption for complete regeneration is so gigantic. The huge consumption of the purge gas is attributed to the CO₂ isotherm on the 13X being nearly irreversible (Figure 4A). The desorption pressure has to be at least 0.07 bar, to have the H₂ recovery positive. It may not be practical operating the process at such a low pressure from the industrial perspective. The tail gas contains much less hydrogen than the syngas, as around 90% of the hydrogen contained in the syngas is recovered as a high purity of hydrogen product at a hydrogen purification PSA (see Table 1). The adjusted H₂ product recovery was also plotted in Figure 6A for the tail gas case, based on the total hydrogen product recovered by H₂ PSA as well as CO₂ VSA.

As for CO₂ product recovery, Eq. 9, the desorption pressure affects the amount of CO₂ produced during the blowdown step, while the other quantities remain constant. The CO₂ recovery relies on the amount of the CO₂ being desorbed by depressurisation only, without using a purge gas. In this respect, the highly irreversible isotherm of CO₂ on the 13X must be so disadvantageous, as it is very hard to desorb CO₂ by reducing the pressure. The desorption pressure has to be decreased down to 0.01 bar to achieve 90% CO₂ capture. In contrast, 92% CO₂ capture is achievable at the desorption pressure of 0.1 bar in case of syngas capture.

The effect of desorption pressure on the bed productivity (Figure 6B) is by and large similar to its effect on the product recovery (Figure 6A). It should be noted that the CO₂ molar flowrates in the two feeds are almost the same as each other, whilst the H₂ molar flowrate of the syngas is six times larger than that of the tail gas. Such a high bed productivity with respect to hydrogen in the syngas case can be explained by the very large difference of H₂ flowrate. At very low desorption pressures up to 0.05 bara, the bed productivity with respect to CO₂ in the tail gas case is superior to that in the syngas case. But this is merely down to the difference of two bed volumes, and the two CO₂-based bed productivities must be comparable to each other if they were expressed with respect to adsorbent mass instead of volume. At the desorption pressures being greater than 0.05 bara, the syngas case exhibits far greater bed productivity with respect to CO₂.

**Energy Consumption**

Figure 7 shows the specific power consumptions of the 5-step VPSA with the desorption pressure ranging from 0.01 to 0.6 bara. The power consumption for pressurising the CO₂ gas needed for the rinse step remains constant regardless of desorption pressure. However, the power consumptions for pulling a vacuum during the blowdown and purge steps vary greatly with the desorption pressure. The adiabatic efficiencies for gas compression and evacuation were fixed at 0.8, while

---

**TABLE 2 | Physical properties of the adsorbents and adsorption column design data (Park et al., 2016; Park et al., 2021).**

| Adsorbent                      | Syngas capture | Tail gas capture |
|-------------------------------|----------------|-----------------|
| Adsorbative mass fraction [-]  | 0.256          | 0.284           |
| Adsorbent particle density, ρ | 750            | 1,050           |
| Adsorbent particle diameter [nm] | 1.7 - 2.4 | 2.0 - 2.2 |
| Column length, L [m]          | 9.39           | 1.66            |
| Column diameter [mm]          | 3.01           | 5.90            |
| Column volume [m³]            | 66.8           | 45.3            |
| Adsorption time [s]           | 600            | 600             |
| Actual interstitial gas velocity at the feed step [m s⁻¹] | 1.77 | 0.109 |
| Pressure drop along the column at the feed step [bar] | | |

---

**FIGURE 5 | z-t diagram of a five-step VPSA process for syngas capture case. Lines represent the characteristics. The light grey area and the dark grey area indicate penetration of CO₂ (0 < y < 1) and pure CO₂ (y = 1), respectively.**

