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Exergetic and Exergoeconomic Analysis of Three Different Technologies for Post-combustion CO2 Capture / Ferrara, Giandomenico; Ho, Minh T.; Lanzini, Andrea; Leone, Pierluigi; Wiley, Dianne E.. - In: ENERGY PROCEDIA. - ISSN 1876-6102. - 114:(2017), pp. 6455-6464. (Intervento presentato al convegno 13th International Conference on Greenhouse Gas Control Technologies, GHGT 2016 tenutosi a che nel 2016) [10.1016/j.egypro.2017.03.1782].

*Availability:*

This version is available at: 11583/2683345 since: 2017-09-28T14:56:48Z

*Publisher:*

Elsevier Ltd

*Published*

DOI:10.1016/j.egypro.2017.03.1782

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13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18  
November 2016, Lausanne, Switzerland

## Exergetic and Exergoeconomic Analysis of Three Different Technologies for Post-combustion CO<sub>2</sub> Capture

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### Abstract

The last decades have seen a fast rise in global greenhouse-gas (GHG) emissions by more than one-quarter, with CO<sub>2</sub> accounting for 60% of all anthropogenic GHG emissions and the energy sector representing two-thirds of the total. Carbon Capture and Storage (CCS) has been acknowledged as a technology for CO<sub>2</sub> reduction, however development in lowering the cost and energy consumption remains an important challenge. One tool that can be used for optimizing the energy consumption of capture is the application of an exergy-based analysis including an exergetic and exergoeconomic analysis. This paper aims to develop an exergy-based analysis and compare the results of different post-combustion CO<sub>2</sub> capture technologies using MEA chemical absorption, gas separation membranes and vacuum/pressure swing adsorption (VPSA). The results show that liquid/gas processes such as chemical absorption using MEA solvent has a total irreversibility almost double that of gas/gas processes such as gas separation membranes or vacuum /pressure swing adsorption.

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Peer-review under responsibility of the organizing committee of GHGT-13.

*Keywords:* Exergy, Thermoconomics, PCC, MEA, Membranes, VPSA

### 1. Introduction

The last decades have seen a fast rise of global greenhouse-gas (GHG) emissions by more than one-quarter with CO<sub>2</sub> accounting for 60% of all anthropogenic GHG emissions and energy sector representing two-thirds of the total.

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Carbon Capture and Storage (CCS) has been acknowledged as a technology for CO<sub>2</sub> reduction, however developments in lowering the cost and energy consumption of implementations remains an important challenge.

One tool that can be used for optimizing the energy consumption of capture is the application of an exergy-based analysis including an exergetic and exergoeconomic analysis. The exergy of a thermodynamic system is the maximum theoretical useful work obtainable as the system is brought into complete thermodynamic equilibrium with the thermodynamic environment with which the system interacts [1]. An exergetic analysis reveals the locations and causes of inefficiency and loss in an energy conversion system and provides improvements that cannot be found with an energetic analysis. An exergoeconomic (or thermo-economic) analysis uses exergy, rather than energy, as the commodity of value and the rational basis for assigning the monetary costs to the energy conversion system.

A number of studies have investigated energy consumption and the theoretical exergy analysis for post-combustion CO<sub>2</sub> capture using chemical solvent absorption [2-7]. The largest exergetic losses were identified to occur in the absorber and stripper (including the reboiler and condenser). Following the absorption/desorption stages, the next highest exergy losses in a solvent absorption process occurs in the CO<sub>2</sub> compressor. An exergy analysis investigating a two-stage gas separation membrane process for post-combustion carbon capture in a coal power plant has also been undertaken by [8]. The exergy analysis indicates that the main energy bottleneck of a membrane technology is located in the membrane units operation, which has relatively low exergetic efficiency. Currently there are no published studies focusing on an exergy analysis of a CO<sub>2</sub> capture process using Pressure Swing Adsorption (PSA) or Vacuum Pressure Swing Adsorption (VPSA) technologies.

This paper aims to develop an exergy-based analysis and compare the results of different post-combustion CO<sub>2</sub> capture (PCC) technologies including chemical absorption, gas separation membranes and adsorption. The analysis will quantify the total exergy losses, the exergoeconomic costs and the exergoeconomic factors of each technology and identify the components in the process with the most opportunity for exergy improvement.

