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### Full Length Article

# CO<sub>2</sub> capture and amine solvent regeneration in Sotacarbo pilot plant

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#### ABSTRACT

The removing CO<sub>2</sub> from fossil fuel based power plants has got increased interest due to environmental reasons. CO<sub>2</sub> absorption by chemical solvents is an attractive and commercial applicable CO<sub>2</sub> capture technology.

In that field ENEA, together with Sotacarbo, is developing different activities on their pilot plants to test the use of gasification technologies for the combined production of hydrogen and electric power in medium and small scale commercial plants and to test CO2 absorption and regeneration technologies. This paper reports the first results achieved during preliminary experimentations carried out to assess the CO2 absorption performance with monoethanolamine. Different plant operating conditions have been tested. The absorption CO<sub>2</sub> efficiency has been evaluated and the main parameters of the regeneration process are discussed.

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#### 1. Introduction

The European Strategic Energy Technology Plan (SET-Plan), adopted by the European Union in 2008, is a first step to establish an energy technology policy for Europe. Fossil fuels will continue to be used in Europe's power generation [1] as well as in other industrial processes despite the growing deployment of renewable energy generation. Therefore, the EU 2050 target of decarbonization can only be achieved if the GHG emissions from fossil fuel use are reduced by between 93 and 99%. [1]. For this reason the EU supports Carbon Capture, Utilization and Storage (CCUS) with legislative and policy framework and through a framework program for research and innovation and other mechanisms in order to support a shift to low carbon generation technologies. In order to realize the long term decarbonization targets set by the Union, research and innovation on CCS is needed to lower the energy penalty induced by the adoption of capture technologies.

Three CO<sub>2</sub> capture processes are being intensively studied: oxy-fuel combustion, pre-combustion and post-combustion. In

Abbreviations: CCS, carbon capture storage; CEM, continuous emission monitoring; ESP, electrostatic precipitator; FOAK, first of A kind; GHG, green house gases; IGCC, integrated gasification combined cycle; LHV, lower heating value; LPG, liquefied petroleum gas; MEA, monoethanolamine; NGCC, natural gas combined cycle; PCSP, pulverized coal supercritical plant; PSA, pressure swing adsorption; R&D, research and development; R&I, research and innovation.

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the pre-combustion capture, CO<sub>2</sub> is removed before the combustion of gas fuel. E. g.: in IGCC plants coal is fed to a pressurized gasifier, with steam and oxygen, to produce a syngas, constituted mainly by a mix of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>. Downstream a carbon capture section operates with solvent, at high partial pressure of CO<sub>2</sub>, producing a decarbonized effluent with high H2 content that it's sent to gas turbine combustor. The efficiency loss due to CO2 capture for IGCC plants is estimated to be in the range of 5-11% points using the Selexol process. In the post-combustion capture, CO<sub>2</sub> is removed after the combustion of solid or gas fuels. E. g.: in PCSC plants or NGCC plants fuel is burn and downstream a carbon capture is operated on flue gases in atmospheric pressure conditions. This means to work with higher volumes and lower partial pressure of CO<sub>2</sub>. Typical efficiency penalty due to CO<sub>2</sub> capture is in the range of 10% points for PC and 8% points for NGCC [2].

Post-combustion capture can be considered the most mature process that could be implemented faster for application in existing processes, although it is also one of the most challenging approaches due to the diluted concentration of CO2 and its low pressure in the flue gas [3].

Therefore the main challenge facing the implementation of this process on large scale is high capital and operational cost [4].

Several Industrial Companies and R&D Institutions perform research activities on CO2 post combustion process. As a matter of facts different pilot scale plants are running worldwide deploying various forms of solvents dedicated to chemical absorption. R&D groups include: CSIRO, the University of Texas, the University

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#### Nomenclature

- $\alpha$  CO<sub>2</sub> amine loading
- v viscosity
- ρ density

of Regina, NTNU and University of Melbourne. Industrial Companies that provide amine technologies include: Fluor (Econamine FG PlusTM technology), MHI (KM-CDR process), Aker Clean Carbon, BASF (aMDEA technology), Cansolv [5] (Cansolv absorbent DC), Alstom (Chilled Ammonia process), Siemens (PostCap amino acid salt technology), Babcock&Wilcox (Regenerable Solvent Absorption Technology), HTC Purenergy, Toshiba, Powerspan (ECO2®) and Hitachi. The most commonly used solvents in these pilot plants are MEA, KS-1, chilled ammonia, and Cansolv solvents. The capacity of operating pilot plants ranges between 0.5 and 50 tons of CO<sub>2</sub>/day [6].

Between the chemical solvent aqueous amine are the state of the art technology for the post combustion capture and the amine solvent most frequently encountered for  $CO_2$  capture is monoethanolamine (MEA) [7].