---

**FIGURE 6A |** The H₂ recovery of the tail gas case is superior to that in the syngas case. Among the terms in Eq. 8, only the moles of light product consumed for purging and depressurisation, NDT and NDJ, are affected by desorption pressure. By rearranging Eq. 8, it turns out that only the pressure ratio, Ψ, is varied by changing the desorption pressure while the other terms’ values remain constant, which leads to the linear changes of H₂ recovery with desorption pressure as shown in Figure 6A. The H₂ recovery of the tail gas case is way too low, as the gas consumption for complete regeneration is so gigantic. The huge consumption of the purge gas is attributed to the CO₂ isotherm on the 13X being nearly irreversible (Figure 4A). The desorption pressure has to be at least 0.07 bar, to have the H₂ recovery positive. It may not be practical operating the process at such a low pressure from the industrial perspective. The tail gas contains much less hydrogen than the syngas, as around 90% of the hydrogen contained in the syngas is recovered as a high purity of hydrogen product at a hydrogen purification PSA (see Table 1). The adjusted H₂ product recovery was also plotted in Figure 6A for the tail gas case, based on the total hydrogen product recovered by H₂ PSA as well as CO₂ VSA.

As for CO₂ product recovery, Eq. 9, the desorption pressure affects the amount of CO₂ produced during the blowdown step, while the other quantities remain constant. The CO₂ recovery relies on the amount of the CO₂ being desorbed by depressurisation only, without using a purge gas. In this respect, the highly irreversible isotherm of CO₂ on the 13X must be so disadvantageous, as it is very hard to desorb CO₂ by reducing the pressure. The desorption pressure has to be decreased down to 0.01 bar to achieve 90% CO₂ capture. In contrast, 92% CO₂ capture is achievable at the desorption pressure of 0.1 bar in case of syngas capture.

The effect of desorption pressure on the bed productivity (Figure 6B) is by and large similar to its effect on the product recovery (Figure 6A). It should be noted that the CO₂ molar flowrates in the two feeds are almost the same as each other, whilst the H₂ molar flowrate of the syngas is six times larger than that of the tail gas. Such a high bed productivity with respect to hydrogen in the syngas case can be explained by the very large difference of H₂ flowrate. At very low desorption pressures up to 0.05 bara, the bed productivity with respect to CO₂ in the tail gas case is superior to that in the syngas case. But this is merely down to the difference of two bed volumes, and the two CO₂-based bed productivities must be comparable to each other if they were expressed with respect to adsorbent mass instead of volume. At the desorption pressures being greater than 0.05 bara, the syngas case exhibits far greater bed productivity with respect to CO₂.

**Energy Consumption**

Figure 7 shows the specific power consumptions of the 5-step VPSA with the desorption pressure ranging from 0.01 to 0.6 bara. The power consumption for pressurising the CO₂ gas needed for the rinse step remains constant regardless of desorption pressure. However, the power consumptions for pulling a vacuum during the blowdown and purge steps vary greatly with the desorption pressure. The adiabatic efficiencies for gas compression and evacuation were fixed at 0.8, while
FIGURE 6 | Effect of desorption pressure on (A) product recovery and (B) bed productivity.
they may need to be adjusted to different values that the manufacturers provide for specific machines, particularly in case of a vacuum pump running at a very low vacuum pressure. The total specific power consumption of the syngas case is relatively low, decreasing monotonously from 1.1 to 0.4 MJ/kg CO₂ with the desorption pressure. In stark contrast, the total specific power consumption of the tail gas case reaches its minimum value of 0.7 MJ/kg CO₂ at 0.02 bara, and it increases rapidly with desorption pressure, mainly due to the drastic decrease of the CO₂ recovery. In general, the syngas case is superior to the tail gas case in terms of specific power consumption except for the very low desorption pressures below 0.05 bar.