## 2. Methodology

### 2.1. Process assumptions

#### 2.1.1. Emission source

A supercritical black coal power plant with net power generation of 500 MW was chosen as the baseline emission source. The flue gas is assumed to be pre-treated to remove ash and acid gases, such as SO<sub>2</sub> and NO<sub>x</sub>, before entering the CO<sub>2</sub> capture process. The flue gas composition is assumed to be 75% N<sub>2</sub>, 13% CO<sub>2</sub>, 5% O<sub>2</sub> and 7% water.

Figure 1 shows the three configurations of the three CO<sub>2</sub> capture technologies investigated in this paper including a) MEA chemical solvent absorption, b) two-stage gas separation membrane process using the MTR Polaris membrane, and c) VPSA using zeolite 13X. Each process is divided into three sections: flue gas cooling and compression; CO<sub>2</sub> separation; and CO<sub>2</sub> compression. For all the systems, the operating conditions were selected to match those in the NELT report [9] and the capture rate was set equal to 90%. Table 1 outlines the operating conditions assumed for all processes.

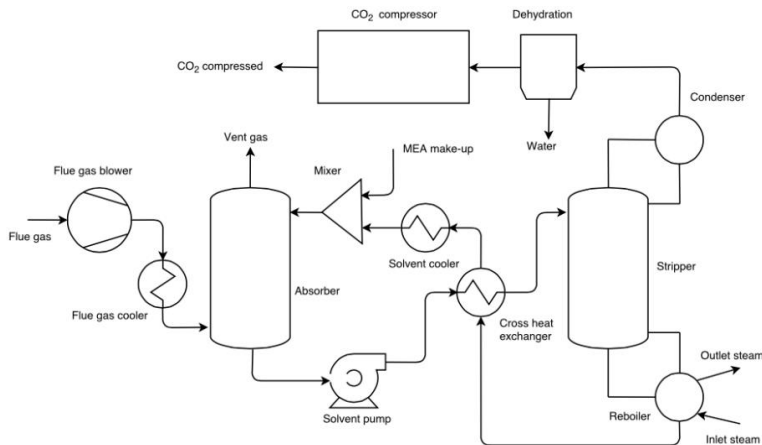


Figure 1a Flow diagram of MEA-solvent absorption process

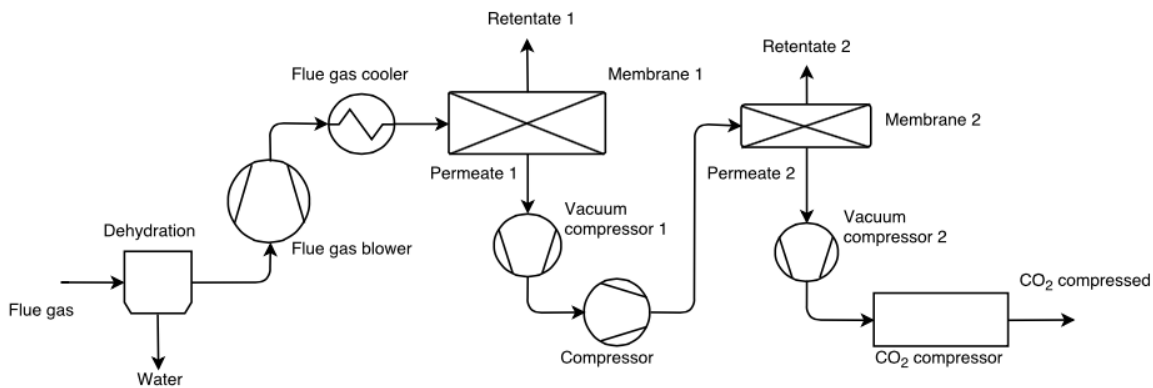


Figure 1b Flow diagram of two-stage membrane process 1

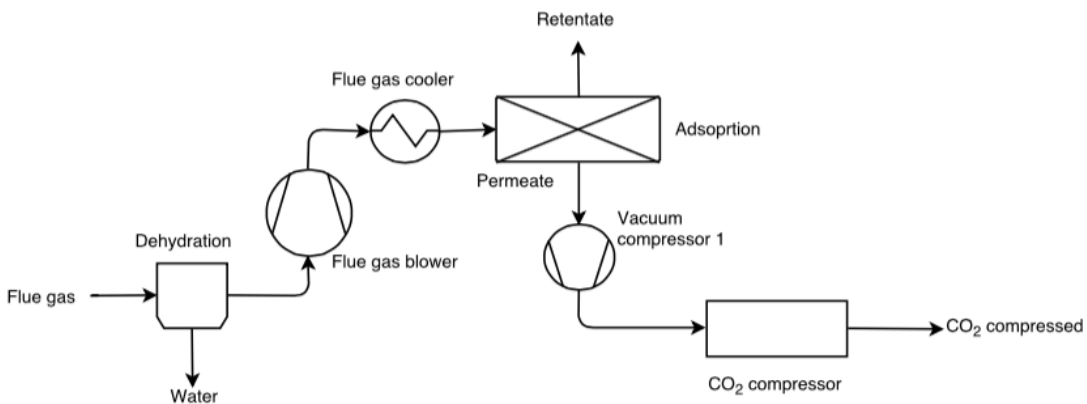


Figure 1c Flow diagram of VPSA process

**Table 1** Operating conditions assumed for the three capture technologies

Parameters	Unit	Value
<b>MEA solvent absorption</b>		
Solvent mass fraction	wt%	30
Lean Loading	mol%	0.229
Rich Loading	mol%	0.455
Absorber pressure	bar	1.5
Stripper pressure	bar	1.6
Steam temperature	°C	130
Specific reboiler duty	kJ/kgCO <sub>2</sub>	5112
Electricity consumption	MW	66.6
Cooling water needs	kg/s	9783
<b>2-stage membrane</b>		
Membrane permeability	Barrer	430
Membrane selectivity	-	35
1 <sup>st</sup> membrane pressure	bar	1.2
1 <sup>st</sup> membrane temperature	°C	62
2 <sup>nd</sup> membrane pressure	bar	1.2
2 <sup>nd</sup> membrane temperature	°C	62
Permeate pressure	bar	0.2
Electricity consumption	MW	146.6
