# Experimental study of an innovative process for landfill gas quality improvement

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**Abstract:**

Landfill gas is generated by anaerobic biodegradation of biodegradable material present in the disposed waste. Generally its composition is adequate for combustion with energy recovery in reciprocating engines, which require the methane content be higher than 39-40% by volume. If this condition is not satisfied the landfill gas is flared. If the landfill gas methane content is lower than the required value, it is possible to pre-process it by removing the inert carbon dioxide present in it and increasing the methane content.
An innovative process, based on the carbon dioxide capture by means of accelerated carbonation of alkaline residues – namely bottom ash - was proposed and studied for the above purpose. The process was investigated at laboratory scale by setting up a process for realizing the direct contact between the bottom ash and the simulated landfill gas in a fixed bed reactor. Different landfill gas compositions were simulated, considering decreasing methane contents (30-25-20% in volume) and evaluating the possibility of obtaining the required minimum methane content in the exiting gas.
An average of about 38 kg of bottom ash per $Nm^3$ of low methane content landfill gas are required to obtain the minimum methane content at the exit of the process.
For an industrial scale plant, processing 100-200 $Nm^3/h$ of poor methane content landfill gas and assuming the same bottom ash specific requirement obtained from the experimental tests, about 30000-60000 t of bottom ash are required for one year of operation.

**Keywords:**

Landfill gas, upgrading, accelerated carbonation, bottom ash, $CO_2$ capture.

# 1. Introduction

Landfill gas is generated from biodegradable waste anaerobic degradation in landfills and is roughly made by 50% in volume of methane ($CH_4$) and 50% in volume of carbon dioxide ($CO_2$). As a matter of fact, European directives about waste management and landfills (2008/98/EC and 1999/31/EC) defined a rigorous strategy in which the landfill has a residual role in the waste management systems. Only pre-treated waste and waste from which it is not possible to recover material or energy can be landfilled. In particular biodegradable waste landfilling must be strongly reduced, being this type of waste the responsible for methane emissions, contained in the escaped landfill gas to atmosphere. In this view biodegradable waste will be diverted from landfills and a reduction of landfill gas production and quality is expected for the future years. However, the biological degradation of the already landfilled waste will take several decades to complete and it will be worth to exploit the produced landfill gas for energy recovery, since this is a beneficial effect in terms of overall greenhouse gas balance and primary energy saving [1].

The most common way for recovering energy from landfill gas is combustion in internal combustion engine (ICE) for combined heat and power production. However, a minimum of about 39-40% in volume of $CH_4$ is required for proper combustion in ICE. In old landfills or in landfills where the amount of biodegradable waste is progressively reduced, the methane content might be lower and the only way to process the gas is flaring.

As matter of fact several processes are commercially available for removing the $CO_2$ from biogas and increasing the $CH_4$ content [2]. Such processes are generally applied to treat normal quality

landfill gas or biogas with the aim of producing biomethane to substitute natural gas. However, such processes are too expensive to be applied to improve the quality of low $CH_4$ content landfill gas for feeding ICE.

An alternative process, less expensive, based on the $CO_2$ capture by means of accelerated carbonation of alkaline residues was studied for the above purpose [3]. Previous studies investigated this type of process for producing biomethane [4-6], using bottom ash (BA) from waste incineration as the alkaline residues for capturing carbon dioxide, showing that the process is suitable for small scale upgrading plants, due to the high amount of BA annually required [7]. For this reason, a slightly different type of application, aimed at improving low quality landfill gas and that requires lower amount of BA, is proposed in this work.

In this type of process, a direct gas/solid contact is realized, by flowing the $CO_2$-rich gas through the BA fixed bed. $CO_2$ is quickly removed by direct carbonation of readily reactive Ca-oxide phases (e.g. $Ca(OH)_2$) contained in the BA, see Equation (1),

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O \quad (1)$$

The process was investigated at laboratory scale exploring different landfill gas compositions and evaluating the possibility of obtaining the required minimum methane content in the exiting gas.

