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This is an Accepted Manuscript of an article published by Elsevier in **Applied Energy** Vol. 253, on November 2019, available at: <https://doi.org/10.1016/j.apenergy.2019.113519>

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Partial oxy-combustion technology for energy efficient CO₂ capture process

F. Vega, S. Camino, J. A. Camino, J. Garrido, B. Navarrete

Chemical and Environmental Engineering Department, School of Engineering, University of Seville, C/ Camino de los Descubrimientos s/n 41092 Sevilla, Spain, Phone: 954481397, fvega1@etsi.us.es

Abstract

Partial oxy-combustion is considered a promising carbon capture and storage technology that can lead to further energy penalty reductions in the regeneration stage. It is based on the generation of a highly CO₂ concentrated flue gas prior to be separated by chemical absorption. The presence of large amounts of CO₂ in the flue gas should enhance the driven force in the bulk gas and the absorption performance. A novel concept namely Shift to Low Temperature configuration has been developed in order to strengthen the potentialities of partial oxy-combustion over the CO₂ separation process. This novel configuration aims at relaxing the operating conditions in the stripping section based on the benefits – kinetics and driven force - observed in the absorption unit by means of shifting the operational CO₂ cyclic capacity of the solvents towards lower energy requirements for solvent regeneration. In this work, three levels of StLT operations were tested in a bench-scale CO₂ capture experimental facility. Results from the test campaign were further compared with both post-combustion and partial oxy-combustion operated at conventional operating conditions. The energy requirements were further improved as this novel configuration was applied, particularly using 118 °C as stripping temperature in combination with 60%v/v CO₂ in the flue gas. Under this operating conditions, the energy penalty was reduced by 11% respect to conventional partial oxy-combustion operation using the same flue gas composition - from 4.55 to 4.05 GJ/t CO₂ using MEA 30wt% as solvent -. The energy penalty was further decreased up to 64% in comparison with the post-combustion test. Results recommend the use of large CO₂ cyclic capacity solvents to enhance the potentialities of the Shift to Low Temperature configuration for carbon capture applications.

Keywords: bench-scale; CCS; CO₂ capture; regeneration; partial oxy-combustion

Glossary

Symbols and constants

Q	Weight specific heat duty (GJ/ton CO ₂)
T	Temperature (K)
C _p	Molar heat capacity (kJ/(mol K))
α	CO ₂ loading (mole CO ₂ /mole solvent)
Δα	CO ₂ cyclic capacity (mole CO ₂ /mole solvent)
PM	Molecular weight (g/mol)
X	Molar fraction of each component (g/g)
Δh	Molar enthalpy (kJ/mol)
P _i	Partial pressure of each component (kPa)
P	Total pressure (kPa)
R	Universal gas constant (8.314 J/(mol K))

Indices

reb	reboiler
sen	sensible
vap	vaporization
des	desorption
ref	reference
S	saturation
*	equilibrium
sol	solution
solv	solvent
vap,H ₂ O	water evaporation
abs,CO ₂ CO ₂	CO ₂ absorption

1. Introduction

Post-combustion based on CO₂ chemical absorption is a close-to-market CCS technology applied either for new or existing industrial facilities. It provides a high CO₂ removal efficiency at CO₂ diluted flue gas, i. e. those derived from both fossil-fuels power plants and energy-intensive industries. There are some drawbacks hindering the deployment of post-combustion at industrial scale, mainly due to the excessive energy penalty related to the solvent regeneration [1]. According to Rubin et. al., the energy penalty for retrofitting existing coal-fuelled power plants is ranging between 9-12% in respect to the total thermal energy input [2]. This energy penalty falls in the window 7-12% points for natural gas combined cycle power plants [3]. In this context, alternative solvents, improvements in process integration, energy optimization and numerous configurations from the conventional equipment arrangement proposed by Bottoms have been taken in order to improve the overall efficiency of the CO₂ capture process [2, 4].

The use of advanced solvents and blends has been studied in numerous works in order to minimize the energy requirements of the overall CO₂ capture process. Osagie et. al. evaluated a 25-30wt% AMP aqueous solution in a post-combustion capture process for capturing CO₂ in a natural gas combined cycle power plant. The AMP-based process resulted in a 25.6% decrease of the reboiler duty compared with MEA 30wt%. The energy savings of AMP-based process provided a 7.1% of energy penalty of the gross power of the combined cycle power plant whereas the use of MEA 30wt% increased this energy demand up to 9.1% [3]. Thermomorphic biphasic solvent (TBS) has been also proposed in combination with intensification methods such as agitation, ultrasonic and nucleation is shown as a promising alternative for solvent regeneration [5]. TBS can reduce the reboiler duty up to 50% in comparison with MEA 30wt% benchmark. A novel proposal from Zhang et. al. based absorption heat transformer coupled with flash evaporation has shown a great potential for stripping performance. In this novel process, the heat of the high-temperature condensate of the reboiler is recovered to be used during the regeneration stage. A 2.62% reduction of the specific energy consumption was achieved in comparison with a conventional CO₂ capture layout applied to

a 660 MW pulverized coal power plant [6]. Recent studies on non-aqueous solvents has demonstrated a high absorption performance for CO₂ capture application. In particular, 2-methoxyethanol and 2-ethoxyethanol blended with MEA resulted in around 55% energy reduction of the solvent regeneration in respect to the benchmark (MEA 30wt%) [7].

In recent years, many efforts have been made to provide new concepts of process integration and novel configurations [8]. One of the approaches is the heat integration between the power plant and the CO₂ capture unit that can enhance the overall plant efficiency [9]. In this sense, new tools for evaluating different configurations based on superstructures has been recently proposed for optimization of the CO₂ capture process [10]. Assessment of such modification or measure might be previously evaluated by the use of simulation tools coupled with either further energy reduction considerations or economic evaluations [11]. Ahn et. al. [12] evaluated up to ten different configurations of a CO₂ capture unit using MEA 30wt% as solvent, adapted for a 550 MW_e sub-critical pulverized coal (PC) boiler power plant. Conventional configurations of an amine-based chemical absorption unit were extracted from the literature and patents, such as absorber intercooling [13], condensate heating [14], stripper overhead compression [15], lean amine flash [16], multi-pressure stripping [17], heat integration [18] and split-flow were proposed [19]. The multiple alteration configurations, in which the absorber intercooling was combined with condensate evaporation and lean amine flash, results in a 36.9% reduction in the reboiler heat duty in comparison with the conventional configuration and leads to around 2.2 MJ/kg CO₂ of energy requirement for solvent regeneration. Ahn et. al. estimates the gain of the overall efficiency of a fossil-fuel power plant coupled with a carbon capture unit at about 1%, from 27.9% for the baseline case to 28.8% for the multiple alteration case, with a 37% reduction in the steam consumption applied to solvent regeneration when multiple integration strategies were set in a fully integrated power plant [12]. A similar evaluation was performed by Li et. al. [20]. In this work, the combination of absorber intercooler, rich-split and stripper inter-heating leaded to 13.6% reduction of the reboiler duty compared with the benchmark, proving a 3.1 GJ/ t CO₂ as a lowest specific energy consumption for