Cooling water needs	kg/s	3457
<b>13X VPSA</b>		
Adsorption pressure	bar	1.2
Adsorption temperature	°C	45
Desorption pressure	bar	0.07
Electricity consumption	MW	104.6
Cooling water mass flow rate	kg/s	2630
<b>CO<sub>2</sub> compressed properties</b>		
CO <sub>2</sub> compressed pressure	bar	152.7
CO <sub>2</sub> compressed temperature	°C	43
CO <sub>2</sub> compressed mass flow rate	kg/s	100

### 2.1.2. Process simulation

Simulation of the MEA absorption process was undertaken using ASPEN Plus™ Version 7.3 (Aspentech, USA) using the NRTL and Pitzer thermodynamic models for vapour liquid systems and vapour liquid solid systems, respectively. The flowsheet was modelled as an open-loop simulation as this allows easier convergence and facilitates multiple runs. The absorber was modelled as a RADFRAC column, while the stripper was modelled as a RADFRAC column with kettle reboiler. The CO<sub>2</sub> compressor was modelled as a four-stage reciprocating compressor with cooling in between the stages. The required capture rate is achieved through a Design Specification which was imposed at the absorber to regulate the amount of CO<sub>2</sub> that is vented from the top of the absorber by varying the amine flow into the absorber column. AspenPlus calculations have been performed using ‘apparent’ components. This means that the results are reported in terms of neutral components (MEA and CO<sub>2</sub>) and not in

terms of the electrolytes. As a result, the change in exergy of a stream containing electrolytes is found in the mixing exergy instead of in the chemical exergy. Geuzebroek et al. [2] have also used this mode of calculation showing that it enables much faster convergence, without loss of quality of the result.

The gas separation membrane model was simulated using the CO2CRC UNSW techno-economic model which adopts the cross-flow model described by Shindo et al. [10] to describe the CO<sub>2</sub> recovery across a single membrane [11]. Simulation of the VPSA process was undertaken using the simplified adsorption model developed by et al. [12].

