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Multi-Objective Optimisation of Hybrid CO_2 Capture Processes Using Exergy Analysis

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Carbon dioxide (CO_2) purification is an essential step in the carbon capture and storage (CCS) process. The leading technology consists of a solvent absorption carbon capture process followed by a multi-stage CO_2 gas compression into supercritical state for sequestration. This study considers a hybrid system of vacuum swing adsorption (VSA), membranes and cryogenic separation. Replacing the multi-stage gas compression with the cryogenic separation has two main advantages: firstly, it further purifies the CO_2 stream, which is valuable for both VSA and membrane processes since both processes struggle to achieve high purity product. Secondly, it produces liquid CO_2 that can be pumped to the supercritical state, which is required for transport and sequestration. Due to the higher degree of freedom available in hybrid processes, a new methodology using multi-objective optimisation combined with exergy analysis was used to optimise the process. This allowed different decision variables to be considered to find the range of optimum operating conditions for each of the processes. It was determined that the refrigerant flow rate, multi-stage compression and cryogenic minimum temperature had the biggest impact on the recovery rate. Furthermore, it was observed that the total specific shaft work had a linear relationship with the specific exergy loss rate.

1. Introduction

The negative effects of greenhouse gases (GHG) in the atmosphere have been widely reported. The IPCC fifth assessment report increased the scientific certainty that changes in the anthropogenic CO_2 concentrations and atmospheric temperature are related (Edenhofer and Seyboth, 2013). Therefore, reduction of CO_2 from major sources such as fossil fuel power generation is critical. Among a portfolio of technologies required to mitigate those emissions, integration of Carbon Dioxide Capture and Storage (CCS) into coal fired power stations is a technology that can significantly reduce the carbon emissions from stationary sources. Post-combustion CCS involves the separation and capture of the CO_2 from the flue gas generated by the power plants, compressing the separated CO_2 into a supercritical fluid and then storing it in geological structures such as deep saline formations.

In order to implement CCS, equipment needs to be installed to capture and compress the carbon dioxide. Heat and electrical energy are required to operate the equipment, which reduces the efficiency of the power plant. The main post-combustion CO_2 capture methods involve: solvent absorption, adsorption, membranes, cryogenic separation and hybrid processes. (Pires et al., 2011). Each of these technologies has different advantages and disadvantages. For example, solvent absorption can achieve the high CO_2 purity and recovery rate by having a high solvent loading; however this comes at a high recovery heat energy required to regenerate the solvent. On the other hand, membranes and adsorption processes have a relatively low environmental impact due to the fact that they do not require solvents but both of these processes draw a large amount of electrical energy. It is possible that by combining two or more capture processes, the advantages and disadvantage of each process can complement each other to have a

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better overall performance. For example, adsorption and cryogenic separation could be a natural fit due to fact that adsorption produces low purity CO_2 and cryogenic separation can further purify the stream. Several studies have investigated different configurations of hybrid process. Both Scholes et al. (2013) and Belaissaoui et al. (2012) proposed hybrid processes which involved a solvent and membrane system. Although the hybrid performed better in terms of both energy consumption and CAPEX than the membrane process, it could not match the base MEA solvent absorption.

While energy analysis has been predominantly used to assess the performance of a process, exergy analysis has also been used (Hagi et al., 2013) and is beneficial as it allows the quality of energy being transferred in the process to be studied.

This work aims to optimise the integration of post-combustion hybrid carbon capture with exergy analysis and CO_2 recovery rate as the two main performance indicators. In order to do so, a combination of steady-state mass and energy balance simulation and multi-objective optimisation is used.

2. Methodology and Framework

The post-combustion flue gas properties were based on a 300 MW sub-bituminous coal-fired power station. The flue gas is pre-treated to remove the impurities and water by scrubbing, resulting in a stream composed of a binary mixture of CO_2 and N_2 as shown in Table 1. The pressure drop associated with the pre-treatment is accounted for as an energy penalty.

