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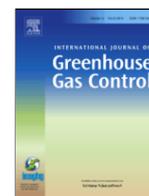


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## ABSTRACT

In biogas upgrading to biomethane, the release of CO<sub>2</sub> off-gas into the atmosphere is generally regarded as a carbon-neutral emission, but a significant loss of CH<sub>4</sub> can occur in this step: considering the global warming potential of this latter compound, methane slip can worsen or even nullify the CO<sub>2</sub> savings associated to biomethane. This study investigates a novel approach for biogas upgrading to biomethane, aimed at reducing the methane loss. A plant based on hot potassium carbonate was fed with 150–200 Nm<sup>3</sup> h<sup>-1</sup> of biogas from municipal waste. CO<sub>2</sub> is removed in a K<sub>2</sub>CO<sub>3</sub> absorption column, with negligible CH<sub>4</sub> absorption. An assessment of biomethane quality was performed to check its compliance with recent National and European standard specifications. Results show that a methane slip below 0.1% can be achieved with this technology, thus significantly reducing the greenhouse gas emissions associated to biomethane industry. This leads to a lower capital expenditure because no off-gas post-treatment is required. Heat and electricity consumption were monitored, and operational expense resulted to be lower than membrane separation in the specific case study, by applying life cycle cost (LCC) methodology.

## 1. Introduction

Biomass has gained a key role in climate change mitigation, in light of its large energetic potential. Several strategies are available for converting biomass to energy, including direct combustion, pyrolysis and gasification, bioethanol and biodiesel production and anaerobic digestion. In the last decade, biogas production through anaerobic digestion has become a consolidated approach for the energetic exploitation of several kinds of biomass, including agricultural and zootechnical by-products, sewage sludge, food waste and energy crops. Biogas is a gas mixture whose main components are CH<sub>4</sub> and CO<sub>2</sub> (85–40% and 15–60%, respectively) (Andriani et al., 2014).

Biogas is generally used for producing heat and/or electricity (Batstone et al., 2015; Demirbas et al., 2016; Bachmann, 2015). On the other hand, biogas conversion into biomethane is being regarded as an interesting application. Biogas upgrading to biomethane aims at obtaining a density and a calorific value comparable to natural gas, by removing CO<sub>2</sub> (Andriani et al., 2014; Munoz et al., 2015; Wesley Awe et al., 2017). The development of biomethane technology allows to in-

crease the share of biomethane end-users: indeed, biomethane can be injected into natural gas grids (Semple et al., 2014; Bekkering et al., 2015) and can be used as vehicle fuel (Yang et al., 2014; Patterson et al., 2011). Biomethane use as gasoil substitute can significantly reduce the contribution of vehicular traffic to urban air quality, due to its lower emission factors for nitrogen oxides, particulate matter and polycyclic aromatic hydrocarbons (EEA, 2016).

The CO<sub>2</sub>/CH<sub>4</sub> separation can be achieved through several approaches, including absorption, adsorption (pressure swing adsorption and vacuum swing adsorption, PSA/VSA), membranes and cryogenic separations (Bauer et al., 2013; Hoyer et al., 2016). Regardless of which separation technique is used, biogas upgrading consists in the production of two gas streams: biomethane and off-gas. While biomethane mostly consists in CH<sub>4</sub> and is used as a fuel, the off-gas is mainly composed of CO<sub>2</sub> and is generally released into the atmosphere. This emission is regarded as “carbon-neutral”, since it corresponds to CO<sub>2</sub> absorbed in previous decades during biomass production. Furthermore, the amount of CO<sub>2</sub> released as off-gas would be similarly emitted in the atmosphere during conventional biogas burning. Nevertheless, high purity off-gas streams might be used in industrial and food appli-

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cations, as well as in carbon capture and storage processes including microalgae growth (Colling Klein et al., 2017).

The choice of the optimum upgrading technology for a specific anaerobic digestion plant depends on a number of factors: in rough approximation, the three main parameters are biomethane purity, energy consumption and methane slip. Biomethane purity is generally defined as the volumetric concentration of CH<sub>4</sub> in biomethane outlet: it affects several parameters which must comply with regulatory requirements, namely density, heating value, methane number, CO<sub>2</sub> concentration etc., depending on the specific Country. Energy consumption (kWh m<sup>-3</sup>) is defined as the energy used, in terms of heat and electricity, for a given volume of processed biogas or produced biomethane. This parameter strongly affects the total operational cost of the plant and is also related to the global balance of fossil fuel saving.