## 2.2. Exergetic analysis

The exergy balance is a statement of the law of degradation of energy, in contrast to the energy balance which is a statement of the law of conservation of energy. Exergy can be consumed or destroyed due to irreversibilities in any process. Thus exergy differs from energy, in that whilst energy is conserved, exergy is not. The greater the exergy destroyed, the more energy input is required to run the process. For an ideal situation, that is a fully reversible process, the exergy flow into the system is equal to the exergy flow out of the system, and the irreversibility rate is zero. For a real process or a non-ideal situation, there is entropy production and hence irreversibilities.

For a considered process, the exergy analysis consists of a system of balance equations, stated at the component level, and a general equation for the overall system. The rate of exergy destruction within component  $k$ ,  $E_{D,k}$ , consists in the irreversibility that occurs in the component and is calculated as the difference between rate of fuel, product and losses exergy of  $k$  component:  $E_{D,k} = E_{F,k} - E_{P,k} - E_{L,k}$ . The exergetic efficiencies of component  $k$  and the overall system consisting of  $n$ - components or process units:

$$\varepsilon_k = \frac{E_{P,k}}{E_{F,k}} = 1 - \frac{E_{D,k} + E_{L,k}}{E_{F,k}}, \quad \varepsilon_{tot} = \frac{E_{P,tot}}{E_{F,tot}} = 1 - \frac{\sum_{k=1}^n E_{D,k} + E_{L,tot}}{E_{F,tot}}.$$

Exergy associated with a heat transfer  $j$  is  $E_j = \left(1 - \frac{T_0}{T_j}\right) \phi_j$ , while work is pure exergy. Exergy associated with mass transfer consists of physical exergy and chemical exergy. The physical exergy is the sum of mechanical and thermal exergy and is defined as  $e_{ph} = (h - h_0) - T_0(s - s_0)$ . For a mixture the physical exergy is evaluated using the formula  $e_{ph} = \tilde{c}_p(T - T_0) - T_0$  with the average  $\tilde{c}_p$  of the mixture, while the chemical exergy can be calculated as  $e_{ch} = \sum_i y_i \cdot e_{ch,i}^0 + RT_0 \sum_i y_i \cdot \ln(y_i)$ , where  $e_{ch,i}^0$  is the standard chemical exergy of each component in the stream.

In undertaking an exergy analysis, an exergy reference environment is required, which is defined in terms of pressure, temperature and reference substances. In this paper the reference conditions defined by [13] have been used, ie.  $T_0=298.15$  K,  $P_0=101325$  Pa and the atmosphere composition, as well as standard chemical exergies for all components except for MEA solvent which was not provided. For this compound the calculated value used in this paper is 1,975,173 kJ/kmol which is the value adopted by [2]. The kinetic exergy and potential exergy have been assumed to be negligible.

## 2.3. Exergoeconomic analysis

Exergoeconomics (also referred to as thermo-economic) analysis combines exergy analysis with conventional engineering economics. The goal is to evaluate and optimize the design and performance of energy systems. [14] states that there is a fundamental difference between a conventional economic analysis and an economic analysis conducted as part of a exergoeconomic analysis: the latter is based on exergy costing and is usually applied at the plant-component level. Exergy not only is an objective measure of the thermodynamic value of an energy carrier but also is closely related to the economic value of the energy carrier, because users only pay for the useful energy.

To perform the exergoeconomic analysis of each CO<sub>2</sub> capture technology, cost balances are expressed at the component level resulting in a system of balance equations as follows:

$$\sum_{i=1}^l c_{i,k} E_{i,k} - \sum_{j=1}^m c_{j,k} E_{j,k} + Z_k = 0$$

Where  $c_{i,k}$  and  $E_{i,k}$  are respectively the specific cost (\$/s) and the exergy of stream  $i$  entering  $k$ , while  $c_{j,k}$  and  $E_{j,k}$  of stream  $j$   $k$ ;  $Z_k$  is the cost rate associated with process unit  $k$ . The exergo-economic cost of capture is calculated as:

$$\text{Cost of capture} = \frac{\sum_{i=1}^l c_{i,k} - \sum_{j=1}^m c_{j,k}}{CO_2 \text{ captured}}$$

In general techno-economic analysis of capture costs, the output streams of a process (such as water and stream vapour) are assumed to have no value. However, in an exergoeconomic analysis these streams are assumed to be re-useable and thus have a value assigned. Hence, the calculated values for capture cost using an exergo-economic methodology differ from the project costs of CO<sub>2</sub> avoided which represents the breakeven carbon price to make a project economically viable.