It is interesting to compare the energy consumption between the CO₂ capture VPSA and an MDEA absorption process, as MDEA is one of the most conventional solvents taken for selective CO₂ removal from a feed gas with a relatively high CO₂ partial pressure. MDEA is one of the components of the ADIP solvent taken for Shell’s Quest CCS project where CO₂ is captured from a high pressure syngas, and the amine solvent was also chosen in the Japan’s Tomakomai project where CO₂ is captured from the PSA tail gas. The process configuration of a MDEA capture plant is similar to those of physical solvent capture plants, such as Selexol process (Kapetaki et al., 2015). The rich solvent leaving the absorber is regenerated by two different mechanisms: depressurisation and steam stripping. In case of the absorber working at a high pressure, the entire rich solvent is admitted to flash drums where CO₂ is partially desorbed. The liquid stream leaving the flash drum is the semi-lean amine. The semi-lean solvent is split into two sub-streams. One is returned to the absorber in the middle, while the rest is regenerated more thoroughly by steam stripping. The lean amine leaving the stripper is fed to the absorber on the top. Therefore, a MDEA process spends both electricity and heat, and the total energy consumption varies with the semi-lean amine recycle ratio, i.e., the ratio of the semi-lean amine being recycled back to the absorber to the total semi-lean amine leaving the flash drum.

In this study, an amine process using 40wt% aqueous MDEA solvent was simulated to estimate its energy consumption for two cases where CO₂ is captured from either the syngas or the tail gas at their actual compositions listed in Table 1. The process simulations were carried out with Honeywell UniSim R461.1 and its associated DBRamine package. In this simulation, the absorber and stripper were designed to have sufficient numbers of stages and large diameters so that the rich and lean loading could not be enhanced notably by increasing the number of stages further. In other words, the absorption system designed in this study can be considered as a limiting case where its performance is controlled by vapour-liquid equilibrium only, similarly to those of the adsorptive capture systems designed by Equilibrium Theory in this study.

Figure 8 shows the energy consumption of the two MDEA processes working to capture CO₂ from either syngas or tail gas. The energy consumption in terms of specific work consumption is affected greatly by the split ratio of the semi-lean amine between recycle to the absorber and steam stripping. It was found that the optimal ratio of the semi-lean recycle to the total semi-lean would be around 0.92, in other words, only 8% of the semi-lean solvent being directed to the stripper. The optimal semi-lean amine recycle ratio may vary slightly depending on what heat-to-work conversion factor to use. In this study, the reboiler heat of low pressure steam was converted to the equivalent work with the conversion factor of 0.3 (Ahn et al., 2013). At the optimal recycle ratio, the specific work consumption was as low as 0.35 MJ/kg CO₂. Therefore the two capture processes are expected to incur the energy consumptions similar to each other in case of syngas capture.
For the low pressure tail gas, the absorption process was designed so that the rich amine was regenerated by steam stripping only. The specific reboiler duty of the tail gas capture was estimated around 3.3 MJth/kg CO₂, greater than 2.2 MJ/kg CO₂ of the syngas capture case at the semi-lean recyle ratio set to zero. The difference of the reboiler duties is mainly down to the difference of the CO₂ partial pressure in the feed that results in different rich loading. In case of the tail gas feed, the VPSA may be competitive over the MDEA unit if the desorption pressure is set as low as less than 0.05 bara.

CONCLUSIONS AND FUTURE WORK

A Pressure Swing Adsorption process incorporating a rinse step has been studied to decarbonise a conventional SMR H₂ plant by capturing CO₂ from either the synthesis gas or the H₂ PSA tail gas. For the sake of quick feasibility study, the 5-step VPSA system was analysed by Equilibrium Theory without conducting complex numerical simulation. As a result of the analysis, it was found out that the shifted synthesis gas would be by and large more advantageous than the tail gas with respect to product recovery, bed productivity and power consumption, unless the VPSAs would be operated at an impractically low desorption pressure, i.e., less than 0.05 bara. The energy consumption of the VPSA was estimated as low as those of the MDEA units with the CO₂ recovery greater than 90%.

The VPSA designed for syngas capture is similar to the Gemini process’ A beds in that they work for CO₂ capture, while the two systems are different in terms of regeneration and repressurisation methods (Sircar and Kratz, 1988). The 5-step VPSA can be easily expanded to function to produce pure hydrogen as well as pure CO₂ by its integration with another adsorption cycle for hydrogen purification. In this respect, the existing H₂ PSA can be repurposed so that it can perform CO₂ capture as well as H₂ purification.

