
Feasibility analysis of CO₂ clathrate production for CO₂ sequestration and transport

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Abstract

The most promising approach in the CO₂ abatement strategies is the use of carbon capture and storage (CCS) systems, because it allows to reduce emissions not only in the energy sector (especially fossil fuels), but also in industrial sectors, such as iron and steel manufacturing, petrochemical, and cement industry. This work focuses on post-combustion technologies in which CO₂ is separated from flue gases. It explores the opportunity to use gas hydrates, also known as clathrates, as an alternative capture process and storage medium. Due to its exceptionally high gas storage capabilities, clathrate-based separation could be an alternative to the existing separation technologies and, by adopting water as a separation medium, it is considered simple and environment-friendly. CO₂ capture technologies add high energy penalties to power plants, therefore the hydrate process is modelled through a simulation software, ASPEN-Plus, to assess the related energetic and capital costs. A comparison between a MEA-based separation and the designed THF-catalysed clathrate system for a supercritical 900MW coal power plant reveals that more than 39% of the net power output is needed to cut up to 90% of the CO₂ emissions. The results show that, at the current EU average CO₂ and electricity market price, the analysed techno-economic conditions deem CO₂ capture systems unprofitable, despite the great potential.

1 Introduction

Nowadays, it is common knowledge that the observed carbon dioxide (CO₂) concentration in the atmosphere has been increasing significantly over the past century. Data show the passage from about 280 ppm in the pre-industrial era to an average concentration greater than 400 ppm (figure 1). The last decade attracted particular attention because of an average growth rate of 2 ppm/year.¹ In recent years, though, governments pushed towards a progressive promotion of sustainable development in the energy sector to fight climate change and face the related environmental issues. Although this paradigm shift is globally occurring, the energy sector remains the largest source emitting Green House Gases (GHG).² The most promising approach in the abatement strategies is CCS because it would allow to reduce emissions not only in the energy sector (especially the fossil fuel based) but also in industrial sectors such as iron and steel manufacturing, petrochemical, and cement industry.³ This work focuses on post-combustion technologies in which CO₂ is separated from flue gases, exploring the opportunity to use gas hydrates, also known as clathrates, as an alternative capture process and storage medium. Due to its exceptionally high gas storage capabilities, clathrate-based separation could be an alternative to the existing

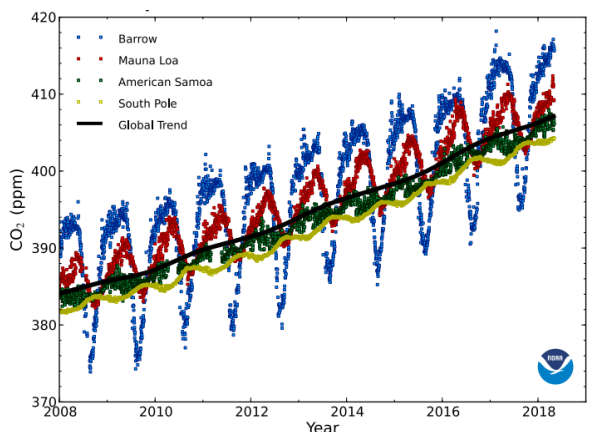


Fig. 1: Averaged CO₂ daily measurements from four GMD Baseline observatories: Barrow (Alaska), Mauna Loa (Hawaii), American Samoa, and South Pole (Antarctica).

separation technologies and, by adopting water as a separation medium it is considered simple and environment-friendly. It is well known that CO₂ capture technologies add high energy penalties to power plants and this translates into higher economic costs. The objective of this analysis is to evaluate the feasibility of producing CO₂ clathrate for CO₂ sequestration and transport.

2 Literature review

CO₂ capture processes are mainly divided in three categories, namely pre-combustion, post-combustion and oxy-fuel combustion. In pre-combustion, the CO₂ sequestration happens before the combustion phase while in post-combustion, the process takes place afterwards. In the oxy-fuel process, oxygen (purity up to 97%) substitute air in the combustion phase to reduce the amount of N₂ and thermal NO_x formation in the exhaust gas.⁴ Due mainly to the commercial deployment and development of the technology in the industrial sector and due to the chance of virtually retrofit any existing power plant, the choice of this analysis fell on the post-combustion option. Table 1 summarise advantages and disadvantages of these capture options. Six main capture technologies are

Table 1: Advantages and disadvantages of CO₂ capture choices

Advantages and disadvantages of CO ₂ capture choices		
Capture choices	Advantages	Disadvantages
Pre-Combustion	Low separation and compression energy needs	Temperature and efficiency issues
Oxy-fuel combustion	Mature air separation technology	Large O ₂ consumption Corrosion due to high SO ₂ concentration
Post-combustion	Full commercial development and deployment Chance to retrofit existing plants	High energy penalty for solvent regeneration High capital & operation costs

currently in use or being developed: chemical or physical absorption, chemical or physical adsorption, membrane and hydrate separation, mineral carbonation and cryogenic distillation. Here is a summary of important aspects on the analysed technologies:

- When aiming at CO₂ removal at low partial pressure, amine absorption systems can reach removal rates higher than 90%.^{5 6 7} This is the most diffused CO₂ capture technology on an industrial scale with a high selectivity, making it very suitable for CO₂ separation.
- Physical adsorption through Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption

(TSA) is also a viable option: PSA for CO₂ recovery is already a commercially available technology that yields efficiencies above 90%^{8 9}; TSA is also a promising technology that, although has a longer regeneration time, yields CO₂ purity higher than 95%, with recovery higher than 80%.¹⁰

