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Novel adsorption processes for carbon dioxide capture within an IGCC process

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Abstract

There is considerable interest in identifying carbon dioxide capture processes that can be incorporated within Integrated Gasification and Combined Cycle (IGCC) systems. In this paper, two novel adsorption based process configurations are proposed to operate in the temperature window (250-500°C) suitable for an IGCC process after the water gas shift reactor. These process configurations are numerically simulated with an in-house simulator MINSA (Monash Integrated Numerical Simulator for Adsorption), and the simulation results indicate that good performance can be achieved with low operating cost. Carbon dioxide purity of greater than 95% and carbon dioxide recovery of greater than 90% can be obtained by both process options.

1. Introduction

There are a number of different separation technologies that can be applied to precombustion carbon dioxide capture including solvent, membrane, and adsorbent based processes. The conventional technology is UOP's liquid absorption Selexol process which is a process option for the removal of hydrogen sulphide and simultaneous capture of carbon dioxide from an IGCC process. However, one potential limitation of this process is that capture occurs at ambient temperature. This necessitates cooling the gas exiting the Water Gas Shift (WGS) reactor, capturing the carbon dioxide and hydrogen sulphide (acid gas removal), and then reheating the gas prior to the power block (gas turbine). These cooling and reheating steps add to the capital cost and reduce the efficiency of the power cycle. By contrast, membrane and adsorbent based processes offer the potential of higher temperature capture thereby eliminating the intermediate cooling and reheating steps. Recently these efforts have further focused on integrated membrane-water gas shift (WGS) reaction or Sorption Enhanced WGS reactions that enable simultaneous hydrogen synthesis and carbon dioxide capture. These are important research directions which merit further consideration. In this paper however, we investigate and assess two moderate/high temperature adsorption-based carbon dioxide capture processes downstream of the WGS reactor. This paper details numerical simulation work to explore the

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potential of these two different process options utilizing two well known adsorbents--13X zeolite and hydrotalcite (HTC). Although there has been much work characterizing and developing adsorbents suitable for high temperature capture, there has been little work on integrating these adsorbents within a specific process configuration. This is the challenge taken up in this paper.

The results reported in this paper are the initial phase of a research project (*Energy Technology Innovation Strategy* (ETIS) project) funded by the Victorian state government of Australia to develop a precombustion carbon dioxide capture strategy within an IGCC process. This work is ongoing and adsorbent screening and numerical simulation is the initial phase. Subsequent process testing will be carried out using real synthesis gas feed from a pilot gasifier. One distinguishing feature of the IGCC process studied here is that the gasifier is air blown, and this results in a significant quantity of nitrogen through the system. There is therefore no need for nitrogen supply prior to the gas turbine as is common in oxygen blown gasifiers. Also, due to the elevated water concentration in the feed coal (lignite containing approximately 60% moisture), there is no requirement for steam injection into the WGS reactor. Lastly, the process operates at a moderate total pressure (27 bar).

Process 1 – Adsorption Process based on Hydrotalcite material

Hydrotalcites (HTC) have been researched extensively as a material suitable for Sorption Enhanced WGS due to their selectivity for carbon dioxide and adsorptive capacity in the temperature range of the WGS [1]. However, the process proposed here utilizes an HTC material as a separate carbon dioxide capture (VPSA) unit operation. This improves the simplicity of the unit operation

Process 2 – 2 Stage Adsorption Process based on 13X for separating water and carbon dioxide

Zeolite 13X has been identified previously as an adsorbent with significant adsorptive capacity of carbon dioxide at moderate temperatures (~ 120°C) [2]. Based on isotherm data, it is possible to extend this operating temperature window to 250°C. While the adsorptive capacity is reduced, the selectivity is enhanced, enabling effective separation of carbon dioxide up to 250°C using zeolite 13X. An additional benefit of using 13X at higher temperatures is that the water isotherm (which is almost rectangular at ambient temperature) becomes much more linear at 250°C. The adsorbent still retains a significant working capacity for water but does not need for deep vacuum or extended purge for bed regeneration (as is the case for ambient temperature operation).