The main reactions that take place in aqueous systems of amine (MEA, which has molecular formula HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and CO<sub>2</sub> are [8]:

$$CO_2 + HOC_2H_4NH_2 \leftrightarrow HOC_2H_4NHCOOH^- \tag{1}$$

$$CO_2 + HOC_2H_4NH_2 \leftrightarrow HOC_2H_4NH_3^+ \tag{2}$$

$$CO_2 + OH^- \leftrightarrow HCO_3^-$$
 (3)

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$
 (4)

Absorption temperature, pressure and pH value in the solvent solution highly influence these reactions [9].

The study of the performance of CO<sub>2</sub> capture processes in pilot and demonstration scale plants is an important research area. It is crucial to provide valuable insights into operating strategies (start-up, operational reliability, control and flexibility) of future full-scale plants, to obtain reliable data and to identify technical bottlenecks [10].

In that field ENEA, together with Sotacarbo, is developing different activities on their pilot plants to test CO<sub>2</sub> absorption and regeneration technologies. The plant is composed of absorption unit and a regeneration unit. The absorption/regeneration section is also inserted in a gasification plant equipped with a gas cleaning section and an internal combustion engine. Therefore in the experimental facility it is possible to carry out tests both on different types of solvents that on different gas mixtures.

This paper presents a short description of the whole experimental equipment and summarizes the first results achieved during preliminary experimentations carried out to assess the  $\rm CO_2$  absorption performance with monoethanolamine. The declared objective of experimental campaign is to test the system behavior and assessing the  $\rm CO_2$  capture pilot plant performance, to check the operability of all components, to improve the knowledge of  $\rm CO_2$  capture pilot plant operation in the different phase of start-up, run and shut down.

Because an accurate knowledge of solvent property is crucial to maintaining high system control and performance, a first solvent characterization was performed. Consequently, density, viscosity, pH, temperature, CO<sub>2</sub> loading and other parameters required to define the solvent properties have been estimate.

Furthermore also the correlation between the density and the  $CO_2$  amine loading (mole  $CO_2$  to mole amine ratio) was investigated, in fact if the temperature and concentration of amine in sorbent are constant, the density of the solution depends only on the content of dissolved  $CO_2$  [11], consequently it is possible to evaluate the  $CO_2$  loading of the solution from the density change.

#### 2. Experimental setup

The Sotacarbo pilot platform has been built up to test different plant solutions at different operating conditions; therefore, a very flexible and simple layout has been designed and constructed. Mainly pilot plant is based on an 35 kg/h up-draft [12], air-blown and fixed-bed gasification process, suitable to be fed with both coal and biomass, follow a gas cleaning section and an internal combustion engine. tar removal. In particular, the pilot plant is equipped with the overall syngas treatment process, in order to produce the hydrogen for the power generation section. The coal gasification section includes the gasifier and the wet scrubber, as well as a wet electrostatic precipitator (ESP), which allows to achieve a fine particulate and tar removal. The clean gas leaves the ESP at atmospheric pressure and, by means of a compressor which increases the pressure to about 1.4 bar, feeds the downstream syngas conversion section. According to the design conditions, downstream the compressor, the syngas is splitted into two streams: the main stream, about 80% of the produced syngas, is sent to a cold gas desulphurization process, whereas the secondary stream, that is the remaining 20% of the produced syngas, is sent to a hot gas desulphurization process, which is followed by the hydrogen production section. In particular, the cold gas desulphurization process is based on a hydrogen sulphide (H<sub>2</sub>S) absorption process (which uses MDEA as sorbent) and it is directly followed by the power generation section, represented by an internal combustion engine. The secondary syngas treatment line includes a dry hot gas desulphurization process (which employs metal oxide-based sorbents) followed by an integrated CO-shift and CO<sub>2</sub> absorption system and a hydrogen purification system, based on the PSA (Pressure Swing Adsorption that works with a fixed bed of zeolites) technology. As indicated in Fig. 1, the two CO<sub>2</sub> absorber reactors and the two (high and low temperature) WGS reactors can be used both in simple consecutive scheme or into a hybrid parallel scheme where a first CO<sub>2</sub> capture reactor is settled downstream the high temperature WGS reactor to enhance WGS reaction in the second low temperature reactor. In all cases the path is closed by the second capture reactor.

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.

The flexible configuration of the pilot syngas treatment line allows to test and characterize some gas treatment processes and materials (solvents, sorbents and catalysts) for syngas desulphurization, water–gas shift,  $\rm CO_2$  removal, hydrogen purification and so on. These specific properties of the pilot unit allow Sotacarbo to provide technical support to third Companies for testing activities on specific fuels, materials and processes .

Since 2008 more than 2000 h of experimental tests have been carried out in the flexible Sotacarbo pilot platform, allowed to optimize gasification process and syngas treatment sections in

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