# 2. Materials and methods

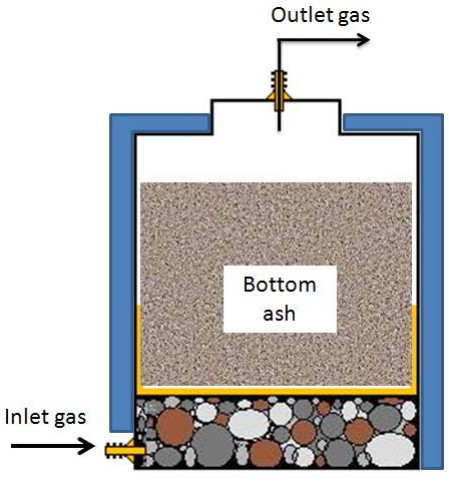
## 2.1. Experimental facility

The experimental facility mainly consists of the BA fixed bed reactor and the measuring systems.

The BA fixed bed reactor is realized by a 15 l stainless steel cylindrical container (diameter 28 cm; height 35 cm) (Fig. 1 (a)). The reactor can be opened from the top, by means of a cover, for loading and unloading the BA. The gas flows into the filter bed from the bottom to the top. The ashes rest on a gravel layer covered by a geotextile fabric, which retains the small particles and allows the passage of the gas (Fig. 1 (b)). For external thermal insulation, an insulating adhesive material, provided in rolls, was used.

Before flowing the gas into the BA reactor, nitrogen is flushed through in order to purge air/$O_2$ from the reactor. The nitrogen supply is stopped when the oxygen content in the output gas is lower than 0.2% by volume, and then the simulated landfill gas is fed to the reactor.

(a)




(b)

*Fig. 1. Fixed bed reactor: a) external view without the insulation cover, b) schematic of the internal arrangement.*

Input and output gas flow rates to/from the BA fixed bed reactor are measured by means of CKD-small size flow sensors FSM2-NVF010-S063, able to measure in the range 0-1000 ml/min with accuracy of +/- 3% f.s. and repeatability < +/- 1% f.s..

The differential pressure of the input and output gas streams to/from the reactor is measured by a differential piezoresistive pressure transducer (Delta Ohm-HD 408T) able to work in the range from -100 to +100 mbar relative to the atmospheric pressure with accuracy of +/- 0.5% f.s. at 20°C.

Atmospheric pressure is measured by means of a barometric pressure transducer (Delta Ohm HD 9908 BARO) able to work in the range from 700 to 1100 mbar, with accuracy of +/- 0.5 mbar at 20°C and resolution 1 mbar.

The inlet/outlet gas temperature and the temperature inside the reactor are measured by electronic thermometers, produced by Hanna Instruments (HI 98501 - Checktemp C), able to measure in the range da -50 a +150°C with precision of +/- 0.3 °C and resolution 0,1 °C.

The gas flow rate, pressure and temperature are measured at sampling rate of 1 khz, the average of the measured values is registered in a discontinuous manner (every 1-5 minutes). The measurement instruments are controlled by a programmable automation controller NI-USB 6008 National Instruments with 8 analog inputs (12-bit, 10 kS/s); 2 analog outputs (12 bit, 150 S/s); 12 I/O digital; 1 counter 32 bit; programming software Labview 10.0.

The volumetric gas composition is measured by means of a portable gas analyzer (PGD3-IR - ENMET Corporation) which measures $CH_4$ and $CO_2$ by infra-red absorption (± 3% absolute accuracy for >15% vol.) and $O_2$ by internal electro-chemical cells. The composition is measured manually every 1-5 minutes.

Besides, the experimental facility is equipped with a gas mixing device (Witt MG 100-3ME EEx), able to produce $CO_2/CH_4/N_2$ gas mixtures of different compositions. The device allows setting the desired volumetric concentration for 5 % steps with an accuracy of ±2 % abs.

## 2.2. Materials

The BA used in the experiments originated from a Municipal Solid Waste (MSW) incinerator located in central Italy equipped with a grid furnace and fed by pre-treated waste. The pre-treatment of the MSW consists of bag opening and waste shredding, followed by size separation by a rotating drum, magnetic metals removal and secondary shredding. The BA are discharged at the bottom of the furnace in a water channel.

$CO_2$ and $N_2$ were provided in gas cylinders by SOL with a purity of, respectively, $N_2$ Lev.5 purity 99.999 % and $CO_2$ Lev.6 purity 99.9999 % .