Processes 1 and 2 are based on a vacuum/pressure swing adsorption technology. Thus the CO2 is adsorbed at syngas feed pressure but recovered under vacuum and delivered at atmosphereic pressure. A disadvantage of this approach is that the carbon dioxide is captured at low pressure (1 bar). Geosequestration will require that these low pressure streams are compressed to approximately 100 bar for storage. It is possible that an alternative adsorbent regeneration strategy, such as TSA, is more favourable in terms of reducing the overall energy penalty for sequestration. However, the VPSA cycles offers potential advantages with respect to simplicity, reduced cycle time, and a small bed sizing factor (less adsorbent required and a lower capital cost).

Ultimately a methodology is required to effectively compare the capture penalty (CAPEX and OPEX) of different capture strategies, such as those based on Selexol, membranes, VPSA and TSA. One example of such a methodology is that of Rubin [3]. The work reported here however only demonstrates the technical feasibility of a novel capture process. Further analysis is required to quantify and compare the specific aspects of this and competing processes.

2. Adsorption parameters from isotherm experiments

A key requirement to enable numerical simulation is determination of adsorption isotherms in the proposed operating temperature ranges. Isotherms for carbon dioxide and nitrogen on zeolite 13X have been measured with a volumetric apparatus (Micromeritics ASAP 2010 and ASAP2020) at 90°C and 120°C. These data were represented with the Dual-Site Langmuir equation with the parameters indicated in Table 1.

$$n_i^* = \frac{m_1 b_i p y}{1 + b_i p y + b_j p(1-y)} + \frac{m_2 d_i p y}{1 + d_i p y + d_j p(1-y)} \qquad (1)$$

$$b_i = b_{oi} \exp\left(\frac{Q_{1i}}{RT}\right); d_i = d_{oi} \exp\left(\frac{Q_{2i}}{RT}\right) \qquad (2)$$

Table 1. Dual-Site Langmuir isotherm constants for Adsorption of CO_2, H_2O and N_2 on 13X Zeolite

Parameter	CO_2	H_2O*	N_2
m_1 (mol/kg)	3.389	2.630	2.02
m_2 (mol/kg)	0.00	11.528	0.00
b_o (1/kpa)	1.21e-8	376.91e-09	2.036e-6
Q_1 (J/mole)	47511	66541.99	14875.2
d_o (1/kpa)	3.301e-6	48.698e-07	0.00
Q_2 (J/mole)	32176.7	52213.92	0.00

*isotherm data from UOP

Isotherms for carbon dioxide on HTC at 400°C is based on data and a chemisorption model by Lee et. al.[4].

$$n^* = \frac{m K_c P[1 + (a+1)K_R P^a]}{[1 + K_C P + K_C K_R P^{(a+1)}]} \qquad (3)$$

$$K_C = K_{C0} \exp\left(\frac{Q_1}{RT}\right); K_R = K_{Ro} \exp\left(\frac{Q_2}{RT}\right) \qquad (4)$$

Table 2. Chemisorption isotherm constants for CO_2 adsorption on HTC

Item	CO_2
m (mol/kg)	0.2365
K_{c0} (atm^{-1})	1.0338
Q_1 (J/mol)	23462.5
K_{R0} (atm^{-1})	2.043e-3
Q_2 (J/mol)	40385.9
a	2.6766

Based on reported literature, it was assumed that N_2, H_2. and H_2O did not adsorb on HTC [5].