solvent regeneration. Recent works from Xu et. al. showed a de-carbonization of a coal-fired power plant by means of supercritical CO₂ (S-CO₂) power cycle combined with an absorption heat transformer. Both recovery process can add 23.8 MW and 119.6 MW to the gross power, respectively. Xu et. al. estimated an increase of 3% points of the energy/exergy efficiency compared to the reference case for this novel configuration [21]. Oyekan and Rochelle [17] evaluated four different stripper configurations and their performance under seven solvents, primarily KS-1 solvent from Mitsubishi Heavy Industries (MHI) and PZ blends with MEA, MDEA and potassium carbonate, respectively. This study concludes that a double matrix configuration for the stripper showed the best performance. In particular, the double matrix using MEA/MDEA blend as solvent offered a 22% energy saving in comparison with conventional MEA-based chemical absorption units with 90% CO₂ capture [17]. Recent stripper modifications have been proposed that can significantly reduce the energy requirement for solvent regeneration. Rochelle proposed the advance flash stripper using PZ, which provided 10% of the overall equivalent work associated with reboiler duty, compression and pumping works [22]. Other novel proposals, such as electrochemically-mediated amine regeneration [23] and the use of ejectors for waste heat upgrading [24], have shown a promising performance in terms of energy reduction of the global carbon capture process.

Other CCS technology, namely oxy-combustion, has been developed as a competitive option for CO₂ capture for fossil-fuel power plants and energy-intensive industrial processes. In this case, the high purity O₂ production is the main drawback that constrains its deployment at full scale. Therefore, efforts have been conducted to achieve relevant improvements on the O₂ production technologies, particularly via cryogenics. According to Perrin, further optimizations of the Air Separation Unit based on heat integration established the separation energy of around 140 kWh/t O₂, with a realistic target around 120 kWh/t O₂ by 2020 [25]. New advances on cryogenic oxygen storage combined with oxy-fired power plants can reduce up to 1.1% the impact of the O₂ production on the net electrical efficiency of oxy-fired power plants [26].

In the above-described framework, partial oxy-combustion emerges as a promising CCS capture

technology that can drastically decrease the energy requirements of the overall CO₂ separation process [27]. It based on the use of an oxygen-enriched oxidizer during the combustion stage followed by a CO₂ separation process based on chemical absorption. Flue gas derived from partial oxy-combustion process provided a higher CO₂ concentration compared with conventional post-combustion. The presence of higher CO₂ concentration in the flue gas enhanced the CO₂ absorption [28] and hence produces further reductions of the solvent regeneration stage [27]. Partial oxy-combustion has shown a high performance and feasibility in industrial processes such cement plants, in which the inherent CO₂ production can lead to elevated CO₂ concentrations in the flue gas [29]. However, techno-economic studies on pulverized coal power plants carried out by Huang showed lower energy conversion efficiencies for partial oxy-fired cases – from 36.18% to 34.87% - than the full oxy-combustion case – 36.24%. In this work, the oxygen-enriched oxidizer was produced by mixing high purity O₂ from an Air Separation Unit (ASU) and ambient air which enhanced the inefficiency of the overall energy production process [30]. Other studies conducted by Cau et. al. reported similar results in terms of the overall energy efficiency of the 1000 MW_{th} pulverized coal power plant operating under partial oxy-combustion conditions [31]. Both post-combustion and oxy-combustion case resulted in higher energy efficiency, 35.9% and 36.13%, respectively. The contribution of O₂ from ASU varied from 10% to 90% in partial oxy-combustion cases and the energy efficiency was found ranging between 34.70% and 31.46%, respectively. Cau et. al. did not consider the direct production of oxygen-enriched air instead of O₂ from ASU-air mix. In addition, the energy consumption of the CO₂ capture and compression process only varied from 32.4 MW (post-combustion case) to 30.4 MW (partial oxy-combustion with 90% O₂ contribution from ASU – 10% contribution from ambient air) [31].

This work studied a novel configuration of the CO₂ capture process based on regenerative chemical absorption under partial oxy-combustion, namely Shift to Low Temperature (StLT). The novel configuration should enhance the potentials and main advantages observed from partial oxy-combustion and therefore make partial oxy-combustion competitive in comparison with both post-combustion and oxy-combustion technologies. The aims of this work is to demonstrate the flexibility, feasibility and performance of a CO₂ capture process based on chemical absorption operated under the StLT configuration and to minimize the energy penalties related to the CO₂ separation stage, mainly focused on the optimization of the operating conditions of the CO₂ capture unit. The StLT configuration was tested in a CO₂ capture bench-scale unit designed to operate at both post-combustion and partial oxy-combustion in a wide range of CO₂ concentrations up to 60%v/v CO₂.

2. Fundamentals

The energy requirements for solvent regeneration account for 50-80% of the total energy consumption in a conventional post-combustion capture process using aqueous amine solution as a solvent [32]. The heat of regeneration (Q_{reg}) consists of the sum of three terms: the solvent sensible heat (Q_{sen}), the heat of CO₂ desorption (Q_{des}) and the water vaporization heat (Q_{vap}), as seen in Eq. 1.

$$Q_{reg} = Q_{sen} + Q_{vap} + Q_{des} \quad (\text{Eq. 1})$$

The sensible heat is required to reach the stripper temperature which depends on the resistance of the solvent to be thermally degraded [33]. It is commonly assigned to 120°C for MEA applications [34]. The high stripper temperature results in a vapourisation of the aqueous solution solvent, which is mainly composed of water. The latent heat of water vapourisation could reach higher values (92.4 kJ/mole CO₂) and leads to the excessive energy consumption in the overall desorption process [35]. In the benchmark case (MEA 30% v/v), the absorption heat accounts for the major portion (50–60% of the total reboiler duty) in the CO₂ desorption process [36]. A detailed expression of each term is shown in Eq. 2. Some assumptions have been suggested such as that the flashing of the solvent does

not occur in the stripper inlet and that equilibrium is not reached in large scale units [34].

