

Experimental and numerical assessment of the CO₂ absorption process in the Sotacarbo pilot platform

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ABSTRACT

CO₂ separation technologies are of prime importance for the prevention of global warming and worldwide climate change. The separation of CO₂ can be achieved by a variety of techniques, including membrane separation, low temperature distillation, adsorption and absorption. The chemical absorption of CO₂ into monoethanolamine (MEA) solutions is one of the most favoured method for the capture of carbon dioxide in fossil fuel power plants. The reactions between amines and CO₂ brings some advantages such as high absorption rate even with low pressure. Moreover, a benefit of chemical absorption into amine solution is that the chemical reaction can be reversed at higher temperatures and MEA recycled.

In this context, Sotacarbo is studying a CO₂ absorption process, which has been tested in a pilot platform which has been recently built up in the Sotacarbo Research Centre in Carbonia, Italy. The process takes place in an innovative bubbling reactor and the absorption experiments were performed in 5 M monoethanolamine solution at 30 °C.

This paper reports the analysis of the preliminary experimental results obtained in the CO₂ separation section. As concern the process performance, the effect of the chemical reactions has been evaluate in terms of the enhancement factor, defined as the ratio between the absorption flux when reaction occurs to that which would occur if there were no reaction. Moreover, CO₂ partial pressure and liquid bulk concentration of all the chemical species present in the solution have been calculated.

Keywords: absorption, carbon dioxide, monoethanolamine, experimental plant.

1. INTRODUCTION

The increasing attention to global warming and climate change, mainly due to the anthropic carbon dioxide emissions, is making more and more interesting all the technologies which allow a CO₂-free power generation.

The diffusion of renewables and nuclear energy sources is currently limited by a series of technical and economical problems [1]; therefore, fossil fuels currently cover about 67% of the worldwide power generation [2].

In this scenario, the development of carbon capture and storage (CCS) technologies from fossil fuels can allow a significant reduction of greenhouse gas emissions in a short and mid-term future.

Carbon dioxide can be separated downwards and upwards the combustion process, operating on flue gas (post-combustion) or syngas (pre-combustion), respectively. Moreover, are currently under development oxycombustion reactors, in which fuel is burned using pure oxygen as oxidant agent and the clean flue gas is mainly composed by steam and CO₂, which can be easily separated through condensation.

Conceptually, post-combustion and pre-combustion separation technologies are similar,

except for the operating parameters, which are strongly influenced by the combustion or gasification process; in any case, the most common technologies used to separate CO₂ from flue gas or syngas are chemical or physical absorption in liquid solvents, adsorption in solid sorbents, low temperature distillation and membranes separation [3]. In particular, the most promising current method for a low-pressure CO₂ separation is chemical adsorption through an alkanolamine solution and, in particular, through monoethanolamine (MEA) [4].

Acqueous alkanolamine solutions are frequently used for removal of acidic gases such as carbon dioxide and hydrogen sulfide from gas streams in natural gas and refinery industries [5]. Despite the advantage of this kind of solvent scrubbing, this technology presents several disadvantages, mainly due to the thermal efficiency losses in the solvent regeneration phase [3]. This involves the need of a further development of this scrubbing technologies, with the main goals to set the process (in its adsorption and regeneration phases) and to optimize the integration between capture section and whole plant.

In this field, Sotacarbo is studying several integrated gasification and syngas treatment process configurations for a CO₂-free combined production of hydrogen and electrical energy. To this goal, a pilot platform has been recently built-up in the Sotacarbo Research Centre in Carbonia (South-West Sardinia, Italy).

The “pilot unit” of the platform, based on a 35 kg/h up-draft Wellman-Galusha gasifier (operating at atmospheric pressure), is equipped with an integrated CO-shift and CO₂ absorption process, which operates carbon capture by using a 5 M monoethanolamine solution in an innovative bubbling reactor [6]. This process, due to its flexibility, allows a large series of experimental tests, currently in their preliminary phase, in order to verify the influence of the main process parameters (pressure, temperature, solvent flow and composition and so on) on the CO₂ absorption process. Moreover, the integration of this section with an on-line solvent regeneration system is currently under design.

This paper reports the main results of a preliminary experimental analysis carried out in the Sotacarbo pilot plant, with reference to CO₂ absorption process. The process performance has been compared to that reported in scientific literature in terms of enhancement factor, defined as the ratio between the absorption flux when reaction occurs to that which would occur if there were no reaction. Finally, a hint about the future development of the experimental tests has been reported.