Methane slip, also known as methane loss, is defined by Eq. 1, where Q<sub>i</sub> and Q<sub>f</sub> are inlet and outlet methane mass flow rate, respectively.

$$\text{Methane slip \%} = 100 \frac{Q_i - Q_f}{Q_i} \quad (1)$$

This latter parameter is a fundamental issue on both an economic and an environmental level. Methane slip are obviously associated to a waste of a fraction of the available biofuel, resulting in a reduced revenue from the unexploited renewable energy. Along this trivial consideration, CH<sub>4</sub> concentration in off-gas can dramatically affect the environmental sustainability of a biogas upgrading plant, since the global warming potential of CH<sub>4</sub> is 28 times higher than that of CO<sub>2</sub> (IPCC, 2013; Paolini et al., 2018a). As a consequence, the release in the atmosphere of low quality off-gas streams would result in the emission of a significant amount of CH<sub>4</sub>. This greenhouse gas would not be emitted if biomass is used in applications different from anaerobic digestion;

similarly, low methane emission factors are observed in conventional biogas burning. Methane slip has been identified as a major contribution to total methane emissions of biogas industry (Liebetrau et al., 2017). The equivalent CO<sub>2</sub> saving of biomethane production considerably raises if methane slip is limited to 0.05%, while the process results no longer sustainable when methane slip reach 4% (Ravina and Genon, 2015).

Table 1 reports a general overview on biogas upgrading technologies available at a commercial scale.

As shown in Table 1, most of commercially available techniques have a methane slip far above 0.05%. Since biomethane production is undergoing a fast development, it is foreseen that a large number of biogas upgrading plants will be installed in the next decade. As a consequence, it is expected that off-gas emissions will have a growing role in the mitigation of climate change. In this framework, biogas upgrading technologies should be thoroughly revised in order to reduce the methane slip.

Currently, the lowest methane slip can be archived by amine absorption, but this technology involves the use of chemicals such as monoethanolamine or diethanolamine. The acute inhalation toxicity of a mixture containing ethanolamines has been investigated in rats and the lethal concentration (LC<sub>50</sub>) was estimated to be 2.48 mg L<sup>-1</sup> (Anon., 2010a). The repeated dose toxicity has also been assessed: the dominant effects of a continuous exposure to 5–6 ppm were skin irritation and lethargy; dogs and rodents exposed to 66–102 ppm ethanolamine vapor had behavioural changes, pulmonary and hepatic inflammation, hepatic and renal damage, and hematological changes; mortality was reported in dogs exposed to 102 ppm ethanolamine vapor for 2 days, and in rodents exposed to 66–75 ppm ethanolamine vapor for 24–28 days (Elder, 1983). The inhalation of ethanolamine can also cause bronchoconstriction (Kamijo et al., 2009). Weak mutagenic effects