$$Q_{reg} = \frac{c_p(T_{reb} - T_{feed})}{\Delta\alpha} \frac{PM_{sol}}{PM_{CO_2}} \frac{1}{X_{sol}} + \Delta h_{vap,H_2O} \frac{P_{H_2O}}{P_{CO_2}} \frac{1}{PM_{CO_2}} + \frac{\Delta h_{abs,CO_2}}{PM_{CO_2}} \quad (\text{Eq. 2})$$

It is obvious that the energy savings in CO₂ desorption should be focused not only on the enthalpy of absorption of the novel solvents but also on the interrelationships of the solvent with the other two members of the equation. In this respect, the partial pressure ratio between both water and CO₂ plays a key role in the overall energy requirements in the stripper. The expressions of both partial pressures (Eq. 3 and 4) can be obtained by applying the Clausius-Clapeyron equation, assuming equilibrium at the top of the stripper [37].

$$P_{CO_2}^* = P_{CO_2,ref}^* \exp\left(\frac{|\Delta h_{abs,CO_2}|}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right) \quad (\text{Eq. 3})$$

$$P_{H_2O}^s = P_{H_2O,ref}^s \exp\left(\frac{|\Delta h_{vap,H_2O}|}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right) \quad (\text{Eq. 4})$$

Therefore, the ratio of both partial pressures is expressed as follows in Eq. 5:

$$\frac{P_{H_2O}^s}{P_{CO_2}^*} = \frac{P_{H_2O,ref}^s}{P_{CO_2,ref}^*} \exp\left(\left[\frac{T - T_{ref}}{RTT_{ref}}\right] [|\Delta h_{vap,H_2O}| - |\Delta h_{abs,CO_2}|]\right) \quad (\text{Eq. 5})$$

As Eq. 5 illustrates, the water-CO₂ partial pressure ratio depends on the enthalpy of absorption and the stripping temperature, which is directly coupled to the operating pressure of the stripper. In the case of solvents with high enthalpy of absorption (fast solvents), the difference between the latent heat and the enthalpy of absorption is negative. This fact implies that the water-CO₂ partial pressure ratio and therefore the heat of vapourisation term from Eq. 1 decrease with an increase of the stripping temperature (or operating pressure). The regeneration of these solvents should be carried out at as high a pressure and temperature as possible. On the other hand, solvents with low enthalpy of absorption obtain a positive value from the difference between both above-mentioned heats and lead to lower energy requirements for CO₂ desorption when the temperature, and hence pressure, of the stripper is as low as possible. In general, for solvents having the same capacity, the one showing the larger heat of absorption can profit from a higher temperature swing between absorber and stripper. Low heat of absorption solvents might benefit from stripping below atmospheric

pressure, which implies low operating temperatures in the stripper [34].

The enthalpy of absorption depends on the temperature and the CO₂ loading of the solvent. It also depends on the solvent composition when blends are used, particularly the composition of the slow kinetic solvent [38]. Based on the experimental data available in the literature, the primary amines are fast solvents for CO₂ absorption and hence exhibit the highest enthalpy of absorption, typically found in the range 80-90 kJ/mole CO₂. The heat of absorption decreases in line with the kinetics. The heat of absorption is about 70-75 kJ/mole CO₂ and 55 kJ/mole CO₂ for secondary and tertiary amines, respectively [35]. In addition, enthalpy of absorption decreases with an increase of CO₂ loading. Most of the solvents maintain high values of enthalpy of absorption at low loadings, but it is observed that the enthalpy of absorption decreases from a certain loading, commonly round about 0.4 – 0.6 mole CO₂/mole solvent [39]. On the other hand, pressure and amine concentration in the aqueous solution do not significantly affect the enthalpy of absorption. The heat of absorption of CO₂ is independent of the partial pressure of CO₂ above the solvent and, therefore, partial oxy-combustion does not have any direct impact on the enthalpy of absorption [38].

3. Materials and methods

3.1 Materials

The solvent used during the test campaign was Monoethanolamine (MEA) in aqueous solution (30wt%). The chemicals were supplied by Acros Organics with a 99 vol.% purity. The aqueous solution was prepared using deionized water. The CO₂/N₂ synthetic flue gas was prepared from individual gas cylinders (99 vol.%). Linde™ supplied the cylinders within ±1% accuracy of the gas purity.

3.2 CO₂ bench-scale pilot plant description

The experimental test campaign was carried out in the CO₂ bench-scale pilot plant. A detailed description of both the CO₂ bench-scale experimental plant and the procedure of key parameters determinations such as specific energy consumption and CO₂ removal efficiency can be found in previous work [27]. The general operating conditions set for the experimental tests are summarized in Table 1.

Table 1. Main characteristics of the absorber and stripper units

Absorber	
Temperature (°C)	50
Operating pressure (bara)	1
ID (mm)	30
Column material	borosilicate glass
Random packing	Raschig rings 6 mm
Packing material	Ceramic
Packing height (m)	0.7
Number of packing beds	4
Volume solvent solution (L)	2
Stripper	
Temperature (°C)	116-120
Operating pressure (bara)	2
Electrical power (W)	750
ID (mm)	25
Column material	316L
Random packing	Raschig rings 6mm
Packing material	316L
Packing height (m)	0.7
Number of packing beds	2

The CO₂ bench-scale pilot plant can operate in a wide range of flue gas CO₂ compositions, from 15 %v/v CO₂ (post-combustion) up to 60% v/v CO₂ (partial oxy-combustion using 80% v/v O₂ in the oxidizer prior to the combustion stage). This experimental unit consists of a 300 mm-ID absorber column and a 250 mm-ID stripper column. Four packing beds with a total height of 3 m were used in the absorber whereas two packing beds with a total height of 1.4 m were used for the stripper. 6-mm stainless steel raschig rings were employed as a random packing for both the absorber and the stripper columns.