2. THE SOTACARBO PILOT PLATFORM

The Sotacarbo pilot platform (figure 1) has been designed considering a very flexible layout, in order to allow experimental tests with different plant configurations and different operating conditions [6]. The platform layout includes two fixed-bed up-draft and air-blown Wellman-Galusha gasifiers: a 700 kg/h demonstrative gasifier and a 35 kg/h pilot gasifier. The choice of this kind of gasification process is a consequence of the particular commercial interest in the field of medium and small scale industrial applications.

2.1 PILOT PLANT

The pilot unit has been designed to develop the syngas treatment process for a combined power generation and hydrogen production. Therefore, it is equipped with a complete and flexible syngas treatment process. In particular, pilot plant includes two different syngas treatment lines: a



Figure 1. The Sotacarbo pilot platform.

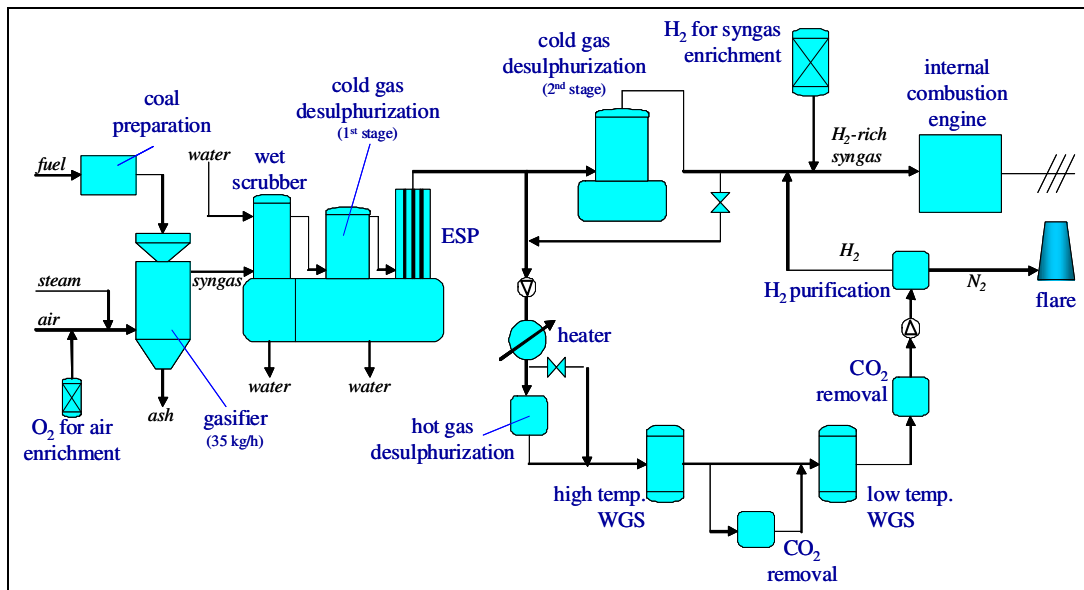


Figure 2. Pilot plant simplified scheme.

power generation line and a hydrogen production line.

As schematically shown in figure 2, raw syngas from the gasification process is sent to a skid which includes a wet scrubber (which reduces syngas temperature from about 300 °C to 50 °C and operates a primary dust and tar separation), a first cold gas desulphurization stage (which currently uses sodium hydroxide as solvent) and an electrostatic precipitator (ESP), which allows to achieve a fine particulate and tar removal.

Downstream ESP, syngas is split into two streams: the main stream, about 80% of the produced syngas, is sent to power generation line, whereas the secondary stream, that is the remaining 20%, is sent to hydrogen production line.

In particular, the power generation line is constituted by the second cold gas desulphurization stage, based on a hydrogen sulphide (H₂S) absorption process (which uses a mixture of sodium hydroxide and hypochlorite, diluted in water, as solvent), directly followed by a syngas-feed internal combustion engine.

On the other hand, in the hydrogen production line syngas is pressurized up to about 0.14 MPa, electrically heated and sent to a two-stages dry hot gas desulphurization process (which employs zinc oxide-based sorbents) followed by an integrated CO-shift and CO₂ absorption system and a hydrogen purification system, based on the PSA (pressure swing adsorption) technology.

The size of the secondary syngas treatment line, even if much smaller than the size of commercial scale plants, should give reliable experimental data for the scale-up of the future plants [7].