The hybrid capture process investigated in this study was a combination of Vacuum Swing Adsorption (VSA), cryogenics and membrane, as shown in Figure 1. All simulations were performed using the Aspen HYSYS® software package, version 8.4, using the Peng-Robinson fluid package throughout the whole capture process plant. The VSA electrical power requirement, which uses the VSA CO_2 recovery rate and the CO_2 outlet purity as the input variable, but does not take into consideration the water removal, was used according to the following mathematical model represented in equations 1-3. Those equations were modelled by using unpublished simulation values obtained from Aspen Adsim® provided by Xiao and Webley (2013).

$$\text{Blower Power (GJ/t } CO_2\text{)} = 2.06 - 5.37\text{E-}02x + 1.08\text{E-}02y + 3.58\text{E-}04x^2 - 1.05\text{E-}04xy \tag{1}$$

$$\text{Vacuum Pump Power (GJ/t } CO_2\text{)} = 4.55 - 1.21\text{E-}01x + 2.66\text{E-}02y + 8.18\text{E-}04x^2 - 2.61\text{E-}04xy \tag{2}$$

$$\text{Total VSA power} = \text{Blower Power} + \text{Vacuum Pump Power} \tag{3}$$

where x is the CO_2 recovery rate in % mass fraction and y is the CO_2 outlet purity in % mass fraction

The CO_2 outlet stream from the VSA was compressed in three stages with inter-cooling using cooling water. A mixed ethane/propane refrigeration system was used to achieve cryogenic temperatures in the cryogenic separation. The tail gas membrane process was modelled using mass transfer equations, specifically developed for applications in carbon capture simulations. (Scholes et al., 2013)

There are a number of key operating conditions, known as decision variables, in capture processes that can be varied to observe their impact on two key objectives; the exergy loss rate and overall CO_2 recovery rate of the hybrid process. As changes to the design variables may result in antagonistic results in the two objectives, MOO should be a useful tool as it provides a range of solutions, called the ‘Pareto-Optimal’ solutions that enable a balance between the two objectives to be considered. Using this range of solutions, the user can make the final selection by either

Table 1: Post-combustion flue gas properties based on a 300 MW sub-bituminous coal fired power station after pre-treatment

Feed Conditions		
Vapour Fraction		1.00
Temperature	(°C)	50.3
Pressure	(kPa)	103
Molar Flow	(kmol/h)	5.78e4
Mass Flow	(kg/h)	1.67e6
Composition	(mol frac)	
CO_2		0.64
N_2		0.36

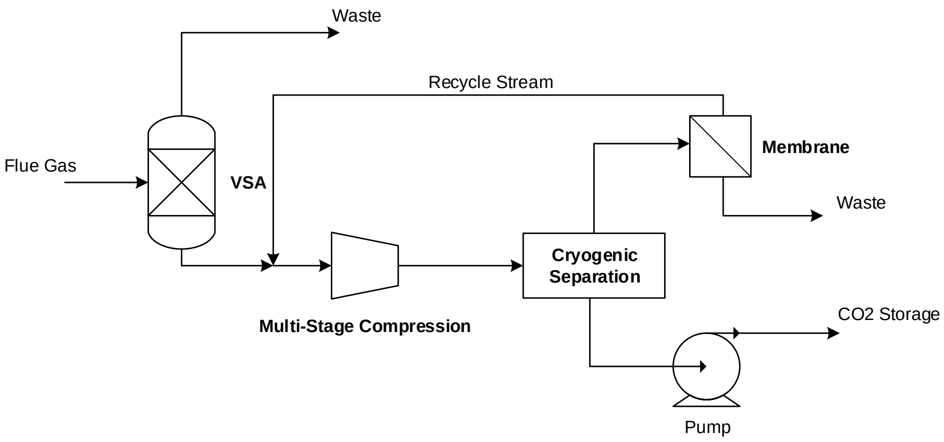


Figure 1: Schematic diagram of VSA, cryogenics and membrane hybrid carbon capture process

looking at the impact the decision variables have on the optimised solution or by performing further analysis on the optimised solutions.