The operating procedure is briefly described as follows. A synthetic flue gas is prepared from two cylinders containing CO₂ and N₂, respectively. The desired composition of the synthetic flue gas is adjusted by using two mass-flow controllers. Then, the composition of the synthetic flue gas is checked using a FTIR - CO₂ analyser (Testo™ XL model 350 XL) prior to be introduced into the absorber and the synthetic flue gas is also saturated at the absorption temperature before entering the absorber. The absorption process occurs along the absorber at a temperature fixed at 50 °C during all the test run planned in the experimental campaign. After the synthetic flue gas is put in counter-current with the lean solvent, the rich solvent is pumped to the stripper using a peristaltic pump. The rich solvent is heated using the lean amine solvent leaving the stripping before being introduced into the stripper. Both the temperature and the pressure of the stripper are controlled using an electrical heater and a pressure transducer for adjusting the desired values, respectively. Once the solvent is regenerated, the lean solvent is pumped back to the absorber. The temperature of the lean amine is adjusted by using a heat exchanger using cooling water after the lean-rich amine heat exchanger. All the experiments require no less than 2 hours to reach the steady state. After that, the experiments are running during three hours, maintaining stable conditions to determine the average values of the representative parameters of the CO₂ absorption process. The CO₂ bench-scale pilot plant is monitoring during the experiments and parameters such as the absorber temperature profiles, the CO₂ concentration of the exhaust gas, the lean and rich solvent flow-rate and their density and the flow-rate of the CO₂ stream leaving the stripper top are continuously reported for further determinations. From all the data reported above, the key parameter determinations are the CO₂ removal efficiency in the absorber and the specific energy consumption for solvent regeneration. The methodology for both calculation are described in detail in previous work [27]. To complete the CO₂ mass balance, several 1-mL liquid samples were withdrawn for both the lean and the rich solvent. The imbalance was found below 10 % of deviation from the CO₂ introduced at the absorber inlet in all the runs.

3.3 Methodology description of Shift to Low Temperature configuration

The Shift to Low Temperature (StLT) operation mode is a novel approach for CO₂ capture applications based on the partial oxy-combustion process [40]. This method provides a novel process control philosophy and stripping operation in addition to the current operation alternatives proposed. Most authors agree with the fact that high pressure operations in the stripper reduce energy requirements for high kinetic solvents [33]. Elevated stripping pressure leads to high stripping temperatures and therefore a further reduction of the reboiler duty as reported in section 2. On the other hand, StLT offers a potential reduction of regeneration energy based on the possibilities shown under partial oxy-combustion conditions that significantly differ from the above-mentioned operation.

In this respect, partial oxy-combustion ensures a significant enhancement of the chemical absorption. Both the saturated CO₂ loading and the absorption kinetic are further improved due to the presence of high CO₂ content in the gas phase [27]. The target proposed for the StLT concept is to transfer these advantages to the stripping process to allow for a reduction of the energy requirements associated with this process.

Figure 1 represents the CO₂ enthalpy of solubility (ΔH_s) plotted versus the CO₂ loading. The CO₂ cyclic capacity ($\Delta\alpha$) is the difference of the CO₂ loading between the rich and the lean solvent. As it can be seen, there is a direct relationship between CO₂ loading and CO₂ enthalpy of solubility. In particular, CO₂ molecules absorbed in low CO₂ loading ranges produce higher values of CO₂ enthalpy of solubility and, hence, high energy requirements for solvent regeneration, whereas CO₂ molecules absorbed at high CO₂ loading ranges are associated with lower CO₂ enthalpy of solubility and also lower solvent regeneration energies. In this Figure, the low CO₂ cyclic capacity solvents (dashed red line) are found in the highest region of the CO₂ enthalpy of solubility and there are not capable to move to lower energy requirements, i. e. MEA. However,

high CO₂ cyclic capacity solvents (dashed blue line) are not only able to reach similar CO₂ cyclic capacities in regions with lower CO₂ enthalpy of solubility but also they can both increase their CO₂ cyclic capacity - i. e. from 0.4 to 0.5 mol CO₂ / mol amine – and also displace towards the lowest CO₂ enthalpy of solubility regions.

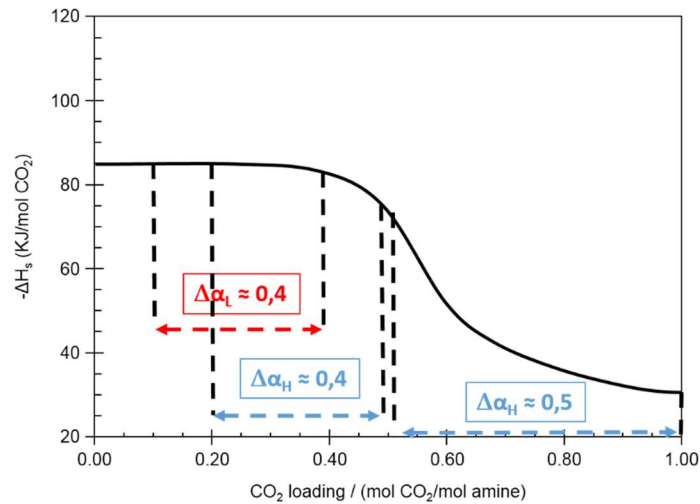


Figure 1. Enthalpy of CO₂ solubility versus CO₂ loading adapted from Ma'mun [39]. $\Delta\alpha_L$ (dashed red line) represents a typical low CO₂ cyclic capacity solvent whereas $\Delta\alpha_H$ (dashed blue lines) represents a typical high CO₂ cyclic capacity solvent

StLT is based on this phenomenon. StLT moves the operating cyclic capacity of the solvent towards low CO₂ enthalpy of solubility regions that result in a low energy requirements during the desorption process. This fact might reduce the kinetic rates that should be balanced by the use of high CO₂ concentrated flue gas. As Fig. 2 illustrates, low cyclic capacity solvents have no chance of shifting the cyclic capacity operation range to low energy regions. This kind of solvents reach a low saturated CO₂ loading. The use of a low cyclic capacity leads to an excessive solvent flow-rate and it likely produces elevated energy requirements. On the other hand, high cyclic capacity solvents can extend the operating range to high CO₂ loading regions and hence low energy requirements. In this case, it may also be possible to increase the cyclic capacity of the solvent if necessary to balance the energy requirements by reducing the solvent flow-rate.

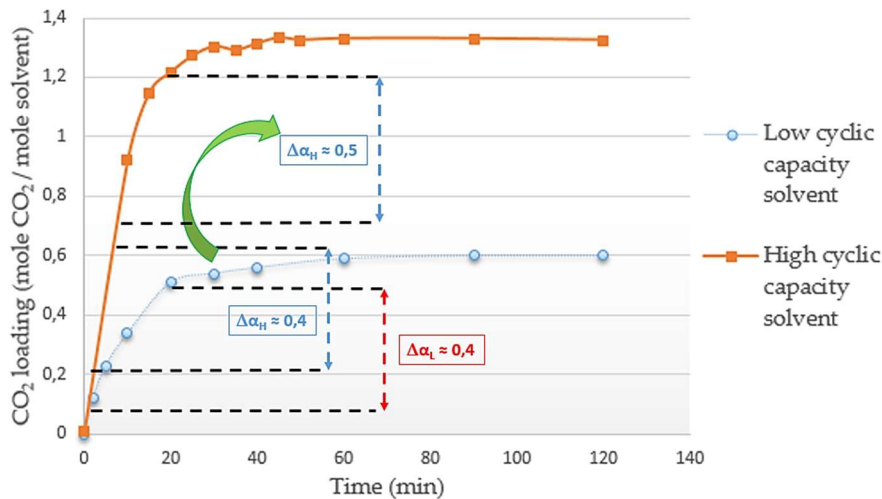


Figure 2. Basic scheme of the StLT operation mode. $\Delta\alpha_L$ represents a typical low CO₂ cyclic capacity solvent whereas $\Delta\alpha_H$ represents a typical high CO₂ cyclic capacity solvent

