Supporting Information:
Cutting the cost of carbon capture: a case for carbon capture & utilization.

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1 Calculating the minimal separation work

The basic equation to estimate the minimum energy ($W_{\text{sep}}^{\text{min}}$) required to separate a two-component gas mixture is given by

$$
\begin{aligned}
-W_{\text{sep}}^{\text{min}} &= T\Delta S \\
&= n_{\text{em}}Ts^{\text{im}}(x_{\text{em}}) + n_{\text{cap}}Ts^{\text{im}}(x_{\text{cap}}) - n_{\text{flue}}Ts^{\text{im}}(x_{\text{flue}})
\end{aligned}
\tag{1}
$$

where n_{em} is the number of moles of the emitted gas, n_{cap} is the number of moles of the captured gas, and n_{flue} is the number of moles of the flue gas. Similarly, x_{em} corresponds to the mole fraction of emitted CO_2, x_{cap} corresponds to the mole fraction of captured CO_2, and x_{flue} corresponds to the initial mole fraction of CO_2 in the flue gas. The mixing entropy is proportional to the total number of configurations,

$$
s^{\text{im}} \propto \ln \Omega
\tag{2}
$$

and given the Stirling approximation

$$
\ln N! \approx N \ln N - N
$$

this results in

$$
s^{\text{im}}(x) = R[x \ln x + (1-x)\ln(1-x)]
\tag{3}
$$

where R is the gas constant and x corresponds to the corresponding mole fraction of CO_2.
There are three cases that need to be considered when calculating the minimum work of separation for flue gas.

(1) First of all, there is the case of perfect separation, where the entire amount of CO_2 in the flue gas is captured and no impurities of N_2 are found in the captured gas. In this case, the total number of configurations Ω to emit pure N_2 and capture pure CO_2 are both 1 and hence, the molar entropies $s^{\text{im}}(x_{\text{em}})$ and $s^{\text{im}}(x_{\text{cap}})$ are equal to zero. As a result, the minimum work is simply

$$
-W_{\text{sep}}^{\text{min}} = -n_{\text{flue}}Ts^{\text{im}}(x_{\text{flue}})
\tag{4}
$$

(2) In case we assume that the emission stream is pure N_2 and the captured gas contains all the CO_2, but may also contain some residual N_2, equation 1 reduces to

$$
-W_{\text{sep}}^{\text{min}} = n_{\text{cap}}Ts^{\text{cap}}(x_{\text{cap}}) - n_{\text{flue}}Ts^{\text{im}}(x_{\text{flue}}).
\tag{5}
$$

(3) Finally, the most general case is the one in which some N_2 may be present in the captured stream, and some CO_2 may be present in the emission stream. We then need to start from the original form of equation 1. To solve this equation, we need to compose both the mass balance for CO_2 and the mass balance for the mixtures:

$$
\begin{aligned}
n_{\text{flue}} &= n_{\text{cap}} + n_{\text{em}} \tag{6}\\
x_{\text{flue}}n_{\text{flue}} &= x_{\text{cap}}n_{\text{cap}} + x_{\text{em}}n_{\text{em}} \tag{7}
\end{aligned}
$$

Using equations (6) and (7), one can determine n_{cap} and n_{em}

$$
n_{\text{cap}} = \frac{x_{\text{flue}} - x_{\text{em}}}{x_{\text{cap}} - x_{\text{em}}}n_{\text{flue}}
\tag{8}
$$

$$
n_{\text{em}} = \frac{x_{\text{flue}} - x_{\text{cap}}}{x_{\text{em}} - x_{\text{cap}}}n_{\text{flue}}
\tag{9}
$$

If a specific CO_2 capture efficiency is desired or required, an additional parameter α is introduced. Then, the captured and emitted CO_2 fractions can be expressed as the ratio of the initial CO_2 concentration in the flue gas. Consequently, n_{cap} and n_{em} are

$$
n_{\text{cap}} = \frac{\alpha x_{\text{flue}}}{x_{\text{cap}}}n_{\text{flue}}
\tag{10}
$$

$$
n_{\text{em}} = \frac{(1-\alpha)x_{\text{flue}}}{x_{\text{em}}}n_{\text{flue}}
\tag{11}
$$

Variable x_{cap} is known for a specific separation process, as it corresponds to the final concentration of captured CO_2. Variable x_{em} on the other hand, needs to be determined by equate equation (9) and (11), which results in

$$x_{em} = \frac{(1-\alpha)x_{flue}x_{cap}}{x_{cap} - \alpha x_{flue}} \tag{12}$$