In a system of balance equations, when the number of unknown stream costs is larger than the number of equations stated, auxiliary statements (that is external values) are required. For each component or process unit, streams entering have been assumed to be known, while streams leaving are considered as unknown. When the number of the outgoing exergy streams of a process unit is higher than one ( $m > 1$ ),  $m-1$  auxiliary equations are needed. The P-principle (on the product side) and the F-principle (on the fuel side) have been used to determine the auxiliary equations as stated by Lazzaretto et al.[15].

As result, the exergy destruction cost  $C_D$ , the exergoeconomic factor  $f$  and the relative cost difference  $r$  are evaluated using:

$$C_{D,k} = c_{F,k} E_{D,k}$$

$$f_k = \frac{Z_k}{Z_k + C_{D,k}}$$

$$r_k = \frac{c_{P,k} - c_{F,k}}{c_{F,k}} = \frac{C_{D,k} + Z_k}{c_{F,k} E_{P,k}}$$

Where  $c_{F,k}$  and  $c_{P,k}$  are the specific costs for the fuel and product.

The exergoeconomic factor ( $f$ ) determines whether the capital cost  $Z$  or the cost associated with destroyed exergy is more influential. Thus higher values of the exergoeconomic factor suggest design improvements or process developments should focus on reducing the investment costs, while low values suggest improvements should focus on reducing the incurred irreversibilities.

### 2.3.1. Economic assumptions

In this paper, the exergoeconomic analysis incorporates the capital and operating costs for the post-combustion CO<sub>2</sub> capture facility including separation/recovery, any necessary pre-separation treatment and CO<sub>2</sub> compression. Table 2 outlines the baseline economic assumptions for all systems. The total capital cost includes all the process equipment shown in Figure 1, plus a general facilities cost. The general facilities cost includes ancillary equipment such as storage tanks, spare pumps, valves and the control system. The operating cost includes fixed general maintenance cost comprising of labour, non-income government taxes that may be payable and general insurance cost. The variable operating costs include costs for cooling water and material replacement such as the membrane, adsorbent and solvent. For further details see Ho et al.[16, 17] and Raksajati et al. [18].