3. Process cycle design and simulation

3.1. MINSA simulation tool

We have used the numerical simulator (MINSA) extensively over the past decade to evaluate air and carbon dioxide separation systems and help guide experiments [6,7,8]. MINSA solves the discretised form of the differential equations describing the mass and energy balance equations governing the adsorption process using a finite volume approach. This simulator has been described earlier [6,7]. Dual-site Langmuir isotherms were used to represent carbon dioxide, nitrogen and water adsorption on 13X zeolite while a chemisorption model was used to describe the adsorption of carbon dioxide on HTC as indicated above. It was assumed that N_2 and H_2O did not adsorb on HTC and H_2 was included with N_2. The kinetic model contains a discrete pellet version implementing the Dusty Gas Model to describe mass transfer within porous materials and is thus suitable for conventional macropore

diffusion limited processes[9]. There has been significant debate in the literature regarding the kinetics of HTC and whether desorption kinetics are much slower as suggested by Ding and Alpay [10].. By contrast, recent work by Lee et.al. [4] suggests uniform and faster kinetics. Future laboratory work is planned to examine this feature and confirm the adequacy of assuming the DGM approach which does not explicitly take account of the nature of chemisorption. The pressure drop in the packed adsorbent bed is calculated according to the Ergun equation. PID (Proportional Integral Derivative) control loops are used to adjust flow-rates (and hence boundary conditions) to achieve design specifications (temperatures, pressures, purities, etc). Cyclic steady state (CSS) is assessed by closure of mass and energy balances to within prescribed tolerances and periodicity of pressure, temperature and composition profiles.

The target in the numerical simulation is to achieve a carbon dioxide stream of purity greater than 95% and a CO_2 recovery greater than 90%.

3.2. Cycle development

An 8 step cycle (2 beds) was used to demonstrate the feasibility of the separation. Half of the cycle is shown below. The remaining half is obtained by replacing bed 1 with bed 2 and duplicating the steps shown below. Increasing the number of beds would improve the recovery of both CO_2 and hydrogen.
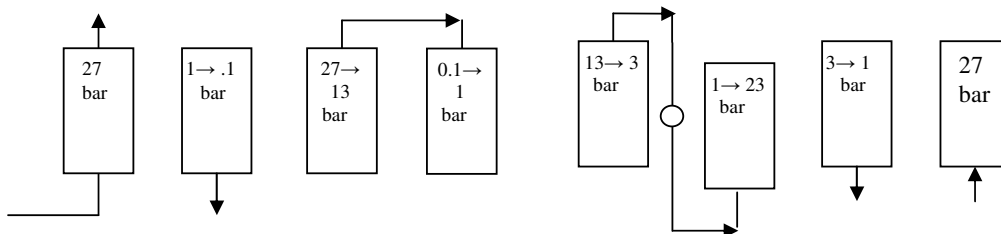

Figure 1. VPSA processing cycle used to capture CO_2 from an IGCC synthesis gas stream

The cycle shown above was designed to remove water and capture carbon dioxide. Four major phases are included: adsorption, equalization, compression, desorption and re-pressurization. In the first phase (adsorption step 1) the feed gas exiting the water gas shift reactor at 27 bar enters the bottom of the bed and exits through the top of the bed. This step causes the preferentially adsorbed species (carbon dioxide or water vapor) to be selectively adsorbed from the bulk gas to the solid phase. The second phase (step II) is equalization where the pressures in the two beds are equalized and the carbon dioxide or water is concentrated in bed 1. Thereafter a compression step is introduced to compress gas flow from bed one to bed two, in which carbon dioxide or water can be further concentrated. The following step is counter-current evacuation which is the primary step removing adsorbed carbon dioxide or water (and co-adsorbed components). In Process 1, a single VPSA cycle captures CO2 and some co-adsorbed water. In Process 2, a two-stage adsorption process is used. In the first stage, predominantly water is removed by blowing down the bed to atmospheric pressure and condensing the water thereby recovering energy. In the second stage, a VPSA process is used to enrich the water depleted stream. These are described in more detail below.

3.3. PSA physical parameters and adsorbent parameters

The simulations are based on adsorbent 13X adsorbent (PSAO2 HP Molsiv®) and HTC (K$_2$CO$_3$ promoted HTC) (8X12 mesh, bulk density of 675 kg/m^3, bed voidage of 0.37 and pellet voidage of 0.6). These properties were measured in our laboratory. The PSA adsorption bed has an internal diameter of 1m and length 1 m. Adiabatic operation is assumed as this would closely represent industrial operation.

