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Research article

Characterisation and cleaning of biogas from sewage sludge for biomethane production

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ABSTRACT

This study investigates the conversion of sewage sludge from wastewater treatment plants (WWTP) into biomethane for automotive fuel or grid injection. A prototype plant was monitored in Northern Italy, based on vacuum swing adsorption (VSA) on synthetic zeolite 13×: this biogas upgrading method is similar to pressure swing adsorption (PSA) and commonly used for other kinds of biomass. Measurements of biogas inlet, biomethane outlet and off-gas were performed including CH_4, CO_2, CO, H_2, O_2, N_2, HCl, HF, NH_3, H_2S and volatile organic compounds (VOCs). Critical levels were observed in the biogas for of H_2S and HCl, whose concentrations were 1570 and 26.8 mg m^{-3}, respectively. On the other hand, the concentration of halogenated VOCs (including tetrachloroethylene and traces of perfluoroalkilated substances, PFAS) and mercaptans were relatively low. A simultaneous and reversible adsorption on 13× zeolite was achieved for H_2S and CO_2, and carbon filters played a minor role in desulfurisation. The presence of HCl is due to clarifying agents, and its removal is necessary in order to meet the required biomethane characteristics: an additional carbon-supported basic adsorbent was successfully used to remove this contaminant. This study also highlights the interference of CO_2 towards HCl if sampling is performed in compliance with the new EU standard for biomethane. High total volatile silicon (TVS) was confirmed in sewage sludge biogas, with a major contribution of siloxane D5: the suitability of this compound as an indicator of total siloxanes is discussed. Results demonstrate that volatile methyl siloxanes (VMS) do not represent a critical issue for the VSA upgrading methodology.

1. Introduction

Urbanisation and the consequent raising of municipal wastewater production is increasing the interest in sewage sludge management: anaerobic digestion is the most common approach, and the produced biogas is generally used for heating and/or electricity production (Bachmann, 2015; Batstone et al., 2015; Demirbas et al., 2016).

On the other hand, biomethane production could be a favourable alternative to biogas in situ combustion (Budzianowski and Budzianowska, 2015). Biogas upgrading to biomethane aims at obtaining a density and a calorific value comparable to natural gas. This is achieved by removing CO_2, whose typical concentration in biogas ranges from 15 to 60% v/v (Andriani et al., 2014). Several technologies are commercially available for CO_2 removal from CH_4, based on absorption, adsorption, membranes and cryogenic separations (Bauer et al., 2013; Hoyer et al., 2016).

Though biogas upgrading is a consolidated approach for most kinds of biomass, few industrial plants exist converting sewage sludge to biomethane (Strauch et al., 2013). This is mainly due to the presence of secondary components able to hamper biomethane production process. Specifically, siloxanes are abundant in sewage sludge, as they are used in cleaning products and foodstuff

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(Kymäläinen et al., 2012; Rasi et al., 2011; Tansel and Surita, 2017). Siloxane level is worthy of technical concerns for subsequent damages to combustion engines. Indeed, biomethane combustion in the presence of organosilicon compounds leads to the formation of amorphous silica particles, able to abrade the inner steel of engines and gas turbines (Álvarez-Flórez and Egusquiza, 2015). Furthermore, siloxanes directly hamper the energy properties of biomethane during its combustion, thanks to their radical scavenger properties (Dewil et al., 2006). Table 1 reports abbreviation and properties of siloxanes considered in this study.

Aim of this research is to improve the current knowledge on the feasibility of biomethane production from sewage sludge. For this purpose, a biogas upgrading unit was monitored during its operations in a sewage sludge treatment plant. The activities described in this study are part of a larger research programme of the Water Agency Gruppo CAP, aimed at identifying the optimal approach to a sustainable management of sewage sludge. In this preliminary step, the considered methodology for CO_2/CH_4 separation is vacuum swing adsorption (VSA): CO_2 is adsorbed on a suitable solid material, which is then regenerated by reducing the pressure; the use of several adsorption columns allows a continuous operating cycle (Andriani et al., 2014). This approach was chosen in light of its stronger resistance to H_2S and siloxanes (Finocchio et al., 2009; Pagliai and Di Felice, 2012).

This study reports the composition of biogas, biomethane and off-gas, including a focus on trace components such as siloxanes. The fate of undesired components at the different stages of biogas cleaning and upgrading modules is then discussed.