**Table 1**  
Overview of biogas upgrading technologies.

Method	Biomethane purity (%v/v)	Electricity consumption (kWh m <sup>-3</sup> )	Thermal energy consumption (kWh m <sup>-3</sup> )	Methane slip (%)
Water scrubbing	96-98 (Singhal et al., 2017)	0.2-0.3 (Bauer et al., 2013; Singhal et al., 2017)	–	1 (Bauer et al., 2013; Singhal et al., 2017)
	>97 (Andriani et al., 2014), (Munoz et al., 2015; Wesley Awe et al., 2017)	0.4-0.5 (Munoz et al., 2015; Wesley Awe et al., 2017)		<2 (Andriani et al., 2014; Munoz et al., 2015; Wesley Awe et al., 2017)
	93-99 (Sun et al., 2015)	0.5-0.9 (Sun et al., 2015)		1-2 (Sun et al., 2015)
	95.5-97 (Abdeen et al., 2016)	0.2-0.43 (Andriani et al., 2014)		
Amine absorption	99.8 (Bauer et al., 2013)	0.12-0.14 (Bauer et al., 2013), (Singhal et al., 2017)	0.5-0.75 (Sun et al., 2015)	<0.1 (Munoz et al., 2015; Wesley Awe et al., 2017; Singhal et al., 2017)
	>95 (Andriani et al., 2014)	0.05-0.26 (Munoz et al., 2015)	0.55 (Bauer et al., 2013; Singhal et al., 2017)	<1 (Sun et al., 2015)
	>99 (Munoz et al., 2015; Wesley Awe et al., 2017; Singhal et al., 2017)	0.05-0.25 (Wesley Awe et al., 2017)		
	97-99.5 (Sun et al., 2015)	0.1-0.15 (Sun et al., 2015)		
	>87 (Abdeen et al., 2016)	0.12-0.65 (Andriani et al., 2014)		
Vacuum/pressure swing adsorption (PSA/VSA)	98-99 (Bauer et al., 2013)	0.24-0.6 (Andriani et al., 2014)	–	1.8-2 (Bauer et al., 2013; Singhal et al., 2017)
	98 (Munoz et al., 2015; Singhal et al., 2017)	0.2-0.3 (Bauer et al., 2013; Singhal et al., 2017)		2-12 (Sun et al., 2015)
	95-98 (Wesley Awe et al., 2017)	0.25-0.46 (Sun et al., 2015)		
Membrane separation	95-99 (Sun et al., 2015)	0.2-0.3 (Singhal et al., 2017)	–	0.5 (Bauer et al., 2013; Singhal et al., 2017)
	98 (Bauer et al., 2013; Singhal et al., 2017)	0.22 (Munoz et al., 2015; Wesley Awe et al., 2017)		<10 (Wesley Awe et al., 2017)
	>96 (Andriani et al., 2014; Wesley Awe et al., 2017)	0.15-0.43 (Sun et al., 2015)		<1 (Munoz et al., 2015)
	91-99 (Sun et al., 2015)	0.2-0.77 (Andriani et al., 2014)		0.19-0.77 (Andriani et al., 2014)
		2-15 (Sun et al., 2015)		2-15 (Sun et al., 2015)
Cryogenic upgrading	96-99 (Munoz et al., 2015)	0.2-1.54 (Sun et al., 2015)	–	0.5-1 (Sun et al., 2015)
	98-99 (Sun et al., 2015)			no loss (Hoyer et al., 2016)
	90-98 (Andriani et al., 2014; Wesley Awe et al., 2017)			

were reported in one study on genotoxicity *in vitro*, and a weak positive response was reported in human lymphocytes (Arutyunyan et al., 1987). Ethanolamine inhalation by humans has been reported to cause immediate allergic responses of dyspnea and asthma and clinical symptoms of acute liver damage and chronic hepatitis (Elder, 1983). A case of occupational asthma in an industrial worker exposed to ethanolamine was reported (Savonius et al., 1994). Exposure to vapours from ethanolamine can irritate the nose, throat, and lungs (Bello et al., 2009). As a consequence, the Occupational Safety and Health Administration (OSHA) permissible exposure level for ethanolamine is  $6 \text{ mg m}^{-3}$  as an 8 h time-weighted average concentration (Anon., 1996). Similarly, the National Institute for Occupational Health and Safety (OSHA) has a recommended exposure limit of  $8 \text{ mg m}^{-3}$  for a 10 h workday and 40 h work week; the short-term exposure limit is  $15 \text{ mg m}^{-3}$ , for periods not to exceed 15 min (Anon., 2010b). Diethanolamine is classified as “possibly carcinogenic” by the International Association of Research on Cancer (IARC) (Anon., 2013).

Aim of this study is to assess a novel approach for  $\text{CO}_2/\text{CH}_4$  separation, with the final goal of reducing methane slip while keeping biomethane purity and energy consumption at a competitive level. The investigated approach consists in the application of hot potassium carbonate (HPC) technology to biogas upgrading. It is basically an absorption on  $\text{K}_2\text{CO}_3$  solutions, through the reaction described in Eq. 2 (Sanyal et al., 1988):