- Due to the constant advancement in membrane separation technologies, it is currently possible to yield separation efficiencies above 90% with product purity up to 95%.^{11 12} Unfortunately, this technology is heavily affected by the flue gas low pressure and CO₂ concentration (~15%) which translate into a low CO₂ permeation driving force.
- Cryogenic distillation can yield recovery efficiencies above 90%, but it is high energy intensive, therefore it is currently discarded from the large scale implementation.¹³
- Mineral carbonation reactions have slow reaction rates and need 2 - 3 tonnes of oxides (rare in nature due to their reactivity) per tonne of captured CO₂. Unless a solution to these issues is obtained, this solution is not viable for industrial applications.¹⁴
- Hydrate separation technology has great potential for future implementations. Assuming the treatment of a 1000 MW thermal power plant emission, the energy consumption for CO₂ capture through hydrates could range from 0.57 to 0.853 kWh/kg-CO₂, accounting for a total energy penalty of 6 to 15.8%.^{15 16} The main disadvantage of this technology are the demanding operation conditions of high pressure (3-50 MPa) and low temperature (265-273K) which lead to high energy penalties. Additives can mitigate this problem, reducing the hydrate formation pressure up to 0.3 MPa, speeding up the hydrate formation process. Moreover, because hydrate slurries can lead to pipe plugging, the handling of clathrates can require substantial maintenance.

The next section will give a brief introduction on hydrates, focusing the hydrate-based separation.

2.1 Hydrate Separation

Hydrate-based separation is a relatively new technology for CO₂ capture: a flue gas mixture passes through chilled water at high pressure (3 - 50 MPa) and low temperature (265 -273K); CO₂ molecules (and part of the other components) freeze with the water molecules

and get trapped into solid crystalline cage-like structures, also known as clathrates. CO₂ and H₂O freeze together forming a slurry of ice crystals in liquid water with other gas components non trapped in the ice crystals. The driving force for mass transfer is the CO₂ concentration difference between the bulk liquid phase and the hydrate interface. To be noted that the bulk concentration will increase at constant pressure and will not follow the concentration lines (figure 2). The hydrates con-

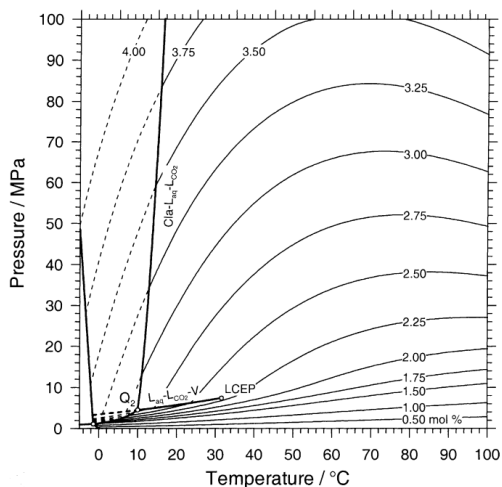


Fig. 2: PT diagram showing solubility isopleths of CO₂(aq) between 0.25 and 4 mol%¹⁷

taining CO₂ molecules is separated from the other components for storage or transport purposes. CO₂ is recovered by heating the slurry, therefore breaking the ice cages and releasing the gas molecules.¹⁷ Gas hydrates are non-stoichiometric, solid compounds in which non-polar gas molecule are engaged in a frame of hydrogen bonded water molecules. These guest molecules, such as CH₄ and CO₂, are bound by van der Waals forces inside the polyhedral cavities of the hydrate structure.^{18 19} Currently, gas hydrates have been found to crystallise in three structure types: I, II, and H. Structures I and II crystallise within a cubic system while structure H follows a hexagonal system. As shown in figure 3, the simplest and smallest cage is formed by twelve five-sided polyhedron (a.) while larger diameter cages can be formed by adding two (b.), four (c.) or eight (e.) hexagonal faces. Structure H has medium-size cavity formed by squared(d.), pentagonal and hexagonal faces. Thanks to the compact hydrate structure, high effective gas packing is possible. A certain number of gas molecules are needed in order to stabilize the hydrate structures and the

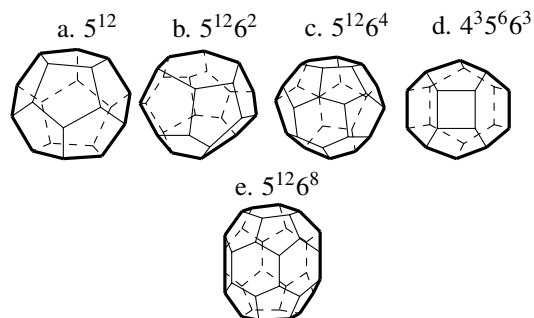


Fig. 3: Crystal structures of gas hydrates: pentagonal dodecahedron (a.), irregular dodecahedron (b.), tetrakaidecahedron (c.), icosahedron (d.) and hextetrahedron (e.)

occupied hydrate cage is a function of the size ratio between guest molecule and host cavity. Structure I and II are most frequently observed during clathrate crystallisation. For structure I and II, table 2 summarise the ratio molecular diameter/cavity diameter for CO₂ and other guest molecules.²⁰ Structural stability of a hydrate com-

Table 2: Ratio of molecular diameter to cavity diameter for few gaseous guest molecules²⁰