Substituting these mole fractions into equation 1 gives

$$-W_{sep}^{min} = T \cdot [(1 - \alpha x_{flue})s^{em}(\frac{(1-\alpha)x_{flue}}{1 - \alpha x_{flue}}) + \frac{x_{flue} - x_{em}}{x_{cap} - x_{em}}s^{cap}(x_{cap}) - s^{flue}(x_{flue})]. \tag{13}$$

To obtain the work per kg of CO_2, this equation should be divided by the mass of the captured CO_2. Hence equation 14 results in

$$-W_{sep}^{min} = \frac{T}{\alpha x_{flue}M} \cdot [(1 - \alpha x_{flue})s^{em}(\frac{(1-\alpha)x_{flue}}{1 - \alpha x_{flue}}) + \frac{x_{flue} - x_{em}}{x_{cap} - x_{em}}s^{cap}(x_{cap}) - s^{flue}(x_{flue})]. \tag{14}$$

Where M_{CO_2} is the molar mass of CO_2, 0.044 kg/mol and T is the temperature of the flue gas. For coal and natural gas-fired power plants, this is 313 K, whereas an air temperature of 288 K is assumed.

In Table 1, several minimum separation energies are calculated at different initial gas compositions, CO_2 capture efficiencies, separation temperatures, and desorption mole fractions.

Table 1: Min. separation work (in kJ/kg$_{CO_2}$) for different initial gas & capture conditions ($n_{flue} = 1$ mol).

| CO_2 capture efficiency α	W_{sep}^{min} of air $x_{cap} = 0.99$	W_{sep}^{min} of natural gas $x_{cap} = 0.99$	W_{sep}^{min} of coal $x_{cap} = 0.99$
1	477.1	245.0	167.7 [1]
0.9	463.2	230.0	153.1
0.75	452.0	218.0	141.5
0.5	439.4	204.6	129.0
efficiency α	$x_{cap} = 0.7$	$x_{cap} = 0.7$	$x_{cap} = 0.7$
1	432.7	196.7	119.5
0.9	418.8	181.7	104.8
0.75	407.6	169.7	93.3
0.5	395.0	156.3	80.7
efficiency α	$x_{cap} = 0.5$	$x_{cap} = 0.5$	$x_{cap} = 0.5$
1	404.7	166.3	89.1
0.9	390.8	151.3	74.4
0.75	379.6	139.3	64.9
0.5	367.0	126.0	50.3

2   The improvement in parasitic energy
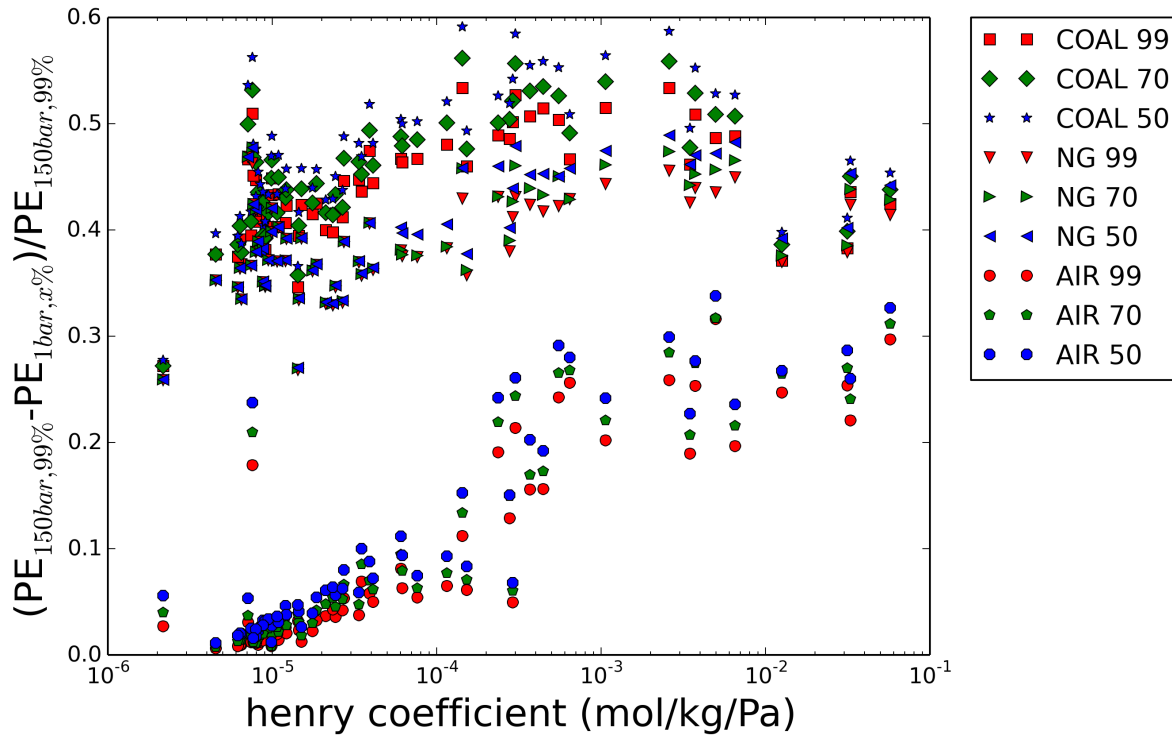
Figure 1: The improvement of the parasitic energy, compared to the reference case of CO_2 at 150 bar and 99% imposed purity, as a function of the Henry coefficient of CO_2.