The obtained  $\text{KHCO}_3$  solution is continuously regenerated by reducing the pressure and increasing the temperature (Kamps et al., 2007). HPC is widely used at industrial scale for  $\text{CO}_2/\text{N}_2$  separation in ammonia synthesis (Mahmoodi and Darvishi, 2017). The advantages of  $\text{K}_2\text{CO}_3$  absorption include good  $\text{CO}_2$  capacity (e.g. 0.7–3.6  $\text{CO}_2/\text{K}_2\text{CO}_3$  ratio, in the temperature range 313–393 K) (Kamps et al., 2007; Imle et al., 2013) and moderate heat consumption (e.g.  $51.64 \text{ kJ mol}^{-1}$  for a  $\text{K}_2\text{CO}_3$  solution 15% in weight, with a loading ratio of 0.86 mol  $\text{CO}_2/\text{mol K}_2\text{CO}_3$  at 303 K) (Kim et al., 2016). In light of these advantages, HPC is being successfully applied to other gas streams, including post-combustion (Hetland and Christensen, 2008; Thee et al., 2012) and gasification (Urech et al., 2014; Li et al., 2014): since these latter applications have significant amounts of dust, tar, sulfur compounds and acidic components, the HPC confirmed to have a good resistance to impurities. Being a consolidated approach for  $\text{CO}_2$  capture, HPC could quickly become a valid and reliable technology for biogas upgrading to biomethane. Despite this potential, to the best of our knowledge no experimental data are available with regard to this topic, even if HPC was recently suggested as a suitable biogas upgrading method in a couple of simulation studies (Arshad et al., 2014; Zhang et al., 2017). Hence, aim of this study is to investigate the technical feasibility of a HPC plant for biomethane production, in terms of long term performances, energy consumption at industrial scale, resistance to biogas impurities, compliance with fuel standard requirements, methane retention and emission in the off-gas. For this purpose, biogas upgrading

to biomethane by absorption on  $\text{K}_2\text{CO}_3$  is investigated for the first time in a pilot HPC plant.

## 2. Materials and methods

### 2.1. Biogas production and cleaning

Tests were performed in a waste management facility located in Este, North-Eastern Italy. The facility includes an anaerobic digestion plant for the treatment of the organic fraction of municipal solid waste. Fig. 1 shows the layout of the plant. The plant is divided into a cleaning module and an upgrading module. The cleaning module aims at removing secondary components such as non-methane volatile organic compounds (VOC) and sulfur compounds. It is basically constituted by a series of activated carbon filters. After the removal of these contaminants, pre-treated biogas is compressed and sent to the upgrading module for the  $\text{CO}_2$  removal, as described in the next paragraph.

### 2.2. Configuration and operation of biogas upgrading plant

The biogas upgrading unit is described in Fig. 2. After cleaning and compression, biogas reaches an absorption reactor consisting of a column with metal random packing. The reactor is operating between at 500–1200 kPa and 60–90 °C. In the reactor, biogas is washed in a counter-current mode with a  $\text{K}_2\text{CO}_3$  aqueous solution, with a flow rate of 150–200  $\text{Nm}^3 \text{ h}^{-1}$ . The flow rate of the solution is 2.5–3  $\text{m}^3 \text{ h}^{-1}$ . According to reaction described in Eq. 2,  $\text{CO}_2$  is absorbed and  $\text{KHCO}_3$  is produced, while pure  $\text{CH}_4$  is collected at the top of the absorption column. The operational liquid to gas ratio is about 0.02  $\text{m}^3$  of liquid per  $\text{Nm}^3$  of gas: this value was identified after preliminary tests aimed at optimizing methane purity, energy consumption and methane slip. The produced  $\text{KHCO}_3$  solution is continuously sent to a regeneration column, where the reaction of Eq. 2 is performed backward by reducing the pressure and increasing the temperature, at 10 kPa and 100–105 °C. This results in the regeneration of the  $\text{K}_2\text{CO}_3$  solution, with a release of  $\text{CO}_2$  as off-gas. The upgrading unit also contains a flashing vessel between the regeneration column and the off-gas outlet into the atmosphere, in order to further reduce the methane slip. The solution pump includes a filter able to remove precipitates and suspensions, if present. The absorber is 7000 mm height and 400 mm diameter, while the regeneration column is 6000 mm height and 500 mm diameter. As a common practice in biogas upgrading plants, stainless steel was used, in order to prevent corrosion and reduce maintenance costs.

### 2.3. Monitoring methods

The plant was monitored from late May to the end of June 2017. Subsequently, a second monitoring campaign was repeated in October 2017 in order to further assess the methane slip.