Guest Molecule Diameter (Å)	Molecular diameter/Cavity diameter			
	Structure I		Structure II	
CO ₂ (5.12)	5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴
CH ₄ (4.36)	1.00	0.834	1.02	0.769
N ₂ (4.1)	0.855	0.744	0.868	0.655
O ₂ (4.2)	0.804	0.700	0.817	0.616
	0.824	0.717	0.837	0.631

posed of a single gas is reached for ratios of molecule to cage size of about 0.9; for ratios significantly lower than 0.9, the molecule will not stabilise enough the cage; when this ratio exceeds 1, the gas will not fit into the cavity; molecules larger than 7.5 Å will not fit into structure I and II cavities while molecules smaller than 3.5 Å will not stabilize the hydrate crystals. The formed structure will depend on the largest molecule hosted.²⁰ Gas hydrates are identified with the chemical formula nM · H₂O, with M referring to gas molecules and n referring to the number of gas molecules. Naturally, the formation of type I structure dominates and, with all the cavities occupied by a CO₂ molecule, the clathrate brute formula is:



Therefore, every mole of hydrate can retain 8 moles of CO₂. Equation 2 identify the total amount of hydrate formed.

$$\dot{n}_H = \frac{1}{8} \frac{dn}{dt} \quad (2)$$

Improving the hydrate formation rate while reducing the clustering pressure can improve the CO₂ capture efficiency. This can be achieved with catalysts, such as Tetra-n-butyl ammonium bromide (TBAB) or Tetrahydrofuran (THF, figure 4), that are water-miscible solvents acting as a thermodynamic promoter of the hydrate formation. In case the production process involves the use

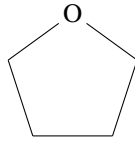


Fig. 4: Tetrahydrofuran, THF

of these catalysts, the formation will shift towards the type II structure, with a clathrate brute formula shown in equation 3. Equation 4 shows the less common, type III formula.



In general, CO₂ can form hydrates easier than other gases, starting clustering at lower pressures²¹. Studies also show that, for gas mixtures of CO₂ and N₂, through the use of THF, TBAB or other promoters, the operating pressure can be lowered up to 0.2 MPa with recovery efficiencies greater than 75%.^{22 23 24} Clathrate formation happens in supersaturation conditions and can be divided into three steps: nucleation, transferring of the solute to the hydrate surface and incorporation of the solute into the hydrate matrix. The Gibbs free energy plays an important role in the crystals nucleation: under supersaturated conditions the dissolved gas free energy is higher than the one of the hydrate. This condition favours the new hydrates nucleation but requires the formation of an interface. Equation 5 shows the Gibbs free energy equation of the system.

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta g_v \quad (5)$$

Where Δg_v is the free energy change per unit volume and σ is the surface tension at the hydrate-liquid interface. The Gibbs free energy reaches the maximum when the critical growth radius (r_c) is reached. The nucleation time is defined as the time interval between the moment

the supersaturated condition is established and the moment the first clusters with $r = r_c$ is formed. The nucleation time depends on various parameters such as operating temperature and stirring rate. A positive variation on the operating temperature can significantly increase the nucleation time, while an increase in the stirring rate decrease the nucleation time.²⁵ It is important to note that the hydrate formation is an exothermic process and this works against the crystal growth, therefore the generated heat must be removed. In case of a pure stream of CO₂ need, one viable option is the utilisation of the heat of reaction in a cross heat exchanger to break the Van Der Waals interaction forces between the molecules and the hydrogen bonds to releasing the gas molecules. The hydrate heat of dissociation is given by the Clausius-Clapeyron equation (6)²⁶:

$$\frac{d \ln P^{int}}{d(\frac{1}{T})} = \frac{-\Delta H_d}{zR} \quad (6)$$

Where P and T are the absolute pressure and temperature of the hydrate at the equilibrium with vapour and liquid water, R is the universal gas constant and z is the gas compressibility.

3 Process Model

The processes were modelled and simulated through Aspen Plus V8.4®, a process modelling tool that allows the user to design, optimise, and monitor the performance of a wide variety of chemical and process engineering processes. In order to correctly model the plant scheme, an equation model that can describe correctly the solubility of CO₂ in water and the respective interaction between each molecule is of crucial importance, therefore the process was analysed on the basis of a non-random two-liquid model (NRTL). This is an activity coefficient model correlating, for each component, activity coefficients and its molar fraction in the concerned liquid phase. With this in mind, the ELECNRTL method was chosen: it can handle very low and very high concentrations whether dealing with aqueous or mixed solvent systems, therefore it is considered the most versatile property method for this analysis. The ELECNRTL is fully consistent with the NRTL-RK property method: a non-random two-liquid model that incorporate the Redlich-Kwong equation of state (equation 7).²⁷

$$P = \frac{RT}{V_m - b} - \frac{a/T^{0.5}}{V_m(V_m + b)} \quad (7)$$

where P , T , R , V_m , a and b are, respectively, pressure, temperature, gas constant, molar volume, a correction constant for the molecule attractive potential and a constant for volume correction. The molar Gibbs free energy (G_m^*) is calculated as:

$$G_m^* = x_w \mu_w^* + \sum_s x_s \mu_s^{*,l} + \sum_k x_k \mu_k^\infty + RT \sum_j x_j \ln j + G_m^{*,E} \quad (8)$$

Where the subscripts m, w, s, k, and j refer, respectively, to molar, water, non-water solvent, ion/molecule solute and any component. Both, molar Gibbs free energy G_m^* and molar excess Gibbs free energy $G_m^{*,E}$, are calculated according the asymmetrical reference state (marked with *): pure water and molecular solutes and ions at infinite dilution. The water thermodynamic potential μ_w^* (Gibbs free energy for pure water, also marked with *) is a function of the ideal gas departure function and heat capacity and is calculated accordingly. The departure function is defined as the difference between the ideal potential and the real potential at a specified pressure and temperature and it is obtained from the ASME steam tables. μ_k^∞ is the aqueous infinite dilution potential, calculated from the heat capacity polynomial model for infinite dilution aqueous phase. The non-water solvent contribution $\mu_s^{*,l}$, the ideal mixing term ($RT \sum_j x_j \ln j$) and molar excess Gibbs free energy $G_m^{*,E}$ are calculated according the equation model NRTL activity coefficient model.