In order to support the experimental tests, the plant is equipped with a sampling system which allows the monitoring of the process performances, with particular reference to syngas composition. Syngas analysis has been carried out by using a micro gas chromatograph, which allows to evaluate the concentration of the main chemical compounds (CO₂, H₂, O₂, CO, CH₄, N₂, H₂S, COS, C₂H₆, C₃H₈) in every stream [8].

The pilot gasifier has been tested for about 250 hours between June 2008 and March 2009, in strict cooperation with ENEA (the Italian National Agency for Energy and Environment). During this first phase of experimental tests, a large amount of data has been collected, in order to evaluate the performance of each section and of the whole plant.

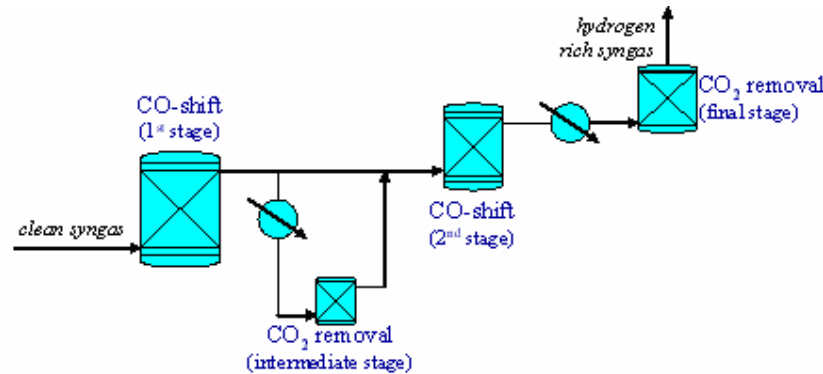


Figure 3. Integrated water-gas shift conversion and CO₂ removal system.

2.2 THE INTEGRATED CO-SHIFT AND CO₂ REMOVAL SYSTEM

As part of the hydrogen production line, an integrated CO-shift and CO₂ absorption system, shown in figure 3, has been realized in order to produce a hydrogen-rich fuel. In particular, the syngas enrichment is carried out by using a two-stage catalytic CO-shift process (operating at about 400 °C for the first stage and about 250 °C for the second stage), with an intermediate and final carbon dioxide absorption stage. A suitable system of shell and tube heat exchangers assures the optimum thermal trend in the system. This integrated configuration has been selected in order to reduce steam consumption into CO-shift process and to maximize the carbon monoxide conversion into CO₂, for a future use of the hydrogen-rich fuel in a high efficiency power generation section (based on micro gas turbines or fuel cells) [9].

Moreover, to optimize heat duty in the integrated process, only a portion of syngas from the high temperature CO-shift is sent to the intermediate CO₂ absorber, so that the CO₂-lean gas (at 30 °C and saturation conditions) and remaining gas (at about 400 °C) are mixed and sent to the low temperature CO-shift at its process temperature.

CO₂ absorption takes place in two innovative bubbling reactors (figure 4), developed by Ansaldo Ricerche S.p.A., with an aqueous solution of monoethanolamine (MEA) at an operating temperature of about 30 °C and atmospheric pressure. The two bubbling reactors, made of stainless steel (AISI 316L), are identical. They are cylinder-shaped with a torus-spherical base, with a 1 m inside diameter and a capacity of 444 dm³. The gas stream (20-30 Nm³/h), monitored by a mass flow-meter, is dispersed

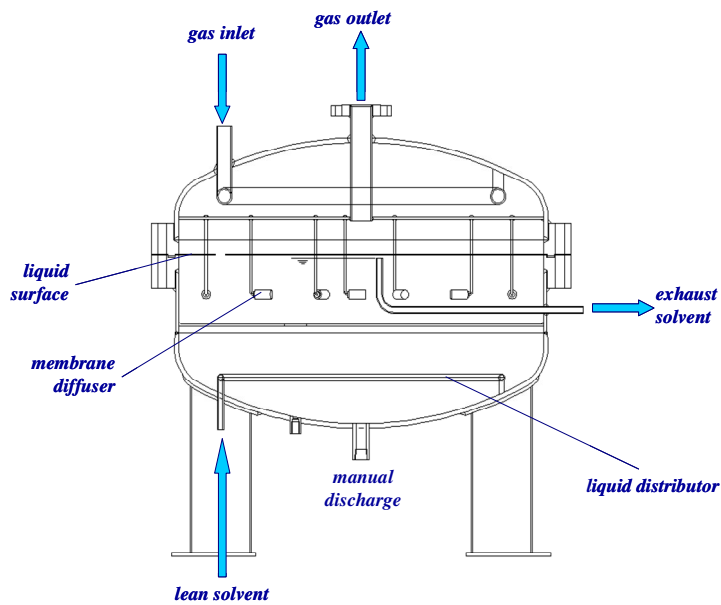


Figure 4. CO₂ absorption bubbling reactor.