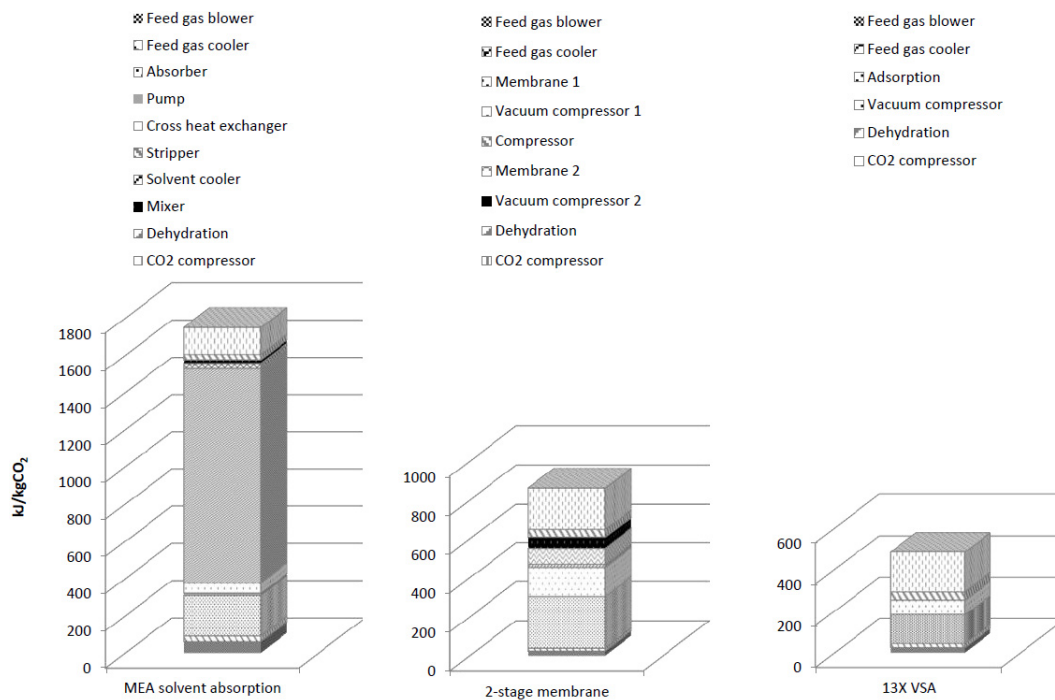
**Table 2** Economic assumptions

Parameter	Value	Unit
MEA solvent cost	1.5	US\$/kg
MEA solvent disposal	20% of MEA replacement	-
Membrane cost	50	US\$/m <sup>2</sup>
Membrane replacement period	4	years
Adsorbent 13X cost	6	US\$/kg
Adsorbent replacement period	3	years
Cooling water cost	0.025	US\$/m <sup>3</sup>
Steam cost	6	US\$/tonne
Electricity cost	42	US\$/MWh
Real discount	7%	-
Project life	25	years

### 3. Results and discussion

#### 3.1. Exergetic analysis

The results of the exergy analysis are shown in Table 3 for all systems, while Figure 2 shows the comparison among them. MEA solvent absorption is a liquid/gas process, while gas separation membrane and adsorption are gas/gas processes.

**Figure 1** Comparison of exergy losses



**Table 3** Exergy losses for key process units of each capture technology

MEA solvent absorption			2-stage gas separation membrane			13X VPSA		
Component	kJ/kg <sub>CO2</sub>	%	Component	kJ/kg <sub>CO2</sub>	%	Component	kJ/kg <sub>CO2</sub>	%
Feed gas blower	60	3	Feed gas blower	24	3	Feed gas blower	24	5
Feed gas cooler	31	2	Feed gas cooler	15	2	Feed gas cooler	15	4
Absorber	217	12	Membrane 1	265	31	Adsorption	71	15
Solvent Pump	12	1	Vacuum compressor 1	15	18	Vacuum compressor 1	139	29
Cross heat exchanger	58	3	Inter-membrane compressor	16	2			
Stripper	1150	65	Membrane 2	81	9			
Solvent cooler	30	2	Vacuum compressor 2	55	6			
Mixer	17	1						
Dehydration	44	2	Dehydration	41	5	Dehydration	411	9
CO <sub>2</sub> compressor	163	9	CO <sub>2</sub> compressor	212	25	CO <sub>2</sub> compressor	190	39
Total exergetic losses	1782	100	Total exergetic losses	862	100	Total exergetic losses	480	100

As a result, MEA solvent absorption has the highest total exergy destruction at about 1780 kJ/kg<sub>CO2</sub> followed by gas separation membrane at about 860 kJ/kg<sub>CO2</sub>, while adsorption has the lowest destruction at 480 kJ/kg<sub>CO2</sub>. The gas separation membrane process has higher irreversibility than the adsorption process because it has two stages/process units for CO<sub>2</sub> capture rather than one, resulting in higher electricity consumption.

With regards to the components for pre-separation treatment such as the feed gas blower and cooler, the irreversibilities in MEA solvent absorption are 91 kJ/kg<sub>CO2</sub>, while the exergy destruction for the other two technologies are around 39-42 kJ/kg<sub>CO2</sub>. The destruction for the membrane and adsorption processes are lower because the pressure of the feed gas after the pre-separation treatment is lower, resulting in lower compression duty and cooling needs.

For MEA absorption, the highest irreversibilities occurs in the stripper which also includes the reboiler and condenser accounting for 65% of the total irreversibility. This is followed by the absorber accounting for 12% of the total irreversibility. In the regenerator the exergy destruction is estimated to be about 1150 kJ/kg<sub>CO2</sub> and is higher than literature values of 425-757 kJ/kg<sub>CO2</sub>. This is because in this paper, the operating pressure of the stripper is lower at 1.6 bar compared to 1.86-2.1 bar. If the stripper pressure decreases, there is an increase of the specific reboiler duty and the efficiency of the stripper also goes down [19].

In the two-stage gas separation membrane process, the total irreversibility is estimated to be 860 kJ/kg<sub>CO2</sub>. The process units with the two highest irreversibility are the first separation membrane stage (which includes the first membrane and the vacuum compressor) and the CO<sub>2</sub> compressor accounting for 48% and 25% respectively.