2. Material and methods

2.1. Description of the plant

Sewage sludge was produced in a wastewater treatment plant located in Bresso, Northern Italy. The plant includes activated sludge tanks and anaerobic reactors. The average flow rate of inlet wastewater is 54464 m^3 per day, resulting in a sludge production of 482 m^3 per day. Sludge (28 kg of total solid per m^3, with volatile solids accounting for 64% of total solids) is digested with a hydraulic retention time of 25 days, at 35 °C. Biomethane potential is 220 $mL_{CH4}\ g^{-1}{}_{VS}$. Biogas production rate is continuously measured in the plant by means of volumetric flow meters; the average flow rate of the plant is 80 $m^3\ h^{-1}$.

A fraction of biogas (10 $m^3\ h^{-1}$) was sent to a prototype for biogas upgrading to biomethane. The prototype was installed by Ecospray Technologies (15050 Alzano Scrivia, Italy) with the layout described in Fig. 1: a cleaning module for the removal of minor components is followed by an upgrading module for CO_2/CH_4 separation.

The cleaning module includes a wet scrubber for the removal of acidic components, designed without pumps nor moving parts, composed by an automatic refill of tap water and an automatic drain of surplus; it operates by means of special sprayers with calibrated holes to maximize the contact surface between biogas and liquid, ensuring a constant pressure drop of 25 mbar (2.5 10^3 Pa); a single-stage side channel blower; a pair of adsorption regenerative dryers (dehumidifier) able to constantly guarantee a dew temperature lower than 0 °C, thus allowing optimal operation of the main VSA reactors; a carbon filter for the removal of minor components. The carbon filter is filled with 30 kg of granular activated carbon (CN5-20 type, Norit Company, the Netherland) with a grain size range of 3–4 mm. The carbon filter has a cylindrical geometry (30 cm diameter, 150 cm height) and the biogas was cleaned with a linear speed of 0.04 $m\ s^{-1}$ (retention time around 15–20 s). The upgrading module is based on vacuum swing adsorption (VSA). The VSA is composed by 3 steel columns filled with 13× synthetic zeolite (Alonso-Vicario et al., 2010), operating at atmospheric pressure with a Skarstrom cycle (Andriani et al., 2014; Arya et al., 2015) to guarantee a constant outlet flow rate of produced biomethane around 7 $m^3\ h^{-1}$. Regeneration takes place by applying a high vacuum phase to release the adsorbed molecules out completely from the molecular sieves. The gaseous byproduct of the VSA unit is called off-gas and mainly contains CO_2; the off-gas flow rate is around 3 $m^3\ h^{-1}$. A proprietary developed in-house software controls pressures and the output composition in order to optimize the cycle times, enhancing the adsorption and desorption phases. After the VSA unit, a finisher unit was added, consisting of a filter containing 20 kg of alkaline-impregnated activated carbon (ROZ type, Norit Company, the Netherlands). The finisher unit has the same geometry of the first carbon filter (30 cm diameter, 150 cm height), but due to the lower flow rate of biomethane, linear speed is 0.03 $m\ s^{-1}$. All the pilot plant components (vessels and piping) are in stainless steel.

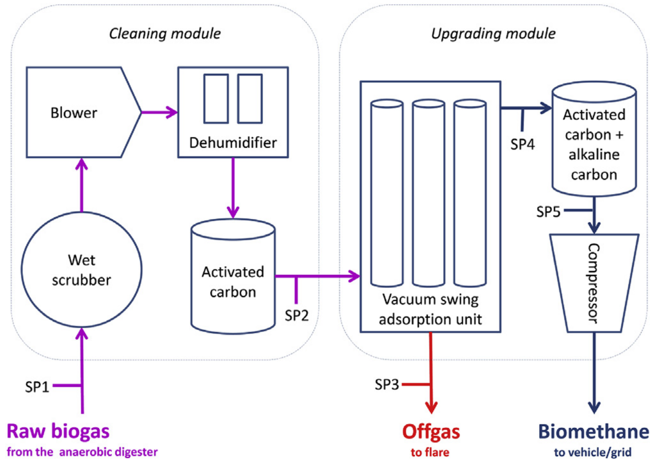

Fig. 1. Layout of the biogas cleaning and upgrading modules, including sampling points indicated with the acronym "SP".

Table 1
Abbreviation and properties of siloxanes considered in this study.

Name	Abbreviation	Molecular formula	Molecular weight (Da)	Boiling point (°C) (De Arespacochaga et al., 2015)
Hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	162.42	107
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	222.46	135
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	236.53	153
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	296.64	176
Decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	310.69	194
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	370.80	211
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_4Si_5$	384.84	232
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	444.93	245