uniformly in the liquid phase through 40 pipe diffusers. At the same time, scrubbing solution (272 dm³/h, during the preliminary tests), is pumped to the bottom of the reactor where it enters through a liquid distributor. An overflow pipe allows to maintain a constant liquid hold-up of 272 dm³. The bubbling gas rises through the liquid head: this brings gas and liquid into contact and CO₂ in the gas phase is absorbed. The CO₂-lean gas leaves the reactor at the top and then is fed to the downstream treatment equipments.

Periodically, the liquid samples are analyzed offline. In particular, CO₂ loading of the amine solution has been experimentally verified by titration methods, based on precipitation of BaCO₃; the methods use a mixture of BaCl₂ and standard NaOH and the excess NaOH is then titrated with HCl [10].

2.3 CHEMICAL SYSTEM OF REACTIVE ABSORPTION OF CO₂

The mechanism for the reaction of CO₂ with primary amine have been extensively studied in the literature [10-13] and can be represented by the following reactions:

Ionization of water



CO₂ hydration



Dissociation of bicarbonate



Formation of bicarbonate



Reactions of CO₂ with MEA



Carbamate to bicarbonate reversion



In reaction 5, 6 and 7, R represents CH₂-CH₂OH.

The reaction of CO₂ with water (2) is very slow while the reaction between CO₂ and hydroxyl ions (4) is fast and can enhance mass transfer even when the concentration of hydroxyl ion is low. As concern the reactions with MEA, is important to underline that reaction 6 is ionic and virtually instantaneous, whereas reaction 5 is a second order and is the rate controlling [10].

Finally, in addition to these reactions, comes the dissolution of the gaseous carbon dioxide into the liquid MEA solution:



3. RESULTS AND DISCUSSION

As reported above, a series of experimental tests on CO₂ absorption by 5 M MEA solution have been carried out in the Sotacarbo pilot plant. Globally, the plant has been tested for about 250 hours between June 2008 and March 2009. During the experimental tests, a large amount of data has been collected, in order to evaluate the performance

	Raw Syngas	CO ₂ absorber (inlet)	CO ₂ absorber (outlet)
Operating parameters			
Mass flow (kg/h)	112.89	23.06	12.26
Molar flow (Nm ³ /h)	5.74	1.21	0.96
Pressure (MPa)	1.07	1.29	1.29
Temperature (°C)	300	30	30
LHV (MJ/kg)	7.5	6.98	13.13
Specific heat (kJ/kg K)	1.55	1.65	2.36
Dry syngas composition (molar fraction)			
CO	0.2241	0.0190	0.0241
CO ₂	0.1120	0.2473	0.0470
H ₂	0.3720	0.4869	0.6165
N ₂	0.2676	0.2271	0.2875
CH ₄	0.0201	0.0170	0.0216
H ₂ S	0.0010	0.0000	0.0000
COS	0.0001	0.0000	0.0000
Ar	0.0031	0.0027	0.0034

Table 1. Steady state syngas compositions.

of each section and of the whole plant. As reported in a previous work [14], through data processing, a global mass balance of the plant has been developed and, for every section, performance and properties of the flows have been determined with good accuracy. Table 1 shows a synthesis of this evaluation with particular reference to gasification and CO₂ absorption sections. In particular the composition, expressed in terms of molar fractions, of raw syngas from the gasification section and of inlet and outlet of absorption section have been reported.

Pilot gasifier has been fed with low sulphur South African coal and air has been used as gasification agent. As can be seen in table 1, according to the design condition, only 20% of produced syngas is sent to CO₂ absorption section.