The StLT operation mode combines a partial oxy-combustion process with a more relaxing stripping conditions, based on the use of lower stripping temperatures. The cyclic capacity range of each solvent can be shifted by changing the stripping temperature to lower values than conventional values, i.e. 120°C. A decrease of the stripping temperature leads to a lower stripping of the solvent and, therefore, a high CO₂ loading of the lean amine. This fact also reduces the three terms included in the reboiler duty equation represented in Eq. 1, showing a large potential to produce a significant reduction of the overall capture process [40]. It should be noted that the reduction of the stripping temperature does not only decrease the solvent regeneration leading to a higher CO₂ loading of the lean amine and, therefore, reducing the reboiler duty, but also reduces the absorption capacity and kinetics leading to higher L/G ratios in the absorber. However, the lower CO₂ absorption capacity and kinetics regarding the higher CO₂-loaded lean amine is balanced in the absorber due to the higher CO₂ partial pressure provided by partial oxy-combustion operations [40]. The operating conditions proposed by StLT operations will be tested during the test campaign.

3.4 Experimental planning

The above-mentioned StLT operation mode was tested in the lab-scale plant for MEA 30wt% as solvent. To extend the capacities of this novel stripping configuration, the experiments were carried out at the highest CO₂ concentration (60%v/v CO₂) using four and two random packing beds for the absorber and stripping columns, respectively. Ten partial oxy-combustion experiments were run under the operating conditions summarized in Table 2. The results obtained were compared with the baseline cases which consisted of both the post-combustion run with the treated flue gas at 15%v/v CO₂ and the partial oxy-combustion runs at 60%v/v CO₂ operated at 120°C as stripping temperature. The CO₂ removal efficiency was set around of the 95% of the total CO₂ introduced in the absorber.

Table 2. Experimental test campaign

RUN	Test description	Stripper Pressure (bara)	T _{strip} (°C)	[CO ₂]g (%v/v)	L/G Ratio (kg/kg)	Random Packing Beds Absorber	Random Packing Beds Stripper
0*	post-combustion*	2	120	15	3	4	2
1	Partial oxy-combustion baseline		120	60	13.3		
2	Partial oxy-combustion test A		118		13		
3					14		
4					15		
5	Partial oxy-combustion test B		117		14		
6					15		
7					16		
8	Partial oxy-combustion test C		115		17		
9					19		
10		21					

*Data extracted from Vega et. al. [27]

For each set of runs, the L/G ratios of intermediate experiments – runs 3, 6 and 9 - were defined in order to achieve similar CO₂ removal efficiency than the baselines cases (95%). In the other two experiments of each set, the L/G ratios were set using values that ensure CO₂ removal efficiencies around 90% (cases 2, 5 and 8) and 100% (cases 4, 7 and 10).

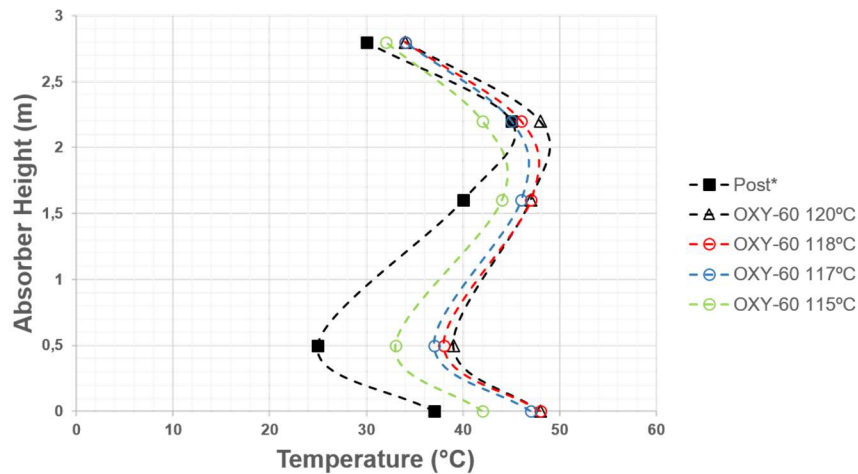
4. Results

The feasibility and performance of partial oxy-combustion has been analyzed as a promising CO₂ capture approach in previous work [27]. A test campaign using MEA 30wt% have been run applying the StLT operating mode described in detail in the methodology section. The operating conditions of those experiments were set to fit the StLT approach, within the tight operating range provided by the use of a low cyclic capacity solvent such as MEA 30wt%. To strengthen the potential of the StLT approach, four packing beds were used in the absorber with a flue gas composition of 60%v/v CO₂. The novel StLT concept was evaluated from the results extracted during the partial oxy-combustion test campaign run at the CO₂ capture bench-scale experimental plant. Those results were further compared with those provided from previous work operating under conventional stripping conditions [27]. The influence of the most relevant operating parameters on the performance of the bench-scale plant have been studied, mainly focused on the stripping performance and the specific energy consumption related to the reboiler duty.

4.1 Effect on the absorber temperature profiles

The absorption performance can be directly evaluated from the absorber temperature profiles. The maximum temperature bulge pointed the optimum L/G ratio for each configuration. The impact on the absorber temperature was studied in this section under variations on the stripping temperature. Figure 3 represents the absorber temperature profiles for the partial oxy-combustion experiments. The absorber temperature profile of the post-combustion case was

reported from previous work for further comparison [27]. The temperature profiles plotted in Figure 3 showed similar behaviour to those obtained from other experimental work found in the literature [49, 55, 56]. It should be noted that the CO₂ capture removal was set around 95% in all the experiments represented in Figure 3 – runs 1, 3, 6 and 9.



* Data reported from Vega et. al. [27]

Figure 3. Absorber temperature profiles from partial oxy-combustion experiments under several StLT operating conditions (experiments 1, 3, 6, 9 from Table 2).