The theoretical model taken for PSA analysis in this study was so simple to use and the PSA performance was estimated effortlessly. But the PSA design/operation and adsorption dynamics that the model considered may not reflect the actual situation exactly. The Equilibrium Theory model will be developed further so as to enhance its accuracy and reliability, by considering incomplete regeneration, coupled isotherm, pressure equalisation steps, etc.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

YC: Equilibrium Theory calculation, wrote the mathematical model section, collected the data HA: Conceived and designed the analysis, wrote the paper, collected the data, performed the analysis, MDEA simulation.

FUNDING

This work was supported by the United Kingdom Engineering and Physical Sciences Research Council (EPSRC) grant EP/J018198/1. HA and YC. are grateful for funding from Birse Trustees to support the PhD study at the University of Edinburgh.
Ruthven, D. M., Farooq, S., and Knaebel, K. S. (1994). *Pressure Swing Adsorption*. New York: VCH.

Scottish Government (2020a). Scottish Government Hydrogen Policy Statement. Available at: https://www.gov.scot/publications/scottish-government-hydrogen-policy-statement/pages/12/.

Scottish Government (2020b). Scottish Hydrogen: Assessment Report [Online]. Available at: https://www.gov.scot/publications/scottish-hydrogen-assessment-report/(Accessed.

Sircar, S., and Kratz, W. C. (1988). Simultaneous Production of Hydrogen and Carbon Dioxide from Steam Reformer Off-Gas by Pressure Swing Adsorption. *Separat. Sci. Technol.* 23, 2397–2415. doi:10.1080/01496398808058461

Soltani, R., Rosen, M. A., and Dincer, I. (2014). Assessment of CO2 Capture Options from Various Points in Steam Methane Reforming for Hydrogen Production. *Int. J. Hydrogen Energ.* 39, 20266–20275. doi:10.1016/j.ijhydene.2014.09.161

Streb, A., and Mazzotti, M. (2020). Novel Adsorption Process for Co-production of Hydrogen and CO2 from a Multicomponent Stream-Part 2: Application to Steam Methane Reforming and Autothermal Reforming Gases. *Ind. Eng. Chem. Res.* 59, 10093–10109. doi:10.1021/acs.iecr.9b06953

UK BEIS (2021). *UK Hydrogen Strategy*. London: HM Government.

Voss, C. (2014). CO2 Removal by PSA: an Industrial View on Opportunities and Challenges. *Adsorption* 20, 295–299. doi:10.1007/s10450-013-9574-8

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**Publisher’s Note:** All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2021 Chen and Ahn. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.
**NOMENCLATURE**

- $A_c$: Cross section area of adsorption column, m$^2$
- $b$: Langmuir isotherm parameter, bar$^{-1}$
- $L$: Column length, mL Light product pressurisation step
- $N$: Total moles of either influent or effluent during a step, mol
- $P$: Pressure, bar
- $P_a$: Adsorption pressure, bar
- $P_d$: Desorption pressure, bar
- $R$: Universal gas constant, bar m$^3$ mol$^{-1}$ K$^{-1}$
- $q$: Adsorbed amount, mol kg$^{-1}$
- $q_s$: Saturation adsorption amount, mol kg$^{-1}$
- $T$: Temperature, K
- $t$: Time, s
- $y$: Mole fraction of heavy component, –
- $y_f$: Mole fraction of heavy component in the feed, –
- $z$: Axial position, m

**GREEK SYMBOLS**

- $\beta_B$: $\frac{1}{1 + \frac{y}{y_f}}$
- $\theta(P, y_1, y_2)$: $\frac{1}{\beta(P, P_d, P_f)}$
- $\theta_A(P, y_1, y_2)$: $\frac{1}{1 + \frac{y}{y_f}}$
- $\varepsilon$: Bed void fraction, –
- $\rho_p$: Adsorbent particle density, kg m$^{-3}$
- $\psi$: $P_n/P_L$, –

**SUBSCRIPTS**

- $A$: Heavy component, CO$_2$
- $B$: Light component, H$_2$ or Blowdown step
- $F$: Feed step
- $I$: Influent
- $L$: Column length, mL Light product pressurisation step
- $O$: Effluent
- $P$: Pressure, bar
- $R$: Rinse step