In order to evaluate the performance of the process, it is important to underline that the reactions of CO₂ with MEA enhance the rate of absorption and increase the capacity of the liquid solution to dissolve the solute, when compared with physical absorption systems. So the process performance can be determined in terms of enhancement factor, defined as the ratio of the mass transfer with chemical reactions to that without chemical reactions:

$$E = \frac{k_L}{k_L^0} \quad (9)$$

where k_L and k_L^0 are the liquid mass transfer coefficient with and without chemical reactions, respectively. The liquid mass transfer coefficient can be correlated to the overall mass transfer coefficient by the following simplified expression:

$$k_L \cong H_{CO_2} K_G \quad (10)$$

Since Henry's constant for the CO₂-MEA system (H_{CO_2}) is available in the literature as a function of both MEA concentration and temperature [15], the estimation of overall mass transfer coefficient (K_G) becomes the main issue to evaluate CO₂ absorption behavior and it can be determined by using the following equation:

$$K_G = \frac{G(y_{CO_2i} - y_{CO_2o})}{PaV_L(y_{CO_2} - y_{CO_2}^*)} \quad (11)$$

where G is the gas flow rate, P is the total pressure of the system, V_L is the volume of the liquid phase into the reactor, y_{CO_2i} and y_{CO_2o} are the CO_2 molar fraction in the gas phase at the inlet and at the outlet of the reactor, respectively, and a is the specific interfacial area. The latter depends on the value of the gas hold-up (H_g) and the bubble diameter (d_b) which were experimentally evaluated [16].

Moreover, y_{CO_2} is the mole fraction of CO_2 in the reactor, which has been calculated by the log mean average while, in order to calculate the equilibrium mole fraction of carbon dioxide ($y_{CO_2}^*$), the solubility of CO_2 in amine aqueous solution, i.e. vapor-liquid equilibrium data, must be known. To this aim, based on the proposed reaction mechanisms, a Vapor-Liquid-Equilibrium (VLE) model has been used to estimate the equilibrium CO_2 partial pressure and the liquid bulk concentration of all chemical species. The input data of the model include the initial concentration of MEA ($[MEA]_0$), the initial CO_2 loading of amine solution (α), the solubility of CO_2 into MEA solution (H_{CO_2}) and the equilibrium constants of the reactions. All the chemical reactions have been assumed to be at equilibrium, while the concentration of water has been assumed to remain constant because its concentration is much larger than concentrations of all other chemical species. The independent equilibrium constants can be expressed as:

$$K_1 = [OH^-][H^+] \quad (12)$$

$$K_3 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (13)$$

$$K_5 = \frac{[RNHCOO^-][H^+]}{[RNH_2][CO_2]} \quad (14)$$

$$K_6 = \frac{[RNH_3^+]}{[RNH_2][H^+]} \quad (15)$$

$$K_7 = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]} \quad (16)$$

In addition to these equations, the mass balance equations and the Henry's law relationship, between the equilibrium partial pressure and the free CO_2 concentration, must be considered:

MEA balance

$$[RNH_2] + [RNH_3^+] + [RNHCOO^-] = [MEA]_0 \quad (17)$$

Carbon balance

$$[CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] = \alpha[MEA]_0 \quad (18)$$

Charge balance

$$[RNH_3^+] + [H^+] = [RNHCOO^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (19)$$

Henry's law correlation

$$p_{CO_2}^* = H_{CO_2}[CO_2] \quad (20)$$

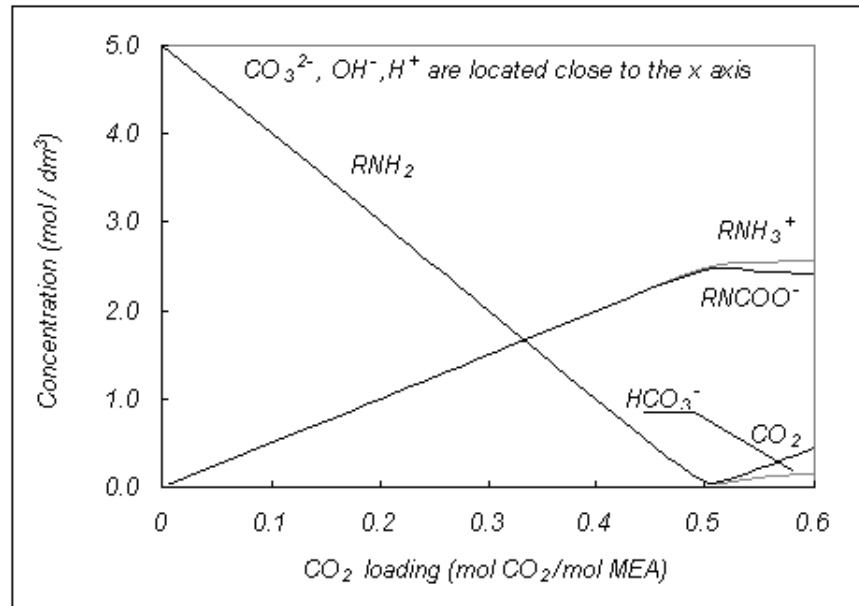


Figure 5. Liquid phase speciation and concentration in 5 M MEA solution at 30 °C.