In general, partial oxy-combustion cases showed higher temperature profiles than post-combustion experiment due to the higher amount of CO₂ absorbed. The temperature bulge varied from 44.5 °C (stripping temperature @ 115 °C) to 49.2 °C (stripping temperature @ 120 °C) whereas the post-combustion run obtained 44.7 °C [27]. Experiments run at low stripping temperature provided highly CO₂ loaded lean amine and hereby they required higher L/G ratio to balance the decrease on the absorption kinetics. For example, the lean amine reached a CO₂ loading up to 0.28 mole CO₂ per mole solvent at 115 °C whereas this value was almost half at 120 °C as stripping temperature (0.15 mole CO₂ per mole solvent). The increase on the solvent flow-rate implied a decrease on the overall temperature profile in the absorber observed in the partial oxy-combustion experiments, as Fig.3 illustrates. The amount of CO₂ absorbed was similar in all the partial oxy-combustion experiments represented in Fig 3. – 95% CO₂ removal

efficiency – and therefore the heat released in the absorber due to the CO₂ enthalpy of solubility was equal for those experiments. The use of more solvent flow-rate reduced the temperature along the absorber, as it was observed in Fig. 3.

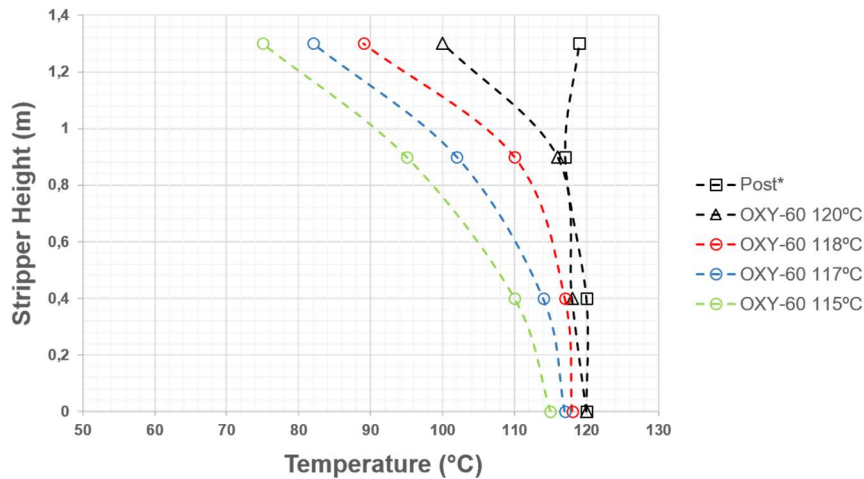
Respect to the temperature bulge, it observed a displacement towards the absorber bottom as the stripping temperature decreased from 120°C to 115°C. The increase of the L/G ratio associated to the higher loaded lean amine from low stripping temperature experiments produced a shift of the temperature bulge location, from 2.1 m (stripping temperature @ 120 °C) to 1.7 m (stripping temperature @ 115 °C). In the post-combustion case, the temperature bulge was located at 2.3 m from the absorber bottom [27].

4.2 Effect on the stripping temperature profiles

The novel StLT configuration modifies the conventional operating conditions in the stripper. Therefore, it had a substantial impact on the temperature profiles in the stripping section. Figure 4 summarizes the stripper temperature profiles of the partial oxy-combustion experiments set at 95% CO₂ removal efficiency.

As it can be seen from Fig. 4, the overall temperature profile in the stripper showed lower temperatures in comparison with conventional post-combustion reported from previous work [27]. In the post-combustion run, the temperatures profile showed a homogenous trend along the stripper, with values close to 120°C. Respect to partial oxy-combustion experiments, the temperature profiles decreased, particularly in the top section of the stripper. This phenomenon was mainly observed in low stripping temperature experiments. The elevated L/G associated to these experiments reduced the resident time of the rich amine in the lean-rich amine heat exchanger before the stripper inlet and therefore the temperature of the rich amine entering the stripper also decreased. In fact, the temperature of the lean amine leaving the stripper was slightly lower and it also limited the performance of the lean-rich amine heat exchanger. Lower temperatures at the stripper inlets produced further decrease along the stripper, mainly

observed in the first random packing bed of the stripper. It should be pointed out that a specific design of the stripper unit should be done for a defined stripping temperature in order to improve the performance of this unit.



* Data reported from Vega et. al. [27]

Figure 4. Stripper temperature profiles from partial oxy-combustion experiments under several StLT operating conditions (experiments 1, 3, 6, 9 from Table 2).

4.3 Effect on the CO₂ cyclic capacity

Regarding the CO₂ cyclic capacity, the CO₂ loading of the rich amine ranged between [0.26 - 0.37] mole CO₂ per mole solvent in 60%v/v CO₂ experiments using MEA 30wt%, with the stripper temperature set at 120 °C, as it was obtained from previous works [27]. Values over 0.6 mole CO₂ per mole solvent were reached during the partial oxy-combustion characterization tests running at 60%v/v CO₂ for MEA 30wt% at equilibrium using the semi-batch rig apparatus [28]. The CO₂ loading of the rich amine respect to StLT operations can fit within the gap existing between the lab-scale plant experiments and the equilibrium CO₂ loading, defined as [0.37 - 0.60].

Figure 5 shows the operational range regarding cyclic capacity at various stripping temperatures. As can be seen in Fig. 5, lower stripping temperatures shifted the absorption-desorption cyclic

capacity towards higher CO₂ loadings of both lean and rich amine. In these experiments, the lean amine loading was increased from 0.14 - 0.15 mole CO₂ per mole solvent at 120°C to 0.31 mole CO₂ per mole solvent at 115°C. The stripping temperature variation also affected the rich amine loading, which reached CO₂ loadings close to 0.5 mole CO₂ per mole solvent. Although a significant increase on the CO₂ loading of the rich amine was achieved at lower stripping temperature, these values were still far from the equilibrium (around 0.6 mole CO₂ per mole solvent).

In general, the cyclic capacity decreased and therefore higher L/G ratios were required to achieve the desired CO₂ removal efficiency. Based on this assumption, the CO₂ loading curves for both lean and rich amine shifted towards higher L/G ratios, as it is observed in Fig. 5. As was stated before, an optimized design of the absorber for a specific stripping temperature may reduce the solvent flow-rate requirements at a previously defined CO₂ removal efficiency.