In this work, the NSGAII genetic algorithm has been applied for this MOO(Rangaiah, 2009); seven decision variables were allowed to be varied including: refrigerant ethane molar fraction, refrigerant molar flow, cryogenic process stream outlet temperature, multi-stage compression pressure and the membrane stage cut (fraction of feed gas that permeates through the membrane). Table 2 shows the range of values that those decision variables were allowed to vary for the hybrid capture process.

All other process unit conditions were specified using industry accepted parameters. The compression stage for both the multi-stage compression and refrigerant compression had an efficiency of 75 %, with inter-stage coolers using cooling water with an approach temperature of 40 °C and a pressure drop of 40 kPa. The heat exchangers in the cryogenic separation were plate-fin heat exchangers with a pressure drop of 50 kPa on both the process side and refrigerant side.

3. Results

3.1 Decision Variables Pareto Charts

The Pareto Optimal Front is the solution obtained from the last generation of the Genetic Algorithm of the non-dominated solution set. The results shown are for a MOO using 100 individuals with 50 generations. The Pareto charts of the first six decision variables are shown in Figure 2 plotted against the objective 1: Maximum CO_2 Recovery.

3.2 Objective Variables Pareto Charts

The Pareto charts of the objective variables are shown in Figure 3(a).

From the objective variables Pareto charts, it could be observed that with increasing recovery rate, there was an increase in exergy loss rate. Therefore, in order to better understand the exergy loss rate with respect to the amount of CO_2 being captured by hybrid capture process, a new graph, using the Pareto-Optimal solutions, of specific exergy loss rate versus recovery rate was generated (Figure 3(b)), where specific exergy loss rate is the exergy loss rate per mass of CO_2 being recovered by the process.

3.3 Additional Results

In addition to the decision variables and objective variables, other key process performance variable were also recorded while performing the MOO. Two of those variables can be seen in Figure 4(a) and 4(b),

Table 2: Table of decision variable range for MOO and optimum operating conditions of hybrid process

Decision Variable		Minimum	Maximum	Optimum
Refrigerant Ethane Molar Fraction		0	0.4	0.22
Refrigerant Molar Flow	(mol/s)	0.2	1.7	1.4
Cryogenic Process Stream Outlet Temperature	(°C)	-60	-30	-56.7
Multi-Stage Compression Pressure	(kPa)	500	4,000	1,797
VSA CO_2 Recovery Rate	%	95	98	95.5
VSA CO_2 Outlet Purity	%	62	65	64.9