3.1 Data used

It is important to notice that with the use of a catalyst, such as THF, the formation of structure of type II dominates the product of the reaction. Considering full occupancy of the hydrate cavities, the ratio between CO_2 and H_2O molecule is $1/4$. In the simulations, only structures type I and II were defined. Although, due to several issues encountered while running simulations with the structure type II, a first approximation was deemed necessary: the formation of solely structure type I with full occupancy of its cavities was considered in the reaction products. The full occupancy of the cavities was assumed to partially compensate, in terms of CO_2 captured, the difference in needed water between the 2 clathrate structures, although this can lead to an overestimation of the equipment size and, consequently of the net power needed. The simulation tool had no inbuilt template on clathrates, therefore all the required data were manually implemented in order to ensure reliable result in the energy calculations. The data is based on a 900 MW supercritical power plant unit that vents to the atmosphere

824.2kg/s of flue gas.²⁸ Table 3 shows the gas composition. Praveen Linga et. all, test solutions at various THF

Table 3: Flue gas composition

Component	Mole fraction
N_2	0.7378
CO_2	0.1416
SO_2	0.0009
O_2	0.0329
H_2O	0.0780
Ar	0.088

concentrations, with gas compositions close to the one of the flue gas stream in exam (16.9% CO_2 and 83.1% N_2). Figure 5 shows the incipient hydrate formation conditions for different THF concentrations, for which infinitesimal amount of hydrate crystals are in equilibrium with gas and aqueous phases. The tests revealed that

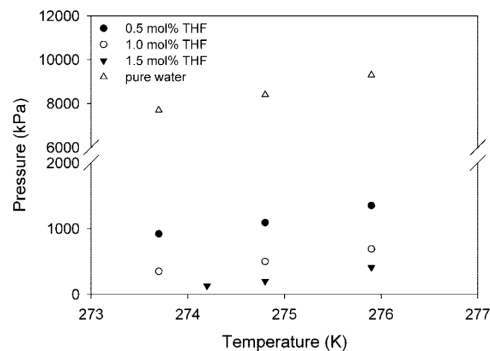


Fig. 5: Incipient equilibrium. 16.9% CO_2 , 83.1% N_2

the use of THF allows for the hydrate reaction to proceed at pressure as low as 10 bar²⁹, but it is possible to increase the total number of moles consumed by increasing the operating pressure, reaching 98% of CO_2 in the hydrate product (this was possible using a series of 3 hydrate formation stages).²³ A conservative approach is adopted for the simulation runs: taking into account the different gas composition a solution 5% mol of THF is used, setting a temperature of -1°C and a pressure of 30 bar for the reactor. Even though it is theoretically possible for the reaction to proceed at higher temperature and pressure, the vessel needs to host already hydrate crystals which function as nucleation initiators. If this condition is not respected, the thermodynamic conditions are not enough for the reaction to proceed to the formation of CO_2 clathrates. Table 4 lists the inlet design general pa-

rameters while table 5 shows the reactor parameters. The CO₂ capture efficiency of the overall process was set to 90%.³⁰

Table 4: Design general parameters

Stream	Mass flow [kg/s]	Temperature [°C]	Pressure [bar]
Flue gas	824.2	45	1
THF	148	15	1
Water	332	15	1

Table 5: Reaction parameters with THF 5% molar

Enthalpy of reaction (10 °C, 5 bar) [kJ/mol]	108.7
Temperature [°C]	-1
Pressure [bar]	30

3.2 Plant Layout

The simplified plant layout is shown (figure 6). The complete scheme has a similar layout, with the flue gas mass-flow split into 5 streams and treated in parallel systems. Although this set-up increases the plant capital cost, the subdivision is needed to operate with smaller mass flows, condition which might lower the O&M costs and help in future works related to sizing and optimisation of the plant equipment. In order for the reaction

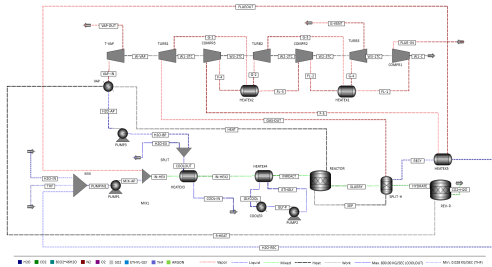


Fig. 6: Hydrate-based process flow scheme

to take place, the feed streams must be brought to the required operating condition (30 bar and -1 °C). Before entering the reactor, flue gases pass through a series of 3 inter-cooled compressions while water and tetrahydrofuran are brought to the required pressure thanks to a pump. Both flows mix and pass through additional cooling units to reach the required temperature. The cooled and pressurised feeds enter the reactor in which the clathrate crystallisation reaction takes place. Part of the water exiting

the heat exchanger is used to keep the reactor at a constant operating temperature. This coolant water is then pressurised and expands in turbine generating power supplied to the necessary utilities. The reactor output is a slurry containing a mixture of clathrates, water, catalyst and non reacted gases. The slurry gets then separated in a gaseous, liquid and mixed fraction using part of the residual heat from the reactor. The gas expands in a series of 3 inter-heated turbine cycles before being vented to the atmosphere, supplying, partially, the power needed by the compressors. The liquid fraction is recirculated to the water feed stream. The mixed stream is heated with the residual heat of the reaction to obtain a pure stream of CO₂ and water. Another option is to directly send the hydrate fraction to the storage facility.