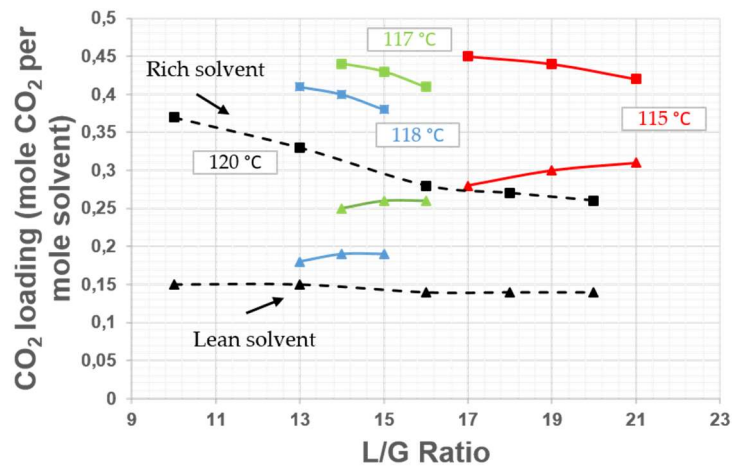


Figure 5. CO₂ loading evolution of lean and rich amine as function of L/G ratio at several StLT operating conditions. Squared dots represent rich amine loadings whereas triangle dots represent lean amine loadings. Dashed black line experiments were reported from previous work [27].

4.4 Effect on the reboiler duty

The energy requirement of the stripping process were plotted as a function of the L/G

ratio for each StLT experiment in Fig. 6.

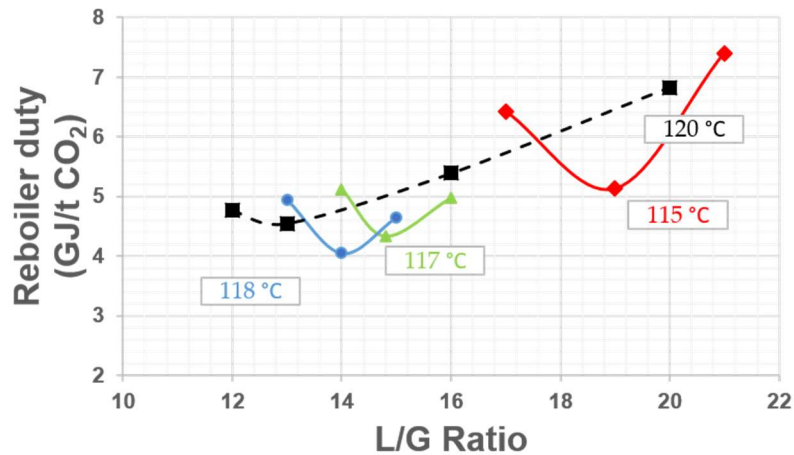


Figure 6. Specific energy consumption in the stripper versus L/G ratio for partial oxy-combustion experiments run at several StLT operating conditions. Dashed black line experiments represents partial oxy-combustion tests at 60%v/v CO₂ and 120 °C from previous work [27].

The stripping temperatures set at 117°C and 118°C provided lower specific energy consumptions than experiments run at 120°C. In particular, the experiments with 118°C set as the stripping temperature achieved a minimal specific energy consumption of 4.05 GJ/t CO₂, which accomplished an 11% reduction in comparison with the specific energy related to 120°C experiment – 4.55 GJ/t CO₂ [27] -. With the temperature set at 117°C, a reduction of 4.5% was achieved, but the specific energy consumption was 7% higher than that achieved at 118°C (Table 3). The experiment carried out at 115°C provided 5.13 GJ/t CO₂. In this case, the trade-off between the gross energy consumed in the stripper during the CO₂ desorption process and the sensible heat associated to a higher solvent flow-rate established an increase of the overall energy requirement of the capture process. The excessive L/G ratio needed for achieving 95% CO₂ removal penalized the reduction of the reboiler duty due to the extremely low operating temperature of the stripper.

Globally, a StLT operation set at 118°C as stripping temperature shifted the operating cyclic capacity to [0.19, 0.40] mole CO₂ per mole solvent (Table 3). The CO₂ capture performance under those conditions reduced the specific energy consumption of the post-combustion case by 64% [27]. A best-defined design of the absorber unit focused on high CO₂ concentrated operations may enhance the rich amine loading and reduce the required L/G ratio. Such enhancement may lead to a further improvement of the overall CO₂ capture process and, thus, a substantial reduction of the specific energy requirements related to the solvent regeneration process might be achieved.

Table 3. CO₂ capture efficiencies and specific energy consumption for solvent regeneration reported from the experimental test campaign carried out at the CO₂ bench-scale pilot plant.

Run	Experiment description	CO ₂ loading Lean amine (mole CO ₂ /mole solvent)	CO ₂ loading Rich amine (mole CO ₂ /mole solvent)	L/G ratio	CO ₂ Capture Removal Efficiency (%)	Reboiler Duty (GJ/t CO ₂)	Ref.
0	Post	0.12	0.35	3	94.0	11.10	[27]
1	Partial oxy baseline	0.15	0.38	13.3	95.9	4.55	[27]
2	Partial oxy A	0.18	0.41	13	91.7	4.95	This work
3	Partial oxy A	0.19	0.40	14	96.2	4.05	This work
4	Partial oxy A	0.19	0.38	15	100.0	4.65	This work
5	Partial oxy B	0.25	0.44	14	92.3	5.12	This work
6	Partial oxy B	0.26	0.43	15	96.1	4.34	This work
7	Partial oxy B	0.26	0.41	16	100.0	4.97	This work
8	Partial oxy C	0.28	0.45	17	88.1	6.43	This work
9	Partial oxy C	0.30	0.44	18	95.9	5.13	This work
10	Partial oxy C	0.31	0.42	19	100	7.4	This work
-	Partial oxy @120 °C – A	0.26	0.41	10	93.3	4.77	[27]
-	Partial oxy @120 °C – B	0.28	0.45	13	95.5	4.65	[27]
-	Partial oxy @120 °C – C	0.30	0.44	16	100	5.39	[27]
-	Partial oxy @120 °C – D	0.31	0.42	20	100	6.83	[27]

The specific energy consumptions determined during the partial oxy-combustion test campaign were with previous work using MEA 30wt%. In particular, Tobiesen et al. [41] obtained a values of the reboiler duty ranging between 3.7 – 10.2 GJ per tonne CO₂ and works from Dugas [42] reported values found in the operating window defined by 5.1 – 14.2 GJ per tonne CO₂. These works operated under similar conditions in terms of stripping pressure – 2 bara and 1.6 bara – and CO₂ loading of the lean amine – 0.22 – 0.41 mole CO₂ per mole solvent and 0.14 – 0.37 mole CO₂ per mole solvent, respectively.