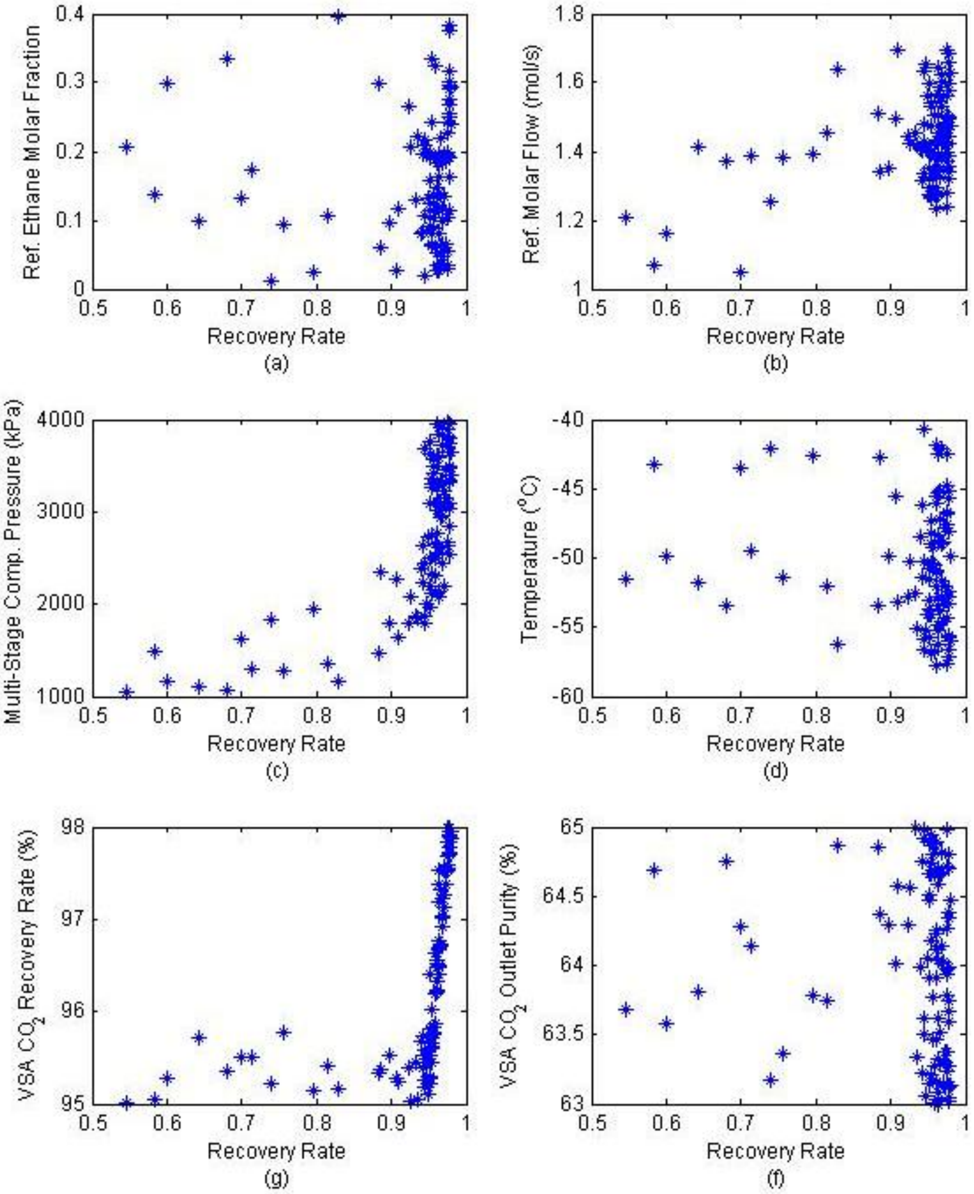


Figure 2: Pareto chart of the six decision variables versus the CO_2 recovery rate (a) Ethane molar fraction (b) Refrigerant molar flow (mol/s) ; (c)Multi-stage compression pressure (kPa); (d) Process stream minimum temperature (°C; (e) VSA CO_2 Recovery Rate (f) VSA CO_2 outlet purity (%)

which were the ‘total shaft work required’ and the ‘total specific shaft work required’. This enabled a relationship between the exergy loss rate and total shaft work required to be examined as in Figure 5.

4. Discussion

It can be seen from Figure 2 that most decision variables seem to have a scattered effect over the recovery rate except for two main decision variables; multi-stage compression pressure and the VSA CO_2 recovery rate. The higher compression pressure increases the partial pressure of CO_2 and therefore facilitates the separation of CO_2 from nitrogen. Also important is the pressure of the stream, which lowers the CO_2 freeze out temperature, which effectively allows the stream to be cooled to the lowest temperature possible before forming solid CO_2. Finally, the VSA CO_2 recovery rate dictates the overall recovery rate since the CO_2 lost in the waste stream from the VSA cannot be recovered.