## 2.3. Experimental tests

Different landfill gas compositions were simulated preparing appropriate mixtures of $CO_2$ and $N_2$, using the gas mixing device. $N_2$ was used as substitute of $CH_4$ in the laboratory tests for safety reasons. The substitution of $CH_4$ with $N_2$, however, does not influence the reliability of the performed tests, since previous experimental results showed that $CH_4$ does not interact with BA, as well as $N_2$ does not [6-7]. In the following, we will address the prepared mixtures as $CO_2/CH_4$ mixtures, to use a language closer to real aims of the work, even if $N_2$ was actually used in place of $CH_4$.

The preliminary tests reported in Table 1 were performed (additional tests are ongoing at the time of writing), adopting a fixed value of the specific gas flow/solid ratio through the BA fixed bed, equal to 4 $Nm^3/(t \cdot h)$, which resulted as preferable value from previous results [7]. The appropriate amount of BA was loaded in the reactor after manual sorting of large metal particles. An additional test, at the same specific flow rate, was performed with a stream of pure $CO_2$, with the aim of comparing the ability of the BA of capturing the $CO_2$ in the best condition with respect to partial pressure.

*Table 1. Main conditions of the experimental tests.*

| Test | Gas composition | | BA [kg] | Target gas flow rate [Nl/h] |
|---|---|---|---|---|
| | $CO_2$ [% vol.] | $CH_4$ [% vol.] | | |
| BA_70_4 | 70 | 30 | 5 | 20 |
| BA_75_4 | 75 | 25 | 5 | 20 |
| BA_80_4 | 80 | 20 | 5 | 20 |
| BA_100_4 | 100 | 0 | 5 | 20 |

The amount of captured $CO_2$ was estimated from the difference between the entering and the exiting volume of gas, at a given time of the experiment, since the captured gas is only $CO_2$, by using equation 2:

$$CO_{2,captured} = \frac{(V_{in,t} - V_{out,t})}{V_m} \cdot M_{CO2} \qquad (2)$$

where $V_{in,t}$ is the volume of gas flowed in in at time t (expressed in $Nm^3$); $V_{out,t}$ is the volume of gas processed flowed out at time t (expressed in $Nm^3$); $V_m$ is the volume of a kmol of ideal gas at normal condition (equal to 22.414 $Nm^3$/kmol); $M_{CO2}$ is the $CO_2$ molar weight (equal to 44 kg/kmol).

# 3. Results

The main results of the preliminary experimental tests are reported in Figure 2-4, representing the trends of volumetric concentration of $CO_2$ and $CH_4$, in the entering and exiting gas to/from the BA fixed bed, plotted against the volume of processed gas.

The process is able to capture completely the $CO_2$ in the beginning phases, as already observed in previous experimental tests [7]. So, in the initial phase, a pure $CH_4$ stream exits from the BA fixed bed. As the process goes on with time, $CO_2$ concentration progressively starts to increase as the solid loading capacity is gradually reduced with time. After a given volume of gas has flowed through the BA fixed bed, the volumetric concentration of $CH_4$ falls below 40%, which is the limit for feeding ICE, and the process is no more useful for this purpose. If one likes to process more gas, the solids in the fixed bed need to be replaced with a new amount.

Observing the results, it is possible to read how much gas has been processed (with reference to the entering stream) before the $CH_4$ volumetric concentration in the outlet gas reaches the 40%, as reported in Table 2. In correspondence of reaching the the value of 40% for the $CH_4$ volumetric concentration in the exiting stream, also other parameters were calculated as the BA specific requirement (in kg per $Nm^3$ of entering volume), the amount of captured $CO_2$ and the specific $CO_2$ up-take per unit of mass of BA, which are reported in Table 2, as well. Values for the different experiments are rather similar among themselves, and it seems not possible to find a trend of these values. As a matter of fact, it is necessary to perform more than one experiment for each operating condition, in order to find average values and to account for the inhomogeneity of the BA. Additional experiments are ongoing at the time of writing.

However, one can preliminarily compare the average specific BA requirement – equal to 38,21 kg of BA per $Nm^3$ of entering landfill gas - obtained for this type of application with the specific requirement for complete upgrading of biogas, obtained in previous experiments [7], equal to 50,51 kg of BA per $Nm^3$ of entering biogas, ascertaining the lower request for the proposed application.