3.3 Model output

Table 6 list the main outputs of the model. Consider-

Table 6: Hydrate-based model outputs

Compressors power	MW	438
Pumps power	MW	8.6
Cooling power	MW	369.1
Turbine power	MW	-458.4
Total required power	MW	357.4
Captured CO ₂	kg/s	155.2
CO ₂ in exhaust gas	kg/s	15.5
Capture power ratio	MW/kgCO ₂	2.3
Energy consumption ratio	MWh/tonCO ₂	0.64
Ton of CO ₂ /energy produced	tonCO ₂ /MWh	0.103
Water re-injection ^a	kg/s	326.5
THF re-injection ^b	kg/s	0.35
Cooling water	kg/s	4500
Ethylene-glycol solution(30%mol) ^c	kg/s	1850

^aPart of the water that participate to the reaction needs to be re-injected to maintain the correct ratio ^b0.1% of the THF is considered to remain in the hydrate flow stream and gets lost during the CO₂ recovery due to its volatility ^cThis is a closed cooling cycle.

ing an average cost for the THF catalyst of 2867€/ton³¹, the annual expenditure to replenish the catalyst is 26 M€. Thanks to ASPEN-Plus ICE (Integrated Cost Estimation), a first capital cost of the capture system can be extracted from the simulated process. Table 7 summarise the THF, capital and operational cost of the capture system based on ASPEN-Plus data-bank. A more accurate estimation is needed to assess the real costs of the implementation, especially for the high O&M and THF cost

Table 7: Initial cost estimation

Total Capital Cost [$M\text{€}$]	306
Total Operating Cost [$M\text{€}/y$]	152.3
THF Cost [$M\text{€}/y$]	26

value.

4 Amine-based absorption

Figure 7 shows the related amine-based flow scheme for CO_2 capture from flue gas. The scheme shows a continuous scrubbing system. It is built around two main elements: an absorber for CO_2 absorption and a regenerator for sorbent recovery and release of CO_2 in concentrated form. Before entering the absorber tower, the

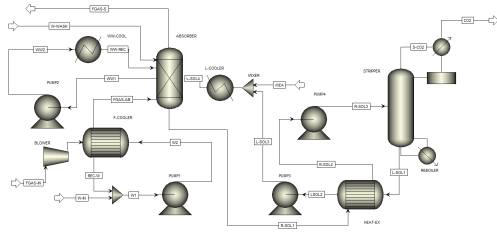


Fig. 7: Amine-based process flow scheme¹⁴

flue gas is pressurised and cooled to 40 - 60°C at atmospheric pressure. Generally, the cooling choice falls onto direct water contact which works also as fine particulate matter remover. The lean solvent (low content of CO_2) enters the absorber tower and gets in contact with the flue gas (counter-current). The separation process uses amines that act like bases, they neutralise acid molecules like CO_2 by forming a weakly bonded component and release heat. The energy released using MEA as sorbent is approximately 3.5 MJ/kg CO_2 . To avoid entrainment and transport of vapour and solvents droplets, flue gas is water washed before it is vented to the atmosphere from the top of the tower. The rich solvent (high content of CO_2) exits from the base of the tower and is heated thanks to the heat recovered from the regenerated solvent cycling back into the stripping tower. Afterwards, the rich solvent is pumped towards the stripping tower that operates at 100 - 140°C and at slightly higher pressure than the absorber. A stream of steam and CO_2 exits the top of the stripping tower and the steam is condensed to obtain a pure CO_2 product stream. The regenerated solvent is cooled and cycled back to the absorber tower. The re-

boiler supplies the heat required to reverse the absorption reaction. Fresh solvent is added to make up for losses in the process.¹⁴

4.1 Amine-based outputs

Table 8 summarise the output of the amine based process.²⁸

Table 8: MEA-based model output

Flue gas	kg/s	824.2
Captured CO_2	kg/s	157.4
CO_2 in exhaust gas	kg/s	17.5
Capture degree	%	90
Capture heat duty	MW	550.2
Heat demand capture ratio	MJ/kg CO_2	3.49
Compressors and coolers power	MW	86.0
Energy consumption ratio	MWh/ton CO_2	0.59
Ton of CO_2 /energy produced	ton CO_2 /MWh	0.111

5 Results

The two separation methods comparison, hydrate and MEA-based, considers the retrofitting of an existing supercritical coal power plant in Gliwice with a net power output of 900MWel. The hydrate capture system requires a total of 357.4MWel to function, while 333.6MWel are needed for the MEA system, cutting off 39.7% and 37% of the plant net power output respectively. For a thermal efficiency of 45%, these values correspond, respectively, to an energy penalty of 17.87% and 16.68%, which means lowering the power plant efficiency to 27% with the hydrate system implementation and 28% through the use of the MEA system analysed. Table 9 summarises the energy comparison main outcomes. A non extensive, ini-