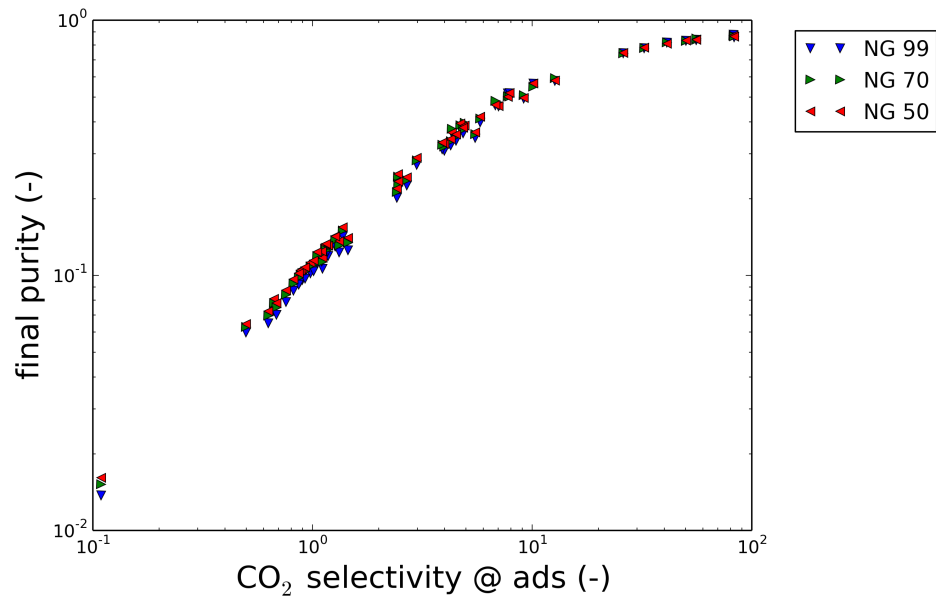# 3   Final purity as a function of CO$_2$ selectivity

Figure 2: Final purity as a function of CO$_2$/N$_2$ selectivity of the material at adsorption conditions for carbon capture from natural gas flue gases at different imposed purities.
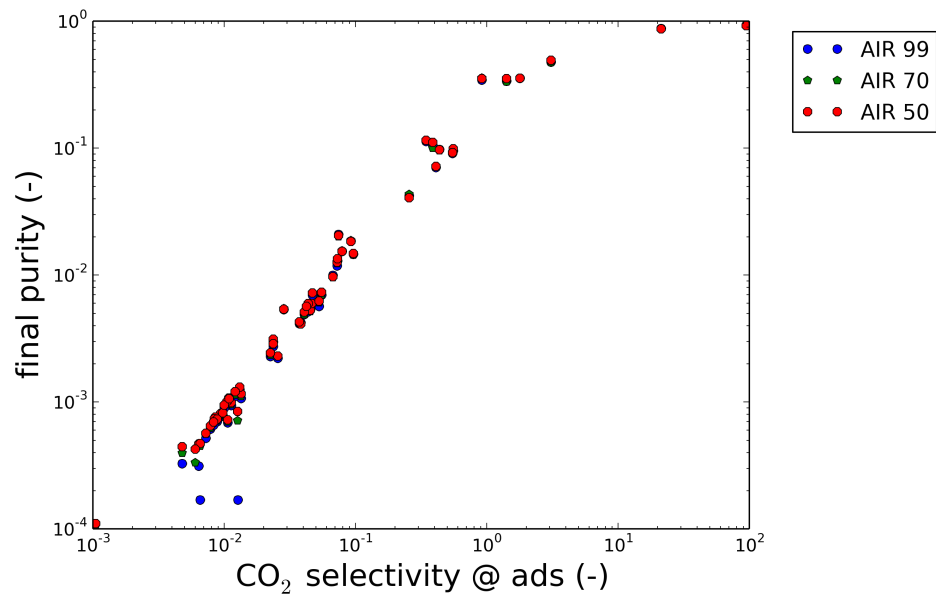

Figure 3: Final purity as a function of CO$_2$/N$_2$ selectivity of the material at adsorption conditions for carbon capture from air at different imposed purities.