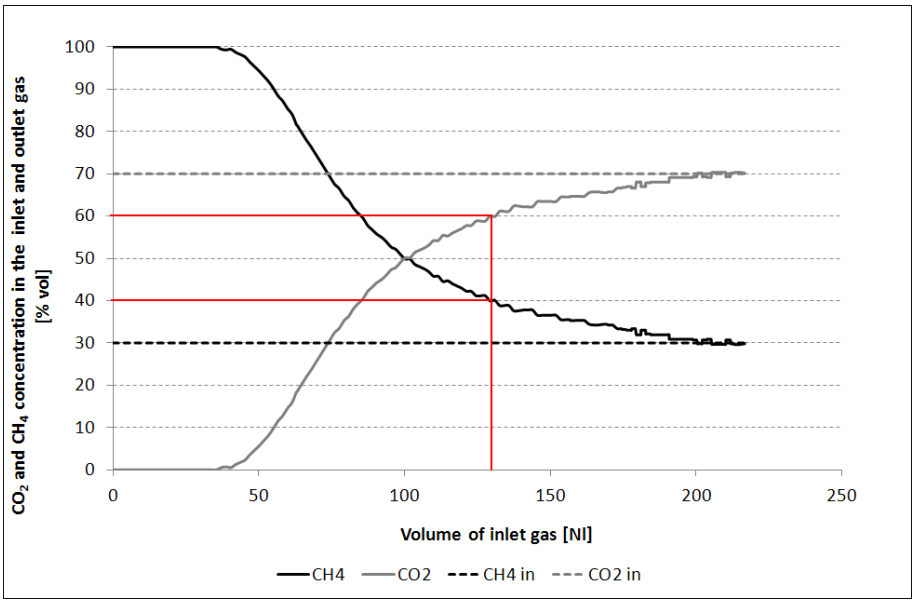



*Fig. 2. Volumetric concentrations of $CH_4$ and $CO_2$ in the entering and exiting gas to/from the BA fixed bed, vs. the volume of processed gas (test BA_70_4).*

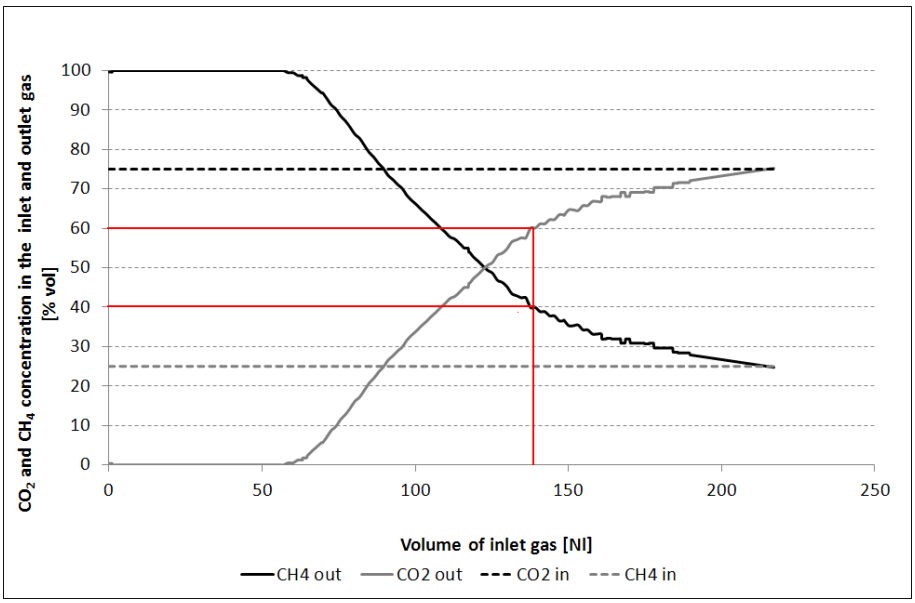



*Fig. 3. Volumetric concentrations of $CH_4$ and $CO_2$ in the entering and exiting gas to/from the BA fixed bed, vs. the volume of processed gas (test BA_75_4).*