Table 9: Energy comparison main outcomes

	No CCS	MEA	Hydrate
System life [y]		25	
Working hours [h/y]		7200	
Power output [MW]	900	566.4	542.6
Efficiency [%]	45	28	27
Energy penalty [%]	0	16.68	17.87
Production [GWh/y]	6480	4078	3907

tial economic analysis was also performed: it takes into

account only the hydrate capture system, excluding the power plant fuel, O&M and income taxes costs. The life expectancy of the capture system is set to 25 years, working alongside the power plants for 7200 h/y. The analysis is based on the average European electricity market price (50 €/MWh³²) and carbon price (12.78 €/tonCO₂³³). Referring solely to the profits obtained through the electricity market, the implementation of the hydrate system lowers the annual net electricity income of the power plant by 28.51% while the MEA process reduces it of the 25.54%. Table 10 summarises the basic cost outputs. It is clear that the implementation of one of these capture

Table 10: Energy comparison main outcomes

	No CCS	MEA	Hydrate
Production [GWh/y]	6480	4078	3907
El. price [€/MWh] ^a		50	
El. income [M€/y]	324	203.9	195.4
CO ₂ product [Mton/y]	4.5	0.5	0.4
CO ₂ captured [Mton/y]	0	4.1	4.0
$\frac{\text{Energy output}}{\text{CO}_2 \text{ emission}} [\frac{\text{tonCO}_2}{\text{MWh}}]$	0.7	0.111	0.103
CO ₂ prod. [$\frac{\text{€}}{\text{tonCO}_2}$]	0	29.44 ^c	32 ^c
CO ₂ price ^b [€/tonCO ₂]		12.78	
CO ₂ cost [M€/y]	57.9	5.8	5.1
Profit [M€/y]	266.1	198.1	190.2

^a Average value reported on the quarterly report on European electricity markets 2018 by the EU Commission³² ^b Due to a great difference with the 1st quarter of 2017 and the present day, the value was updated at the 07-05-2018³³ ^c Value in line with the Global CCS Institute³⁴

systems greatly cuts the CO₂ emission (up to 91%), lowering the carbon footprint by 4 - 4.1 Mton/y. These great savings come with a price: installation, O&M and catalyst costs lower noticeably the net electricity income. At the current average market price of 50€/MWh, considering solely profits obtained from the electricity sale, the hydrate system implementation results to be not economically feasible. This is mainly due to the high O&M costs of the separation system and the chosen average market price for electricity. In order to pay back for the separation system within its life expectancy, with a discount rate of 15%, a minimum price of 59.08 €/MWh must be adopted (see figure 8). This value was obtained through a sensitivity analysis over the net present value (NPV) calculated with the equation 9.

$$NPV = \text{Capital costs} + \sum_t \frac{\text{Revenues} - \text{O\&M costs}}{(1+i)^t} \quad (9)$$

Where i is the discount rate and t indicates the cash flow time. If one of the higher electricity price were to be

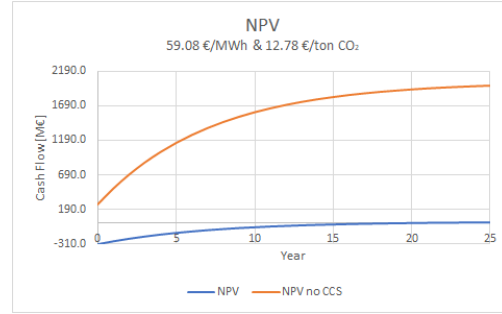


Fig. 8: NPV chart with a payback period of 25 years

considered, (62 €/MWh for example³²), the payback period (PBP) for the capture system would be of ~10 years. Maintaining the same annual profit as the power plant without a CCS installation, considering solely the electricity sale and keeping all the other parameters constants, requires for the electricity price to raise to 69.42 €/MWh (reasonable assumption considering the market trend reported in the EU Commission report³²). In this case, as shown in figure 9, the payback period will go down to ~5 years. Besides the high O&M cost of the

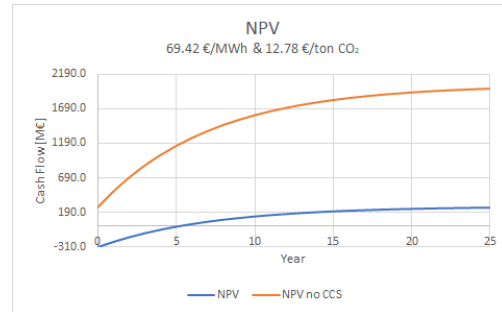


Fig. 9: NPV chart with a payback period of 5 years

CCS system, the low carbon price of 12.78 €/ton of CO₂ plays a crucial role in the system feasibility evaluation. Another sensitivity analysis shows that, with an electricity market price of 62 €/MWh, the increasing of the carbon price to 36.62 €/tonCO₂ would levelise the profits, with a payback period of ~21 years. In all the mentioned scenarios, even though a positive NPV is achievable, the profit over 25 years is noticeably lower when compared to the profit obtainable by the power plant without a CCS system. It is important to notice that no O&M cost for the power plant without CCS were considered, therefore its profit should be lower than the calculated one. If CO₂

sales were to be considered at the same constant average market price of electricity and CO₂, the investment outcome might positively change in economic terms. Due to the market CO₂ need trends, the calculations were carried on considering the total sale of the 4 Mton of CO₂ produced, keeping an average fixed sale price of 5/tonCO₂³⁴ over the years, at the same discount rate. Figure 10 shows the resulting NPV. In this case scenario, despite the conservative approximations, the capture system looks profitable. According to recent reports, the