3.4. Process conditions

Table 3 shows the designed pressure profile and step times for Process 1 and Process 2 (Stage 1 and Stage 2)

Table 3. Operating Parameters for Process 1 and Process 2 (all pressures are bar abs.)

Feed gas condition	Step	Process 1 - HTC VPSA for CO_2 capture	Process 2 – Stage 1 - 13X PSA for water removal	Process 2 – Stage 2 - 13X VPSA for CO_2 capture
Composition:	Step 1 & 5	22s, 27 bar (bed 1);	18s, 27bar (bed1);	7s, 27bar (bed 1)
21.5% CO_2, 16.8% H_2O and remainder N_2/H_2		0.1 bar (bed 2)	1 bar (bed 2)	0.1 bar (bed 2)
	Step 2 & 6	5s, 12.5 bar (bed 1 & 2)	3s, 14 bar (bed 1 & 2)	3s, 12 bar (bed 1 & 2)
Temperature:400°C (HTC)	Step 3 & 7	3s, 1 bar (bed 1);	5s, 3 bar (bed 1)	5s, 1 bar (bed 1)
250°C(13X)		23 bar (bed 2)	24 bar (bed 2)	23.6 bar (bed 2)
Feed Pressure: 27bar	Step 4 & 8	5s, 0.1 bar (bed 1)	5s, 1 bar (bed 1)	5s, 0.1 bar (bed 1)
		27 bar (bed 2)	27 bar (bed 2)	27 bar (bed 2)

4. Results and discussion

4.1. Pressure History

The pressure history in the adsorption beds for Process 1 (HTC) and Process 2 (13X)-Stage 2 are similar and are shown in Figure 2. The pressure drop across the bed is approximate 3kPa resulting in marginal reduction in the pressure of the hydrogen rich stream fed to the gas turbines.
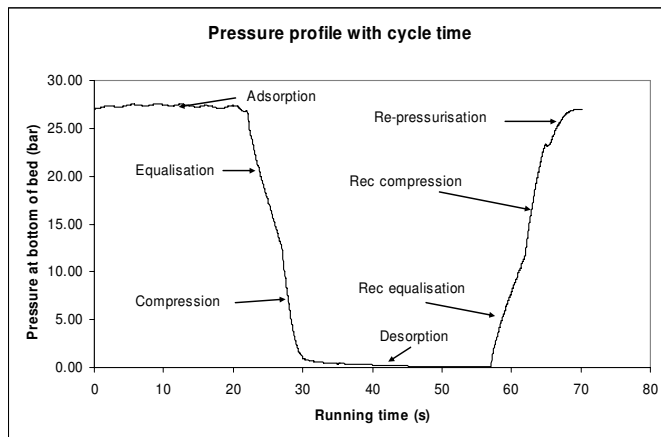

Figure 2. History of Bed Pressure at Cyclic Steady State

4.2. Process 1(HTC) performance

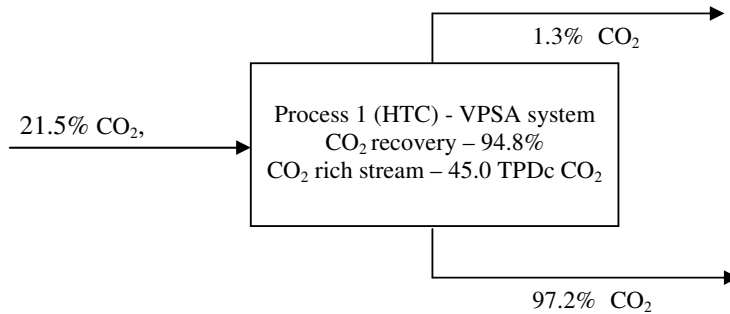The performance for HTC VPSA process is summarized in Figure 3.