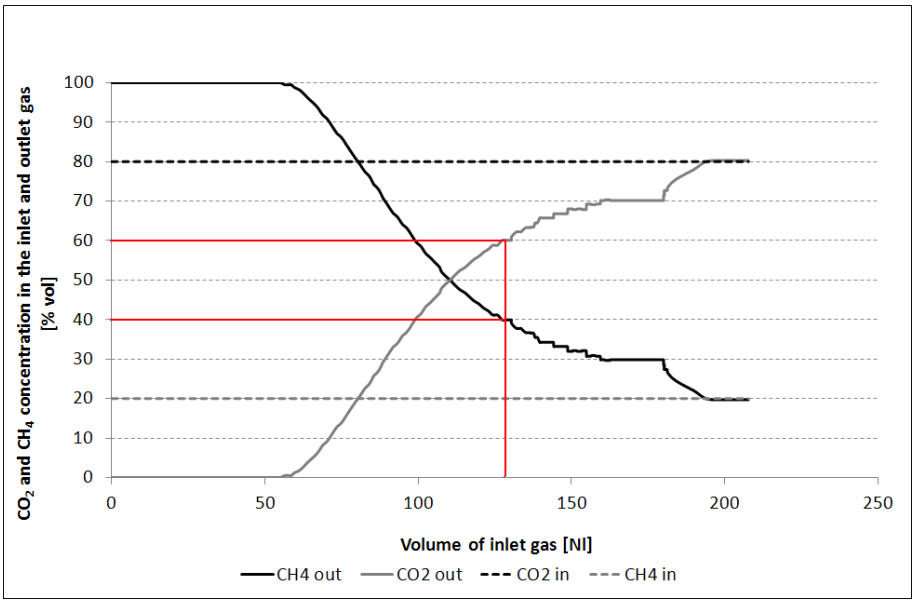



*Fig. 4. Volumetric concentrations of $CH_4$ and $CO_2$ in the entering and exiting gas to/from the BA fixed bed, vs. the volume of processed gas (test BA_80_4).*

*Table 2. Main results of the experimental tests in correspondence of reaching $CH_4$=40% in volume in the exiting stream.*

| Test | Volume of processed gas [Nl] | BA specific requirement [kg/Nm$^3$] | Captured $CO_2$ [kg] | Specific $CO_2$ up-take [kg/kg$_{BA}$] |
|---|---|---|---|---|
| BA_70_4 | 131 | 38.18 | 0.140 | 0.028 |
| BA_75_4 | 136 | 36.74 | 0.173 | 0.035 |
| BA_80_4 | 132 | 37.88 | 0.174 | 0.035 |

As additional information, the estimated captured $CO_2$ was plotted against the time for the four experiments (including the one performed with pure $CO_2$ in the entering stream) and reported in Figure 5. As expected the ability of BA to capture $CO_2$ decreases with the decreasing of $CO_2$ volumetric concentration in the entering stream (i.e. decreasing partial pressure). The trends for BA_80_4 and BA_75_4 experiments are however rather similar, with larger difference with respect to BA_70_4 experiment. The different behaviours are also due to the huge inhomogeneity of BA. The values of specific uptake at the end of the experiments (same duration equal to 780 min), reported in Table 3, are rather similar for the mixed streams, while the pure $CO_2$ test shows a higher value.

*Table 3. Values of specific up-take of $CO_2$ at the end of the experiments.*

| Test | Specific final $CO_2$ up-take [kg/kg$_{BA}$] |
|---|---|
| BA_70_4 | 0.037 |
| BA_75_4 | 0.043 |
| BA_80_4 | 0.043 |
| BA_100_4 | 0.056 |