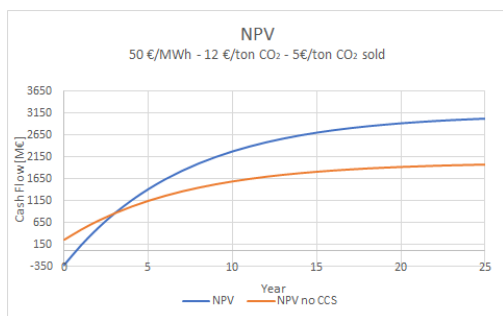


Fig. 10: NPV chart in case of CO₂ sales at 5/ton

energy market proceeds towards a lowering of the current energy prices while the cost of CO₂ emitted will increase^{32 33}. On these terms, although the overall profit will be lower, the capture process might become economically feasible. Further work is needed to assess this possibility.

6 Conclusions

This work mainly compared two CO₂ separation technologies, MEA-based absorption and THF-catalysed hydrate capture. The choice of this specific comparison was mainly based on data availability and reliability, therefore these outcomes may not fully apply to other models. Applying either one of these two technology to an existing 900 MWel power plant requires a great amount of power, but between the two there is not a large difference in terms of energy penalty (16.68% for MEA absorption, 17.87% for THF-catalysed hydrate). If no monetary income streams related to the CO₂ sale is taken into account, at the current techno-economic conditions, the obtained results deem CO₂ capture systems unprofitable. At the current CO₂ and EU electricity average market price (12.78 /tonCO₂ and 50 /MWhel), the analysed separation technologies greatly lower the electricity sale profits (28.51% less for hydrates, 25.54% less for

MEA) when compared to the power plant without CCS implementation. In order to change this situation, government support is essential, not only at the investment stage but also in defining a more appropriate carbon price and adopting an effective green certificate regulation system. For the analysed technology, a great amount of CO₂ emissions can be avoided: more than 4 MtonCO₂ can be captured, stored, sold or reused every year. Thus, considering selling the captured CO₂ at a fixed price of 5/tonCO₂, at the current CO₂ and EU electricity average market price, the calculated income positively changes turning the modelled capture system profitable. Still, research on CO₂ capture through hydrates, aiming not only at power plants but also at other sectors for future commercialisation, is mainly done through computer simulation. This is a huge disadvantage if compared with the possibility to test other technologies in pilot and plant scale: despite the numerous advantages and potential of clathrates, gas absorption remains the most promising solution for CO₂ recovery because it is an industrially developed technology, implemented in other gas treatment processes and easily adaptable to CO₂ capture. With the proper solvent choice (a different MEA blend, for example) and system optimisation, greater energy savings could be achieved. Nevertheless, all the results are in accordance with theory and scientific literature, which allows to say that catalysed-hydrate separation is a promising technology that deserve more in-detail analysis and field tests.

References

- 1 NORA, *Trends in Atmospheric Carbon Dioxide*, National oceanic and atmospheric administration earth system research laboratory, global monitoring division data, 2018.
- 2 IEA, *CO₂ emissions from fuel combustion highlights*, International energy agency report, 2016.
- 3 IEA, *Carbon Capture and Storage: The solution for deep emissions reductions*, International energy agency publication, 2015.
- 4 M. M. M.-V. Dennis Y.C. Leung, Giorgio Caramanna, *An overview of current status of carbon dioxide capture and storage technologies*, Department of mechanical engineering: The university of hong kong, hong kong; centre for innovation in carbon capture and storage: Heriot-watt university, uk publication, 2014.
- 5 E. M. et. al, *CO₂ Capture Performance of MEA and blended amine solvents in CSIRO's pilot plant with flue gas from a brown coal-fired power station*, Csiro energy technology, bayview av7e, clayton, vic, australia publication, 2010.
- 6 N. A. H. Ralph H. Weiland, *Post-combustion CO₂ Capture with Amino-Acid Salts*, Optimized gas treating, inc. publication, 2011.
- 7 S. C. Aroonsri Nuchitprasittichai, *Optimization of CO₂ Capture Process with Aqueous Amines Using Response Surface Methodology*, Department of chemical engineering, the university of tula, usa publication, 2011.

