Economic evaluations of an innovative biogas upgrading method with CO$_2$ storage

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ABSTRACT

The paper reports the preliminary design and the economic evaluation of an innovative carbon dioxide removal process from biogas, characterized by the capture and storage of the removed carbon dioxide. The studied process uses industrial residues for carbon dioxide capture and storage, through an accelerated carbonation process. The considered industrial residues are APC (air pollution control) residues from waste-to-energy plants, which are characterized by a high content of alkaline earth metals, calcium in particular, in the form of hydroxides, oxides or silicates. The carbon dioxide is removed from the biogas by alkali solution absorption. The spent solution, containing carbonate and bicarbonate ions is regenerated through reaction with calcium contained in the APC residues, forming calcium carbonate (APC carbonation) and reproducing – at least in part – the original alkali compound. A technical feasibility assessment of the method was carried out, based on pilot plant operation results, highlighting some constraints on the possibility of operating at very large scale, due to the high amount of required residues. Then a preliminary economic assessment of the method was carried out, with the aim of estimating the specific cost of treatment on appropriate industrial scale and comparing it with the costs of commercial methods.

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1. Introduction

Biogas is produced during anaerobic digestion of organic substrates, such as manure, sewage sludge, the organic fractions of household and industry waste and energy crops. Biogas is produced in large scale industrial digesters and it is also produced during anaerobic degradation in landfills and is then referred to as landfill gas. The production in the European Union (EU 15) was estimated to be around 10,547 Mtoe in 2010 (10,943 Mtoe in EU 27 in 2010), generated by landfills (27%), by sewage sludge (9%) and by other substrates (64%) [1]. The biogas production in the European Union has steadily increased over the last years [2].

Biogas produced in AD (anaerobic digestion) plants or landfill sites is primarily composed of CH$_4$ (methane) and CO$_2$ (carbon dioxide) with smaller amounts of H$_2$S (hydrogen sulphide), NH$_3$ (ammonia) and N$_2$ (nitrogen). Trace amounts of H$_2$ (hydrogen), VOCs (volatile organic compounds) and O$_2$ (oxygen) may be also present in biogas and landfill gas [3]. Usually, the gas is saturated with water vapor and may contain dust particles. Additionally,

organic silicon compounds (e.g.: siloxanes) are usually present in particular with reference to landfill gas, however their presence was highlighted also in AD biogas [4]. The heating value of biogas is determined mainly by the methane content of the gas.

Biogas can be used for heat and steam production, electricity production and/or co-generation, vehicles fueling, chemicals production and injection into the natural gas grid. The most common way of use, at present, is electricity production by using reciprocating engines [2]. However, using biogas as vehicle fuel or injecting it into the natural gas grid is applications that are gaining interest at international level [5,6]. In both the last cases, an appropriate upgrading of the biogas – i.e. removal of CO$_2$ and trace contaminants – is required. The output gas from the upgrading process is generally called biomethane and it is characterized by an increased content of methane with respect to the entering biogas.

At present, international technical standards for biomethane injection into the natural gas grid are not available, but some countries have developed their own national standards and procedures, such Sweden, Switzerland, Germany and France [6]. The standards have been set to avoid contamination of the natural gas grid or at end use. In general, in the standards requirements on Wobbe index values and limits on the concentration of certain components such as sulfur, oxygen, dust and the water dew point,

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as well as a minimum methane volumetric concentration of 96% are defined. These demands are in most cases achievable applying existing upgrading processes.

There are several different commercial methods for reducing the carbon dioxide content of biogas [6]. The most common are HPWS (high pressure water scrubbing) [7,8], amine scrubbing [9], PSA (pressure swing adsorption) and separation membranes [10–13]. Other technologies are, for example, cryogenic upgrading and molecular sieves [14–16].

The commercial technologies available for biogas upgrading have the common feature of removing CO_2 from biogas without focusing on the fate of the separated CO_2, which is usually re-emitted into the atmosphere during the system regeneration phase. It should be anyhow pointed out that these CO_2 emissions are of biogenic origin and should hence not be accounted for as an effective contribution to greenhouse gas emissions.
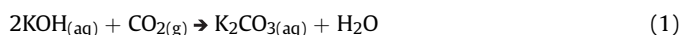
As a matter of fact, the innovative aspect of the upgrading process evaluated in this work, and previously developed and investigated in the framework of the European Life+ project UPGAS-LOWCO2 (UPgrading of landfillGAS for LOWering CO_2 emissions), is to definitely store the CO_2 removed from biogas in a solid form [17]. The subtraction of carbon dioxide of biogenic origin from the atmosphere can contribute as a negative emission (sink) to the overall greenhouse gases balance. In addition, the innovative upgrading process may allow to achieve also other specific environmental benefits that will be highlighted in the following paragraphs.