The absorption solution was regularly analysed in order to assess the absence of turbidity due to precipitations and suspensions. During all the monitoring campaigns, no turbidity was detected.

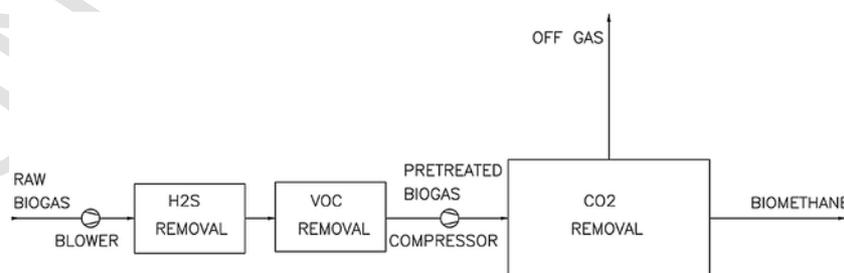


Fig. 1. Plant layout for biogas cleaning and upgrading.

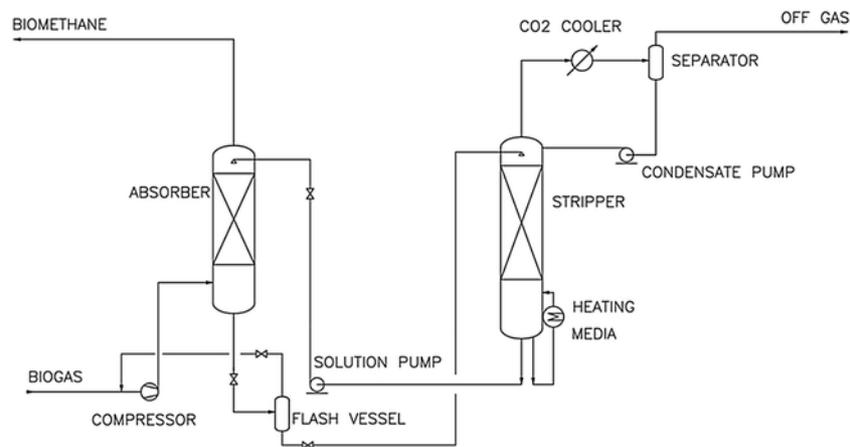


Fig. 2. Upgrading unit.

$\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}$  were sampled in hydrogen-tight, aluminium coated polyvinylfluoride sampling bags, and quantified by means of an INFICON 3000 Micro GC Gas Analyzer (SRA Instruments, Via alla Castellana, 3, Cernusco sul Naviglio, Italy); the instrumental method is reported in a previous study (Petracchini et al., 2017). For all gases, accuracy and limit of quantitation (LoQ) were 0.01% v/v and 0.1% v/v, respectively. Gas composition was used for calculating density, Wobbe index and higher heating value according to ISO 6976:2016 standard method (ISO, 2016); methane number was calculated according to Annex A of EN 16,726 standard method (CEN, 2016).  $\text{HCl}$ ,  $\text{HF}$  and  $\text{NH}_3$  were analysed as described in a previous study: basically, impinger sampling was followed by ion exchange chromatography; analytical uncertainty was 0.1, 0.01 and  $0.02 \text{ mg m}^{-3}$  for  $\text{HCl}$ ,  $\text{HF}$  and  $\text{NH}_3$ , respectively (Paolini et al., 2018b). Hydrogen sulfide was determined by means of a Biogas 5000 analyser (Geotech, Leamington, UK), equipped with a suitable electrochemical sensor. Accuracy and maximum concentration limit are 1.5 and  $7500 \text{ mg m}^{-3}$ , respectively (Paolini et al., 2016). Volatile methyl siloxanes were sampled on carbon cartridges and analysed by thermal desorption followed by gas chromatography and quadrupole mass spectrometry, as described in a previous study (Paolini et al., 2018b).

### 3. Results

#### 3.1. Biomethane purity

Fig. 3 shows the  $\text{CH}_4$  and  $\text{CO}_2$  concentration in biomethane produced by the prototype during four operational days, representative of the average performance of the plant. The average  $\text{CO}_2$  concentration is  $1.2 \pm 0.4\% \text{ v/v}$ , following absorption in the potassium carbonate solution. This result shows that, in terms of biomethane purity, the considered methodology is competitive with the currently used alternative approaches (Andriani et al., 2014; Ryckebosch et al., 2011).