- 8 J. K. Thi-Huong Pham, Byeong-Kyu Lee, *Novel improvement of CO₂ adsorption capacity and selectivity by ethylenediamine-modified nano zeolite*, Department of civil and environmental engineering, university of ulsan, daehakro r93, nam-gu, ulsan 680-749, republic of korea publication, 2016.
- 9 O. B. Luca Riboldia, *Overview on Pressure Swing Adsorption (PSA) as CO₂ capture technology: state-of-the-art, limits and potentials*, Energy and process engineering departament, the norwegian university of science and technology, norway publication, 2017.
- 10 D. S. S. Ambarish R. Kulkarni, *Analysis of Equilibrium-Based TSA Processes for Direct Capture of CO₂ from Air*, School of chemical and biomolecular engineering, georgia institute of technology, atlanta, united states publication, 2012.
- 11 S. Z. et. all, *Status and progress of membrane contactors in post-combustion carbon capture: A state-of-the-art review of new developments*, Department of environmental sciences - macquarie university and csiro energy, australia. department of chemical engineering - norwegian university of science and technology, norway. Irgp-cnrs universit de lorraine and universit clude bernard de lyon, france. college of engineering - huazhong agricultural university, china. unesco centre for membrane science and technology - school of chemical engineering - the university of new south wales, australia. membrane science and technology research centre - nanjing tech university, china publication, 2016.
- 12 E. S. R. Haibo Zhai, *Techno-Economic Assessment of Polymer Membrane Systems for Postcombustion Carbon Capture at Coal-Fired Power Plants*, Department of engineering and public policy, carnegie mellon university, pittsburgh, united states publication, 2013.
- 13 C. S. et. all, *Advanced cryogenic CO₂ capture process based on Stirling coolers by heat integration*, Tianjin key laboratory of indoor air environmental quality control and key laboratory of efficient utilization of low and medium grade energy - school of environmental science and technology - tianjin university, china. graduate school of life and environmental sciences, university of tsukuba, japan publication, 2017.
- 14 S. A. Rackley, *Carbon Capture and Storage (Second Edition)*, Butterworth-Heinemann, 2017.
- 15 X. L. Shuanshi Fan, Yanhong Wang, *CO₂ capture in form of clathrate hydrate - problem and practice*, School of chemistry and chemical engineering, key lab of enhanced heat transfer and energy conservation, ministry of education, south china university of technology, guangzhou, china publication, 2011.
- 16 F. K. Hideo Tajima, Akihiro Yamasaki, *Energy consumption estimation for greenhouse gas separation processes by clathrate hydrate formation*, National institute of advanced industrial science and technology, tsukuba, japan publication, 2004.
- 17 N. N. A. Larryn W. Diamond, *Solubility of CO₂ in water from -1.5 to 100C and from 0.1 to 100 MPa: Evaluation of literature data and thermodynamic modelling*, Institute of geological sciences, university of bern, baltzerstrasse, switzerland publication, 2003.
- 18 C. Zou, *Unconventional Petroleum Geology (Second Edition)*, Johnathan Simpson, 2017.
- 19 J. D. F. et. all, *Advances in CO₂ capture technology* The U.S. Department of Energys Carbon Sequestration Program, National energy technology laboratory, u.s. department of energy and science applications international corporation, national energy technology laboratory, pittsburgh, united states publication, 2008.
- 20 C. K. E. Dendy Sloan, *Clathrate Hydrates of Natural Gases, Third Edition*, CRC Press, 2008.
- 21 J. H. et. all, *A literature research on the performance evaluation of hydrate-based CO₂ capture and separation process*, Key laboratory of efficient utilization of low and medium grade energy (tianjin university), ministry of education of china, china - sir joseph swan centre of energy research, newcastle university, uk publication, 2017.
- 22 J. T. et. all, *Study on the influence of SDS and THF on hydrate-based gas separation performance*, Natural gas hydrate laboratory, college of pipeline and civil engineering, china university of petroleum (east china), shandong - petrochina coalbed methane co., beijing - west-east gas transmission company pipeline branch, shanghai, china publication, 2013.
- 23 P. E. Praveen Linga, Adebola Adeyemo, *Medium-pressure clathrate hydrate/membrane hybrid process for postcombustion capture of carbon dioxide*, Department of chemical and biological engineering, university of british columbia, vancouver, canada publication, 2007.
- 24 J.-M. H. Nguyen Hong Duc, Fabien Chauvy, *CO₂ capture by hydrate crystallization A potential solution for gas emission of steelmaking industry*, Centre spin, ecole nationale superieure des mines de st-etienne, saint-etienne cedex 2, france publication, 2007.
- 25 P. L. L. Cláudio P. Ribeiro Jr., *Modelling of hydrate formation kinetics: State-of-the-art and future directions*, Programa de engenharia quimica-coppe, universidade federal do rio de janeiro, rio de janeiro, brazil publication, 2008.
- 26 S. Bergeron and P. Servio, *Reaction Rate Constant of CO₂ Hydrate Formation and Verification of Old Premises Pertaining to Hydrate Growth Kinetics*, Dept. of chemical engineering, mcgill university, montreal, canada publication, 2008.
- 27 O. Redlich and J. Kwong, *On the Thermodynamics of Solutions V. An Equation-of-state. Fugacities of Gaseous Solutions*, Shell development company, emeryville, california publication, 1948.
- 28 T. C. Krzysztof Bochon, *Energy and economic analysis of the carbon dioxide capture installation with the use of monoethanolamine and ammonia*, Silesian university of technology, institute of power engineering and turbomachinery, gliwice, poland publication, 2015.
- 29 F. L. P. P. Cláudia F. S. Lirioa, *Enthalpy of Dissociation of Simple and Mixed Carbon Dioxide Clathrate Hydrate*, Ifrj - paracambi, rua sebastiao lacerda, s/n, centro - paracambi, rj. brasil and ufrj- escola de quimica publication, 2013.
- 30 F. K. Hideo Tajima, Akihiro Yamasaki, *Energy consumption estimation for greenhouse gas separation processes by clathrate hydrate formation*, National institute of advanced industrial science and technology, onogawa, japan publication, 2003.
- 31 ICS *Indicative Chemical Prices*, <https://www.icis.com/chemicals/channel-info-chemicals-a-z/>.
- 32 M. O. for Energy of the European Commission, *Quarterly report on European Electricity Markets*, European commission, directorate-general for energy, market observatory for energy, 2018 publication, 2018.
- 33 M. Insider, *CO₂ European Emission Allowances*, <http://markets.businessinsider.com/commodities/co2-emissionsrechte/euro>, 2018.
- 34 G. C. Institute, *The CO₂ Market*, <https://hub.globalccsinstitute.com/publications/accelerating-uptake-ccs-industrial-use-captured-carbon-dioxide/2-co2-market>.