As expected from Figure 3(a), the exergy loss rate increased with increasing recovery rate. That can be explained by the increase in exergy required in the compressors in the multi-stage compression of the

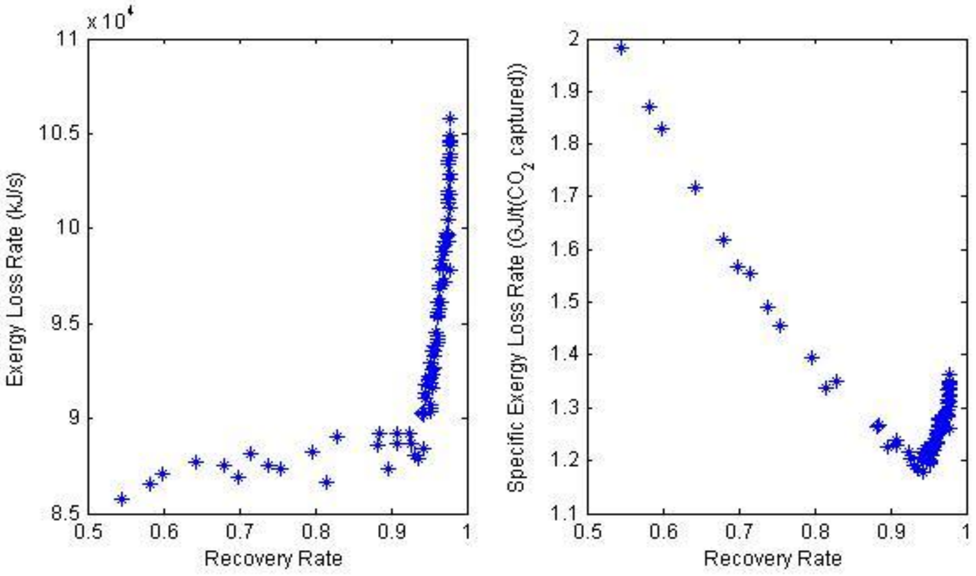
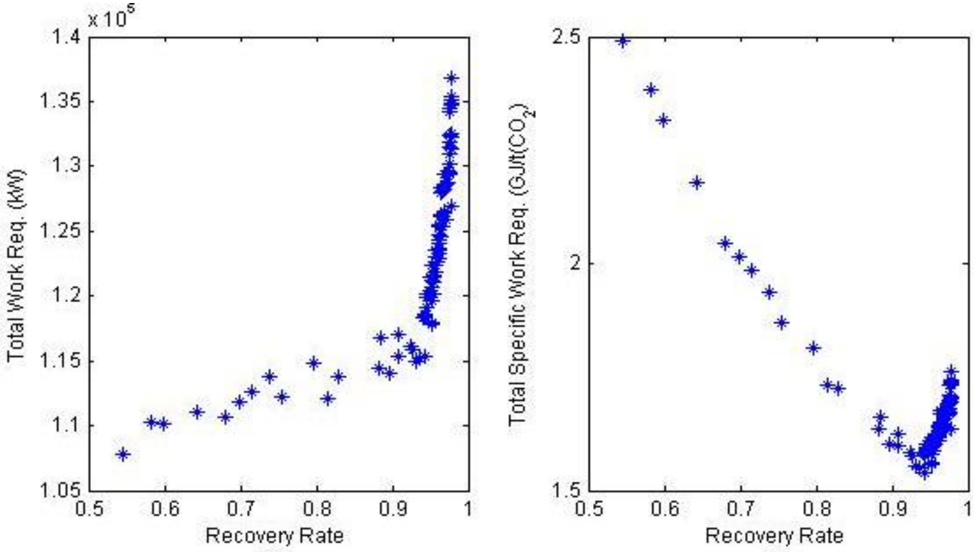


Figure 3(a): Graph of objective variables exergy loss rate (kJ/s) versus recovery rate; 3(b): Graph of specific exergy loss rate (kJ/s) versus recovery rate

process stream. Figure 3(b) shows that the rate of change of exergy loss is lower than the rate of change of CO_2 being captured and thus the specific exergy loss rate decreases with increasing CO_2 being captured up until a capture rate of 95 %. Figure 3(b) shows that the specific exergy loss rate has a minimum point at a recovery rate of approximately 95 % and total specific exergy loss rate of around 1.6 GJ/t (CO_2 recovered).