Figure 3. HTC VPSA processing performance at 400°C

The recovery of CO_2 for Process 1 is 94.8% and the carbon dioxide productivity is 45 tonne per day contained (TPDc). Hydrogen rich product gas (containing only 1.3% CO2) at 27 bar is fed to the gas turbine directly. The carbon dioxide concentration of the waste gas is 97.2%. This process achieves the required purity and recovery targets.

The energy required for the separation occurs in the evacuation and compressing steps. In the evacuation step, the pressure in the bed is reduced to 10 kPa (abs) removing the bulk of the carbon dioxide. The power consumed for both evacuation and compression steps was calculated assuming single stage adiabatic compression with an efficiency of 70%. The total power consumption for the HTC PSA process is 4.15 kW/TPDc CO_2.

4.3. Process 2 (13X) performance

As mentioned earlier, Process 2 involves two separate stages – water removal (Stage 1) and carbon dioxide capture (Stage 2). Both stages operate at 250°C. This 2 stage process is shown in Figure 4. Feed gas enters Stage 1 where water vapor is removed by PSA. The water recovery for the process is 95.3% and 7.6 tonne of water per day contained (TPDc) is recovered. The H_2 product gas exiting Stage 1 contains less than 1% water vapour.

The desorbed stream from the water removal stage (Stage 1) contains water at 87.5%, carbon dioxide 3.6% and the balance hydrogen and nitrogen. The energy of this stream (high temperature and pressure steam) can be recovered through heat integration and turbines. This step is important for the overall process efficiency to enable this process to compete with existing solvent processes that incorporate energy recovery. Following water condensation, the carbon dioxide concentration is be 28.6% and the balance is hydrogen and nitrogen. Importantly in order to recover the hydrogen, this stream can be compressed and enters stage 2 as is shown in Figure 4.

In Stage 2, carbon dioxide is captured by the VPSA process. Carbon dioxide recovery is 91.3% and carbon dioxide productivity is 32.9 tonne per day contained (TPDc). The hydrogen rich product stream contains 2.6% carbon dioxide, 97.4% hydrogen and nitrogen. The waste (carbon dioxide rich) stream contains 93.9% carbon dioxide, 2.3% N_2/H_2 (after water condensation, the carbon dioxide is at 97.7%). The energy consumed in the

evacuation step is 2.0kW/TPDc H_2O and in the compression step is 5.2 kW/TPDcCO_2. The total energy consumption for the two stages is 8.7kW/TPDc CO_2.

Product gas from first stage

Product gas to gas turbine

H_2O 1.7%
CO_2 21.5%
Rest H_2/N_2

STAGE 1
Removal of water vapour at 250ºC by zeolite 13X.
Water recovery –95.3 %
Water rich stream – 7.6TPDcH_2O

CO_2 25.57%
H_2/N_2 – 73.5%

CO_2– 2.6%
H_2O – 0.00%

STAGE 2
Capture of CO_2 at 250ºC by zeolite 13X .
CO_2 recovery – 91.3%,
CO_2 rich stream– 32.9 TPDc CO_2