In the VPSA system, the CO<sub>2</sub> compressor has the highest irreversibility followed by the vacuum compressor and the adsorption unit accounting for 39%, 29% and 15% respectively.

It has been shown that the irreversibilities for the CO<sub>2</sub> compressor increase if CO<sub>2</sub> purity decreases. The highest irreversibility for the CO<sub>2</sub> compressor occurs in the gas separation membrane, i.e. 212 kJ/kg<sub>CO2</sub>, where the CO<sub>2</sub> purity is about 0.68. The same exergy destruction in the VPSA system is 190 kJ/kg<sub>CO2</sub> where the CO<sub>2</sub> purity is around 0.86. The MEA solvent absorption has the highest CO<sub>2</sub> purity and the lowest irreversibility accounting for 0.9 and 163 kJ/kg<sub>CO2</sub> respectively.

### 3.2. Exergoeconomic analysis

Table 4 summarizes the key exergoeconomic results for each capture technology. The gas separation membrane process has the highest project NPV over the life time of the project (and cost rate  $Z$ ), followed by MEA solvent absorption and VPSA system. The exergoeconomic factor ( $f$ ) shows that design improvements and process development should focus on reducing the investment cost.

Of the three capture technologies, the exergy destruction cost  $C_D$  is highest for MEA solvent absorption, followed by the membrane technology with the VPSA process having the lowest exergy destruction cost. MEA has the highest exergy destruction cost because of its very high relative irreversibility, even though its specific fuel cost is lowest. In comparison, the VPSA process has the lowest exergy destruction cost as it has very low irreversibility coupled with moderate fuel cost. The highest total exergoeconomic cost  $C_D + Z$  occurs for the gas separation membrane, followed by MEA-solvent absorption and adsorption.

**Table 4** Key exergoeconomic results for the three capture technologies

Parameter	Unit	MEA	Membrane	VPSA
<i>Electricity consumption</i>	MW <sub>e</sub>	65.6	146.6	104.6
<i>Steam consumption</i>	MW <sub>th</sub>	516	-	-
<i>Cooling water consumption</i>	Kg/s	9,783	3,457	2,630
<i>NPV(Project over 25 years)</i>	million US\$	1,440	1,810	1,080
<i>Exergo-economic cost of CO<sub>2</sub> captured</i>	US\$/ton <sub>CO2</sub>	35.4	56.4	33.7
<i>Irreversibility</i>	kJ/kg <sub>CO2</sub>	1782	861	485
$C_{f,TOT}$	US\$/MWh	19.0	32.8	30.2
$C_{p,TOT}$	US\$/MWh	192.6	246.7	154.3
$r$	-	9.14	6.52	0.81
$C_D$	US\$/s	0.99	0.79	0.41
$Z$	US\$/s	2.05	3.96	2.15
$C_D + Z$	US\$/s	3.04	4.75	2.56
$f$	-	0.68	0.83	0.84

## 4. Conclusions

Based on the results of the exergy analysis in this paper, of the three capture technologies investigated MEA chemical absorption appears to have the highest irreversibility with the stripper and reboiler accounting for most of this irreversibility. The gas separation membrane process also has a relatively high total irreversibility; with about 30% of this occurring in the first membrane unit, 18% in the vacuum compressor and 25% in the CO<sub>2</sub> compressor. The VPSA technology has shown the best exergetic results with most of its irreversibility occurring in the CO<sub>2</sub> compressor.

The CO<sub>2</sub> pipeline compressor has one of the highest exergoeconomic costs for all capture technologies, with exergoeconomic factors of around 0.40-0.55. To reduce cost, one possible process design improvement could be to increase the CO<sub>2</sub> purity after separation to decrease the exergy destruction cost by lowering the amount of incondensable gases and reducing the compression work.

In the MEA solvent absorption process, opportunities to reduce the exergoeconomic costs include reducing the reboiler duty through design improvements such as increasing the stripper pressure or using solvents with lower regeneration energy. Also, alternative solvents with a lower absorption heat could be used to improve the performance of absorption system. For gas separation membranes, opportunities to decrease the area of the membrane could be investigated to decrease the exergoeconomic cost of this process. This could be achieved by

decreasing the permeate pressure or using membranes with higher permeability. For the VPSA technology, the irreversibility and costs could be reduced through increasing the CO<sub>2</sub> purity of the product stream after separation.

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