The aim of this work is to carry out a technical feasibility assessment of the innovative upgrading process, on the basis of pilot plant operation results, accompanied by simplified design and economic assessment.
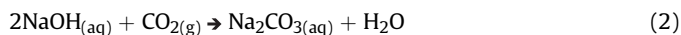
2. Description of the process

The method studied in this work − named AwR (Alkali absorption with Regeneration) − is based on CO_2 chemical absorption by means of an alkali aqueous solution followed by regeneration of the spent solution using APC (air pollution control) residues.
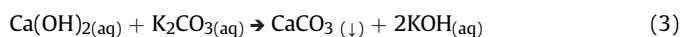
CO_2 is first physically absorbed in the liquid solution and here it reacts with the alkaline compound producing CO_3^{2-} (carbonate) and HCO_3^- ions (bicarbonate) (chemical absorption) [18–20]. The alkaline reactants that can be used in the absorption process are KOH (potassium hydroxide) or NaOH (sodium hydroxide). The reactions that take place during the absorption step are the following:
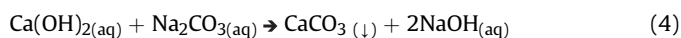
$$2KOH_{(aq)} + CO_{2(g)} \rightarrow K_2CO_{3(aq)} + H_2O \qquad (1)$$

or

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O \qquad (2)$$

The spent solution − i.e. the solution containing the carbonate/bicarbonate ions − can be chemically regenerated by contacting it with $Ca(OH)_2$ (calcium hydroxide) in solid form. In this step, poorly soluble $CaCO_3$ (calcium carbonate) precipitation takes place (carbonation reaction), thus the CO_2 separated from the biogas can be permanently stored in a chemically inert and thermodynamically stable form, whereas KOH or NaOH is recovered for the first step of the upgrading process. The basic reactions that take place during the regeneration phase are the following:

$$Ca(OH)_{2(aq)} + K_2CO_{3(aq)} \rightarrow CaCO_{3\,(\downarrow)} + 2KOH_{(aq)} \qquad (3)$$

or

$$Ca(OH)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3\,(\downarrow)} + 2NaOH_{(aq)} \qquad (4)$$

Since the use of pure calcium hydroxide for such a process would not make sense from a carbon dioxide mitigation perspective, as it is manufactured by calcination of limestone releasing carbon dioxide into the atmosphere, in order to obtain a net reduction of carbon dioxide emissions, in this project industrial waste residues were chosen as alternative alkalinity sources. Several studies have in fact shown the feasibility of using different types of industrial residues, characterized by a high content of calcium hydroxide phases, such as bottom ash and APC residues from waste incineration or steel slag, to sequester CO_2. Such a capture process is known as accelerated carbonation of natural minerals or industrial residues [21–28]. In case of using some industrial residues, the accelerated carbonation allows also improving the leaching behavior of the residues [29–32].

From preliminary investigations, APC residues, which are the product of incineration flue gas treatment with calcium-based products, were selected for the regeneration process owing to their chemical, physical and mineralogical composition [33,34].

In order to define the range of the operating conditions, the regeneration step was first investigated by laboratory works [35–37].

One of the main outcomes of the preliminary analysis concerned the definition of the maximum concentrations of the alkali compounds to be used in the absorption process. In fact, for increasing initial concentrations of KOH or NaOH in the absorption solution and hence of K_2CO_3 or Na_2CO_3 in the solution resulting from the absorption treatment, the yield of the regeneration process showed to decrease owing to the combination of two negative effects: a decrease in KOH or NaOH regeneration efficiency and an increase in solution losses during the solid separation process after regeneration [36]. So it was concluded that a maximum of 4 eq/L of carbonate ions could be acceptable in the solution to be regenerated in order to allow for high regeneration yields during the second stage of the process [36].

The absorption process was first analyzed with the help of computer simulation, using Aspen Plus [38,39]. The layout of the simulation was based on three absorption columns in series, modeled using a radfrac unit. The assumed biogas volumetric composition − entering to the first column − is 50% CO_2 and 50% CH_4. It was estimated that to reach 97% CO_2 removal efficiency at the exit of the third column − which is required to obtain an acceptable upgraded biogas quality (CH_4 volumetric concentration higher than 98%) [6] − a specific ratio of 9 L of solution per each N m^3 (volume calculated at 0 °C and 101325 Pa) of processed biogas is required, using an alkali compound concentration of 3.8 mol/L, which means about 18% in mass of KOH and, alternatively, about 13% in mass of NaOH. Similarly, it was estimated that with lower alkali concentration − i.e. 2.8 mol/L which means about 14% in mass of KOH and 10% in mass of NaOH − a specific of 12 L of solution per each N m^3 of processed biogas is required, that means a layout based on four absorption columns in series.

Experimental tests on pilot absorption column fed by landfill gas (with volumetric concentration of CO_2 and CH_4 respectively 42.3% ± 0.6 and 55.5% ± 1.5) showed that using a solution to gas ratio (L/G) of about 9 L/N m^3, and NaOH concentration equal to 3.8 mol/L, corresponding to about 13% in mass, it was possible to remove about 90.6% of entering CO_2, obtaining in the exiting gas about 87.7% ± 1.6 volumetric concentration of CH_4 [40].

Concerning the regeneration step, specific laboratory experiments were preliminarily carried out to characterize the APC residues and to investigate their capability of regenerating the spent absorption solution rich in carbonate/bicarbonate ions [36]. The amount of calcium phases available for the regeneration reaction was estimated as the difference between the total Ca and the Ca as the $CaCO_3$ content of the ash, and consisted mainly of $Ca(OH)_2$ and CaClOH [36]. The quite high chloride content (around 22% in mass) of the ash, mainly as calcium hydroxychloride proved to hinder the