H_2O 87.5%
CO_2– 3.6%
H_2/N_2 – 8.9%

Down stream gas

CO_2 28.6%
Rest H_2/N_2

Water condensation
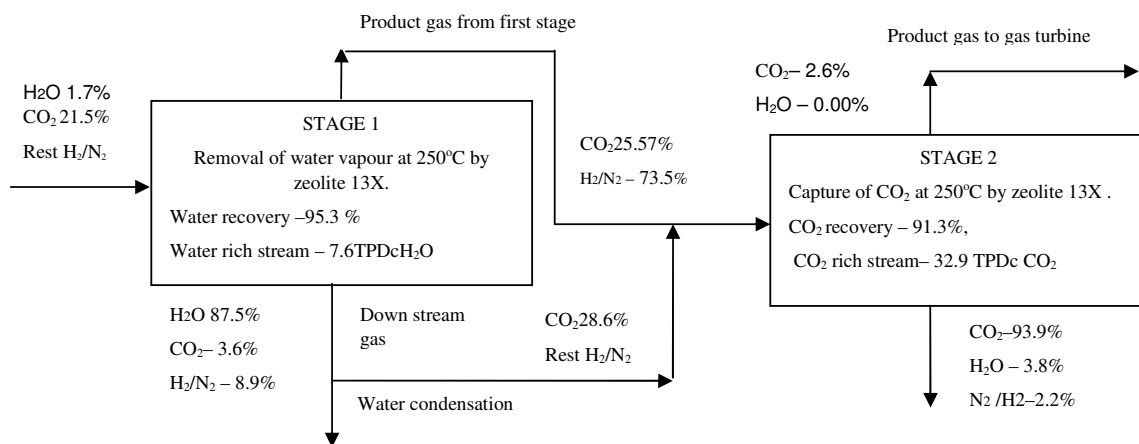
CO_2–93.9%
H_2O – 3.8%
N_2 /H2–2.2%

Figure 4. Process 2 – 2 Stage Water Removal and Carbon Dioxide Capture using 13X

Table 4 – Overall comparison of Process 1 and Process 2

Performance Parameter	Process 1 (HTC)	Process 2 (13X) (Overall)
Overall CO2 recovery (%)	94.8%	91.3%
Overall CO2 purity (%)	97.2%	97.7% (after water condensation /separation)
Bed Sizing Factor BSF (kg/TPDcCO2_)	32.1	32.9
Energy (kW/TPDc CO_2)	4.1	8.7

Although Process 1 appears to be more attractive (about ½ power consumption), it is operating at 400°C and represents a far greater engineering challenge than Process 2 which operates at 250°C. Process 2 has greater heat integration opportunities which will be explored further in future work.

5. Conclusions

In this work, the technical feasibility of two novel precombustion capture carbon dioxide processes by VPSA has been demonstrated using the numerical simulator, MINSA. HTC and zeolite 13X are used as adsorbents in these processes. For both options, carbon dioxide recovery and purity can achieve the target requirements – 95% purity and 90% recovery. Comparing the two options, the advantage of Process 1(HTC) is that the performance is achieved from a single stage separation and lower power consumption. However, for some gas turbines there is a limit on the water concentrations entering the turbine (∼ 13%), and this constraint may not be achieved with Process

1 (HTC). A feature of both processes is that they operate in the temperature range between the exit temperature of the WGS reactor and the inlet temperature to the gas turbine

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Notation:

n : specific equilibrium amount (mol/kg)

m_1: Saturated adsorbed phase loading, gmole/(kg ads)

m_2: Saturated adsorbed phase loading, gmole/(kg ads)

b_{0i}: Term 1 of Pre-exponential term, 1/bar.a

Q_{1i}: Term 1 of Heat of adsorption in J/gmole

d_{0i}: Term 2 of Pre-exponential term, 1/bar.a

Q_{2i}: Term 2 of Heat of adsorption in J/gmole

a: constant which changes with different component

m: saturated chemisorption capacity of chemisorbent surface (mole/kg)

K_{CO}: constant for chemisorption reaction(atm^{-1})

Q_1: molar isosteric heat of chemisorption (kJ/mol)

K_{RO}: constant for additional complexation reaction (atm^{-a})

Q_2: heat of additional surface reaction (kJ/mol)

k: ratio of heat capacities for air, 1.28 for air

Q_f: Instantaneous feed flow (m^3/hr)

P_{low}: Instantaneous vac pressure for evacuation and also pressure for bed 1 (kPa)

η_f: efficiency for vacuum pump or compressor 0.7

P_{high}: atmosphere pressure for evacuation and also instantaneous pressure for compressed bed (kPa)

Δt: scanning time (s)

Power$_{cycle}$: Power number consumed in each cycle (kW/cycle)

$CO_{2cycle}(T)$: carbon dioxide productivity in each cycle (T)