The values of the solubility and the equilibrium constant are required in order to solve these nonlinear algebraic equations. The solubility of CO₂ in the amine solution has been calculated with the equation proposed by Danckwerts [15]. Equilibrium constants, developed by various authors and expressed as function of the temperature, have been used in this work [10, 13, 17-19]. The liquid phase concentration of all chemical species as function of the CO₂ loading has been reported in figure 5.

Finally, the value of the liquid film mass transfer coefficient k_L^0 can be evaluated by experimental tests of physical absorption of CO₂ in water, using the same operating conditions of the chemical absorption experiments.

Therefore, the value of the experimental enhancement factor, for the described system, is about 91. This result can be compared with the predictions of a simple rate model, in which the rate of absorption is predicted by the theory of diffusion with fast chemical reaction. In the fast reaction regime, if MEA concentration gradients in the liquid film can be neglected and represented by their bulk values, the pseudo-first order enhancement factor equals the Hatta number for the system. It depends on the value of amine concentration ([MEA]), the diffusivity of the reactants in liquid phase (D_{CO_2}), the kinetic constants of the reactions evolved in the global process (K_{ov}) and the mass transfer coefficient in absence of chemical reaction (k_L^0):

$$E = \frac{\sqrt{D_{CO_2} K_{ov} [MEA]}}{k_L^0} \quad (21)$$

The kinetic constant of the CO₂ reaction with MEA can be determined by the expression of Aboudheir et al. [20] and the diffusion coefficient of carbon dioxide into MEA solution has been calculated by using the correlation proposed by Sada et al. [21]. The enhancement factor predicted by the simple model is about 103. The pseudo-first order model should represent the overall enhancement accurately with loading less than 0.5 moles of CO₂ per mole of amine [11], such as obtained in the present work. However this enhancement factor accounts for the effect of chemical reactions on the CO₂ absorption rate, but it does not account for reactant depletion or product accumulation at the gas-liquid interface. So, a comprehensive

absorption-rate/kinetics model is under development for interpreting the absorption data of CO₂ into MEA solution.

4. FUTURE DEVELOPMENTS

The tests described in this paper are only a part of the first experimental campaign on the Sotacarbo pilot plant, carried out in order to verify the plant operation and the performance of every equipment in the design conditions. In particular, the tests on MEA-based CO₂ capture section allowed to verify the hypothesis considered for data processing.

A large series of experimental campaigns has been planned in order to verify the performance of every equipment in different operating conditions. In particular, as for CO₂ capture section, a series of tests will be carried out in order to evaluate the effect of the main operating parameters, such as temperature, CO₂ partial pressure, CO₂ loading, gas flow rate and solvent composition.

Temperature influences chemical and physical equilibrium of the process, together with all the chemical-physical parameters such as viscosity, density and so on [22]. Therefore, the need to evaluate the effects of a temperature variation on the absorption system suggests to carry out a series of experimental tests with different operating temperatures.

CO₂ partial pressure can be indirectly modified by varying steam injection in CO-shift process or through a direct carbon dioxide injection upwards carbon capture section. This parameter influences mass transfer and CO₂ reaction into liquid phase, but only a little variation of global removal efficiency is expected [23].

An increasing of gas flow rate (which can be controlled through the compressor which sends syngas to the hydrogen production line) involves a rise of the effective interfacial area between liquid and gas phases; therefore a rise of the whole absorption efficiency, up to a maximum value, is expected.

Obviously, MEA concentration influences the process up to a maximum value, depending to the kind of reactor [23-24]. As a matter of facts, the increasing MEA concentration involves a higher amount of active solvent available to react with carbon dioxide; moreover, this increasing involves a rise of solvent viscosity, which effects will be evaluated in the experimental tests.