Although the displacement towards higher L/G ratios increases the sensible heat term in Eq. 1 and Eq. 2, the StLT operations produced an increase on the CO₂ loading profile along the stripper and therefore the CO₂ partial pressure increased in comparison with conventional stripping operations at 120 °C (Fig. 7). According to Rabensteiner et al. [37], the solvent regeneration process should benefit from the high CO₂ partial pressure at the stripper top. In these cases, low amounts of stripping steam are required as highly loaded solvents are regenerated and the heat of vaporization (Eq. 5) associated to the vapor stripping stream in the desorber drops significantly. The higher CO₂ partial pressures due to StLT operations reduced the vapor-CO₂ partial pressure ratio in Eq. 5, leading to further reductions in this term in Eq. 1 and Eq. 2.

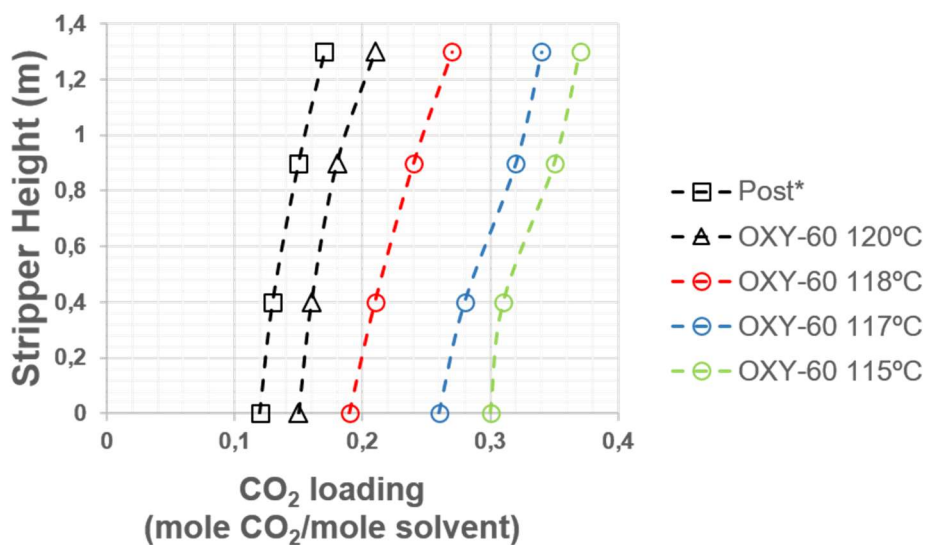


Figure 7. CO₂ loading profile in the stripper. Dashed black line experiments represents partial oxy-combustion tests at 60%v/v CO₂ and 120 °C from previous work [27].

The StTL configuration had impact on the share of the energy terms which contribute to the specific energy consumption defined in Eq 1. and Eq. 2. Figure 8 represents the contributions of each energy terms namely, sensible heat, heat of desorption and heat of vaporization. The decrease of the stripping temperature enhanced the sensible heat required for solvent regeneration. The lower sensible heat requirements related to the use of low stripping temperature could not balance the large amount of solvent needed to balance the highly loaded lean amine. Therefore, the sensible heat increased as the stripping temperature was lower. Opposite effect were observed regarding the heat of vaporization. In this sense, the share of this term changed from 38% at 120 °C to 33% at 115 °C, being the main contributor to the overall specific energy decrease observed in experiments run at 118 °C and 117 °C. Finally, although the variations on the contribution related to the heat of desorption were similar for all the cases, the heat of desorption were decreased at highly loaded lean amine experiments in global terms.

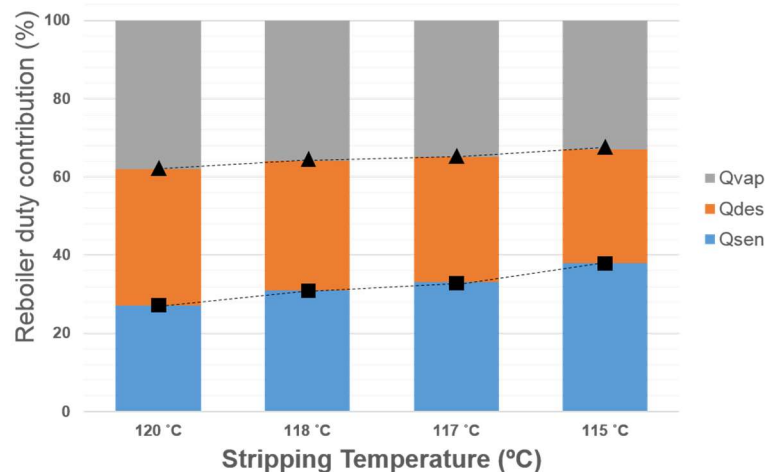


Figure 8. Contribution of the energy terms into the specific energy consumption related to solvent regeneration stage. Square dots represent sensible heat share and triangle dots represent heat of vaporization share.

5. Conclusions

A novel concept for the control philosophy for a CO₂ capture plant based on partial oxy-combustion is proposed in this work. The Shift to Low Temperature approach is based on the idea of shifting the cyclic operating capacity of the solvents towards high CO₂ loadings that can lead to a further reduction in the energy requirements associated with the CO₂ desorption process. The shift in the cyclic operating capacity was achieved by means of variations in the operating conditions of the stripper, particularly the operating temperature of this unit. The energy requirements were further improved when the Shift to Low Temperature configuration approach was applied in combination with 60%v/v CO₂ in the flue gas. The energy penalty was reduced by 11%, being reduced to 4.05 GJ/t CO₂ using MEA 30wt% as solvent. In this respect, results from previous work using MEA 30wt% and 120 °C in the stripper, the energy penalty for the CO₂ desorption process was set at 4.55 GJ/t CO₂.

Based on the results extracted from the test campaign executed in this work, the Shift to Low Temperature configuration should significantly improve the overall CO₂ capture performance of highly CO₂ concentrated flue gas derived from partial oxy-combustion applications. The use of higher CO₂ concentrated gas streams enhanced the CO₂ separation process using amine-based chemical absorption compared with typical CO₂ capture processes applied to flue gas derived from conventional air-fired fossil-fuel power plants. The application of the Shift to Low Temperature approach combined with elevated CO₂ concentrations in the flue gas can lead to further reductions in the solvent regeneration process, mainly based on the CO₂ cyclic capacity of the solvent. Improvements on the specific energy consumption in the stripping section were found in this work using a low CO₂ cyclic capacity solvent as MEA 30wt%. The potentialities of the Shift to Low Temperature configuration should be further strengthened in case large CO₂ cyclic capacity solvents would be used because the operating window in terms of lean-rich amine CO₂ loading would be wider.

Conflict of interest

Authors confirmed that there are no conflicts to declare.

Acknowledgements

This work was carried out with the financial support of the Ministry of Economy and Competitiveness of the Spanish Government (OXYSOLVENT Pro.; ref: CTM-2014-58573-R) co-financed by the European Development Research Fund (EDRF) From European Union.

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