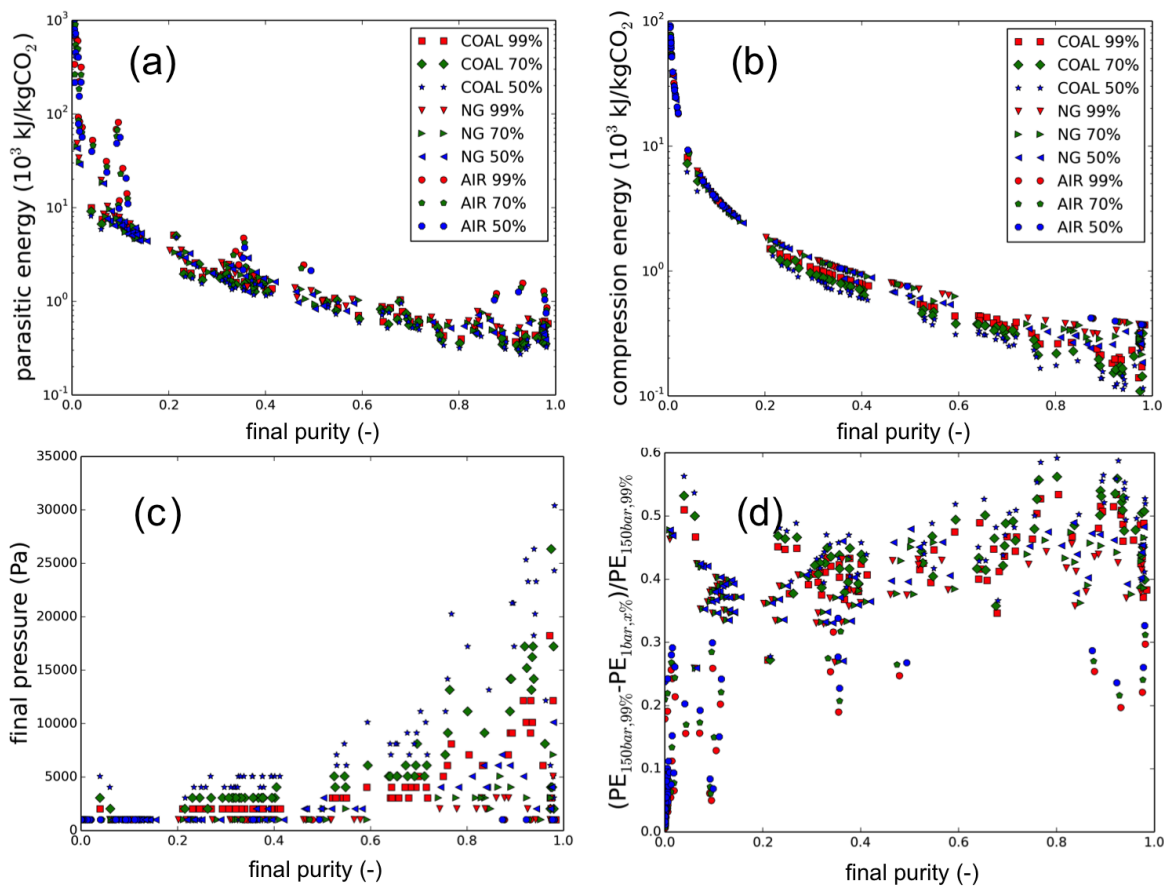# 4 Correlations with purity

Figure 4: (a) parasitic energy as a function of the final purity (b) the compression part of the parasitic energy as a function of the final purity (c) the final pressure as a function of the final purity (d) improvement of the parasitic energy, compared to the reference case of CO_2 at 150 bar and 99% imposed purity, as a function of the final purity.

References

[1] J. M. Huck, L.-C. Lin, A. Berger, M. N. Shahrak, R. L. Martin, A. Bhown, M. Haranczyk, K. Reuter and B. Smit, *Energy & Environmental Science*, 2014, 4132–4146.