A large series of studies demonstrate that it is possible to enhance the reaction rate by using proper additives mixed in the aqueous alkanolamine solution [25-26]. In particular, a significant increasing of absorption performance can be obtained by mixing MEA with piperazine [11] or AMP (2-amino-2-methyl-1-propanol) [27]. A series of experimental tests has been planned in order to verify, in the Sotacarbo pilot plant, the process performance in these operating conditions. Moreover, appears interesting the possibility to carry out a series of experimental tests with different solvent blends [28], with particular reference to an aqueous solution of MEA and MDEA (methyldiethanolamine) [29].

With a relatively simple plant modifying, it will be possible to test the CO₂ absorption system at different pressures. As a matter of fact, being the operating pressure of PSA 0.3 MPa, it is possible to compress syngas before the second CO₂ absorption reactor (see figure 2), using the same compressor for both processes.

Moreover, the design of a solvent regeneration system is currently under development. The introduction of this system will allow the possibility to test the integrated absorption and regeneration process and to reduce the operating costs of the experimental tests. This system will be optimized for the regeneration of MEA-based solvents but, due to its flexibility, it will allow to operate with different solvent solutions.

Finally, the possibility to feed the gasifier with a mixture of oxygen and carbon dioxide as oxidant agent has been investigated with preliminary tests [30]. The effects of these operating conditions on the integrated CO-shift and CO₂ absorption system will be soon investigated, in

cooperation with ENEA (the Italian National Agency for Energy and Environment).

5. CONCLUSIONS

During the first experimental campaign in the Sotacarbo pilot plant, a series of tests has been carried out in order to set the main process parameters of the integrated CO-shift and CO₂ removal system.

Globally, this system includes a double-stage water-gas shift process with an intermediate and a final CO₂ absorption reactors; this integrated system has been designed in order to reduce steam consumption in the process and to optimize CO conversion, with the goal to test a process able to produce a clean gas which could be sent to an advanced power generation system, such as micro gas turbine or fuel cell.

Carbon dioxide absorption process takes place in a bubbling reactor (designed by Ansaldo Ricerche S.p.A.) at about atmospheric pressure and at 30 °C, with a gas mass flow of about 20-30 Nm³/h. During the preliminary tests, only a setting of the main operating parameters has been carried out, with particular reference to the final CO₂ absorption stage. A maximum removal efficiency of about 85% has been obtained, with a CO₂ inlet concentration of about 25%.

The performance of the absorption process have been compared with other processes, which data are available in scientific literature, in terms of enhancement factor, defined as the ratio between the absorption flux when chemical reactions occurs to that which would occur if there were no chemical reactions. This comparison demonstrates a good accuracy of the preliminary evaluations. Moreover, a detailed simulation model of the process is currently under development, in order to evaluate the influence of the main operating parameters (such as temperature, pressure, CO₂ initial concentration, CO₂ loading, gas flow rate and solvent composition) and to define and optimize the next experimental campaigns.

Finally, a flexible solvent regeneration system, currently under design, will allow to analyze and optimize the whole process (absorption and desorption) and to reduce the operating costs (strongly influenced by the high solvent price).

NOMENCLATURE

α	CO ₂ loading of the aqueous amine solution (mol CO ₂ / mol MEA)
a	specific interfacial area (m ² /m ³)
d_b	bubble diameter (m)
D_{CO_2}	diffusion coefficient of CO ₂ into MEA solution (m ² /s)
E	enhancement factor for absorption of CO ₂
G	gas flow-rate (mol/s)
H_{CO_2}	Henry's law constant (Pa m ³ /mol)
H_g	gas hold-up (m ³ /m ³)
K_g	overall mass transfer coefficient (mol/(m ² Pa s))
K_i	equilibrium constant of reaction i
k_L	liquid phase mass transfer coefficient (m/s)
k_L°	liquid phase mass transfer coefficient without chemical reactions (m/s)
L	liquid flow-rate (dm ³ /s)
$[MEA]_0$	initial MEA concentration (mol/dm ³)
P	total pressure of the system (Pa)
$p_{CO_2}^*$	equilibrium partial pressure of CO ₂ (Pa)
V_L	volume of the liquid phase into the reactor (m ³)
ΔV	volume expansion (m ³)

y_{CO_2}	CO ₂ molar fraction in the gas phase into the reactor
y_{CO_2i}	CO ₂ molar fraction in the gas phase at the inlet of the reactor
y_{CO_2o}	CO ₂ molar fraction in the gas phase at the outlet of the reactor
$y_{CO_2}^*$	equilibrium mole fraction of CO ₂

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