Figure 4(a) and 4(b) yielded results that were similar to Figure 3(a) and Figure 3(b), which means that the total shaft work required and exergy loss rate have a linear relationship. This was further proven in Figure 5, where the total specific exergy loss rate and total specific shaft work required showed a linear graph. This relationship can be explained by the fact that approximately 99 % of the exergy input is from the shaft work in the compressors. The optimum result is at a recovery of 94.4 %, which leads to the minimum specific exergy loss rate and shaft work.



(a) (b)

Figure 4(a): Graph of total shaft work required (kW) versus recovery rate. (b): Graph of specific shaft work required (kJ/t (CO_2)) versus recovery rate

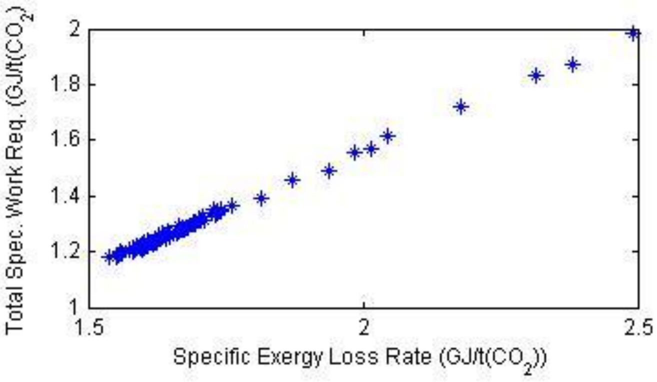


Figure 5: Graph of total specific shaft work required (kJ/t (CO_2)) versus specific exergy loss rate (MJ/t(CO_2))

5. Conclusion

An overall exergy analysis of a hybrid carbon capture system has been performed while optimising the process using MOO. This allowed different key decision variables to be varied to understand the effect that they have on the overall recovery rate and exergy loss rate. It was determined that the multi-stage compression and the VSA recover rate had the biggest impact on the overall recovery rate. A minimum specific exergy loss of 1.6 GJ per tonne of CO_2 was found at a recovery rate of 94.4 %.

Furthermore, it was observed that the total specific shaft work had a linear relationship with the specific exergy loss rate. This is due to the fact that the compressors account for the majority of the exergy going into the system as well as the total shaft work. However, this can be further investigated by selecting an optimum point on the Pareto chart in Figure 3(b) and performing an advanced exergy analysis on each of the individual processes to break down the exergy loss rate to identify further potential improvements. Finally, an exergy analysis should be performed on a solvent absorption capture process, where the exergetic requirement would come from both compressors and thermal energy, and the results could then be compared to this hybrid process.

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References

Belaissaoui B., Le Moullec Y., Willson D., Favre E., 2012. Hybrid membrane cryogenic process for post-combustion CO2 capture. Journal of Membrane Science, 415–416, 424-434.

Edenhofer O., Seyboth K., 2013. Intergovernmental Panel on Climate Change (IPCC). In: SHOGREN, J. F. (ed.) Encyclopedia of Energy, Natural Resource, and Environmental Economics. Waltham, United States: Elsevier.

Hagi H., Nemer M., Le Moullec Y., Bouallou C., 2013. Assessment of the flue gas recycle strategies on oxy-coal power plants using an exergy-based methodology. Chemical Engineering Transactions, 35, 343-348.

Pires J.C.M., Martins F.G., Alvim-Ferraz M.C.M., Simões M., 2011. Recent developments on carbon capture and storage: An overview. Chemical Engineering Research and Design, 89, 1446-1460.

Rangaiah G.P., 2009. Multi-Ojective Optimization. Techniques and Applications in Chemical Engineering, World Scientific Publishing Co. Pte. Ltd, Singapore.

Scholes C.A., Anderson C.J., Cuthbertson R., Stevens G.W., Kentish S.E., 2013. Simulations of Membrane Gas Separation: Chemical Solvent Absorption Hybrid Plants for Pre- and Post-Combustion Carbon Capture. Separation Science and Technology (Philadelphia), 48, 1954-1962.

Xiao G., Webley P., 2013. Personal Communication: VSA Zeolite 13X Experimental Results.