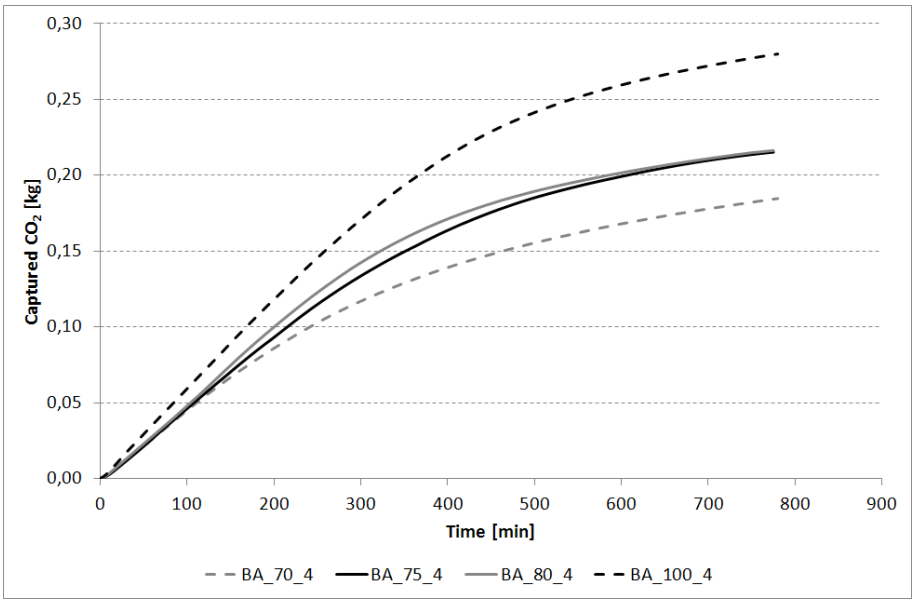



*Fig. 5. Amount of $CO_2$ captured vs. time, for the different tests.*

Finally, using the specific requirement of BA previously reported in Table 2, about 38 kg of BA required to process 1 $Nm^3$ of low $CH_4$ content biogas, it is possible to estimate the annual amount of BA necessary for feeding a plant able to process a given entering flow rate of landfill gas, considering a continuous operation for 330 days per year, according to eq. 3:

$$BA_{annual} = Q_{biogas} \cdot 300 \cdot 24 \cdot BA_{SR} \qquad (3)$$

Where $Q_{biogas}$ is the biogas flow rate (in $Nm^3/h$) and $BA_{SR}$ is the BA specific requirement, assumed equal to 38 $kg/Nm^3$.

Table 4 shows the results of this calculation, using the specific requirements resulted from the three tests and considering increasing plant size, from 100 to 1000 $Nm^3/h$ of entering biogas to be processed. One can compare the results in term of BA requirement with those obtained for a process aimed at complete upgrading of biogas, i.e. $CH_4$ content higher than 96% in volume [7]. In that case [7], for a complete upgrading plant, processing 100 $Nm^3/h$ of entering biogas, about 40000 t/y of BA were required.

One should consider that the amount of BA produced by a municipal solid waste incineration plant is about 15-25% in mass of the of the incinerated waste, according to its content of inert [8-10], thus to produce 30000-90000 t of BA per year a plant incinerating about 150000-450000 t of waste per year is required (or more than one smaller plants). The last raw of Table 4 also reports the size range of the MSW incineration plant able to produce the required amount of BA for each case. The overall amount of BA produced annually by the incineration plants located in the Tuscany region is about 58000 t, while about 1200000 t of BA are produced annually in Italy [11]. The Confederation of European Waste-to-Energy Plants (CEWEP) reports that about 16 millions of t of BA were produced in 2009 in Europe [12].

*Table 4. Annual amount of BA (in t/year) required to run a biogas treatment plant for increasing sizes.*

| Plant size [$Nm^3/h$] | 100 | 200 | 300 | 400 | 500 | 1000 |
|---|---|---|---|---|---|---|
| BA_70_4 | 30237 | 60473 | 90710 | 120947 | 151183 | 302366 |
| BA_75_4 | 29095 | 58191 | 87286 | 116381 | 145477 | 290954 |
| BA_80_4 | 30000 | 60000 | 90000 | 120000 | 150000 | 300000 |
| Average | 29777 | 59555 | 89332 | 119109 | 148887 | 297773 |
| Incineration plant size [t of MSW/year] | 119000 ÷ 199000 | 238000 ÷ 397000 | 357000 ÷ 596000 | 476000 ÷ 794000 | 596000 ÷ 993000 | 1191000 ÷ 1985000 |

# 4. Conclusions

An innovative process to increase the quality of landfill gas was studied. The aim is to process landfill gas with methane content not suitable for feeding engines and to improve such content by removing the carbon dioxide from the landfill gas. The removal process is carried out by accelerated carbonation of alkaline solid residues, i.e. bottom ash from municipal solid waste incineration. The process was studied by an experimental facility. The results confirm that the process is able to increase the methane content of the entering gas and can work until the solid capacity of capturing the $CO_2$ is gradually reduced with time. To obtain at the exit a gas with 40% in volume of methane the process requires an average amount of about 38 kg of bottom ash per $Nm^3$ of entering landfill gas, which is lower than the specific amount required for a complete upgrading of biogas. This means that for an industrial scale plants the bottom ash requirement will range from 119000 to 1985000 t per year, for biogas processing plant size in the range of 100-1000 $Nm^3/h$, respectively. In order to base the calculations on more representative results, additional experiments are ongoing at present. Further an economic analysis of the costs of the process on real scale should be assessed to ascertain the actual applicability.

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