A detailed characterisation of biomethane is reported in Table 2. Data are compared with the recent EU standard specification for biomethane: it can be confirmed that, in the investigated operational conditions, the proposed technology allows to obtain a biofuel suitable for use in automotive engines. Data are also compared with the more stringent Italian regulation, which includes the monitoring of other inorganic contaminants.

Table 2 also reports the composition of the cleaned biogas, after the treatment with activated carbon filters and immediately before the upgrading module. A comparison between the composition of the cleaned biogas inlet and the biomethane outlet gives useful information on the

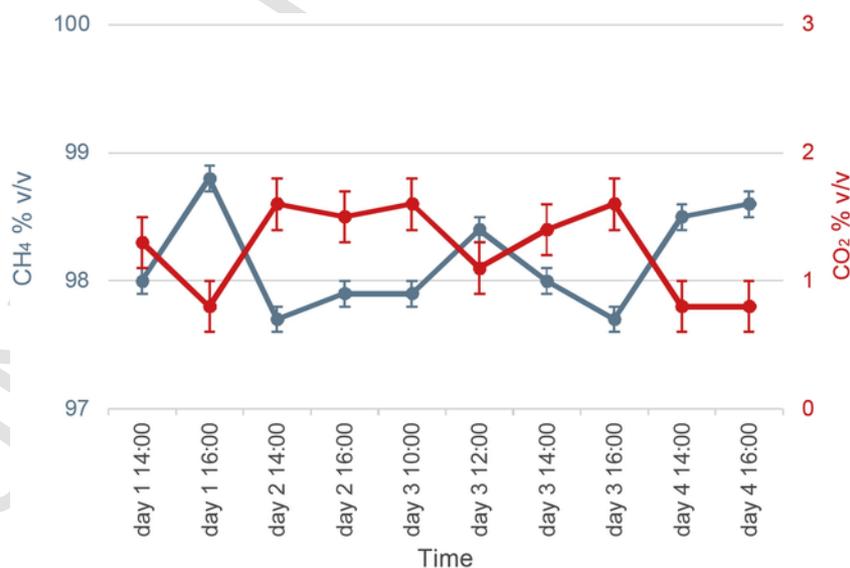


Fig. 3. Methane and carbon dioxide content in biomethane.

**Table 2**  
Biogas and biomethane composition.

Parameter	Cleaned biogas	Biomethane	Italian regulation	EU regulation
			UNI TR 11537	EN 16723-2
Higher heating value MJ m <sup>-3</sup>	22.3 ± 0.2	36.4 ± 0.2	34.95-45.28	
Wobbe index MJ m <sup>-3</sup>	22.9 ± 0.5	48.8 ± 0.5	47.31-52.33	
Relative density	0.94 ± 0.01	0.57 ± 0.01	0.5548-0.8	
Methane number*	n.a.	95.5 ± 0.5	> 65	
Oxygen %	< 0.2%	< 0.2%	< 0.6%	< 1%
Methane %	60 ± 2	98.1 ± 0.5		
Carbon dioxide %	39 ± 2	1.2 ± 0.4	< 3%	
Hydrogen %	< 0.2%	< 0.2%	< 0.5%	< 2%
H <sub>2</sub> S mg m <sup>-3</sup>	1.6 ± 0.9	0.9 ± 0.7	< 6.6	
Mercaptans mg m <sup>-3</sup>	< 0.01	< 0.01	< 15.5	
H <sub>2</sub> S and CS <sub>2</sub> mg m <sup>-3</sup> (sum expressed as S)	1.5 ± 0.9	0.8 ± 0.7	< 5	
Total sulfur mg m <sup>-3</sup>	1.5 ± 0.9	0.8 ± 0.7	< 150	
Carbon monoxide %	< 0.1%	< 0.1%	< 0.1%	
Total volatile silicon mg m <sup>-3</sup>	< 0.04	< 0.04	< 1	< 0.3
Ammonia mg m <sup>-3</sup>	12 ± 1	1.0 ± 0.2	< 10	
Amines mg m <sup>-3</sup>	< 5	< 5	< 10	
Fluorine mg m <sup>-3</sup>	1.1 ± 0.3	0.54 ± 0.03	< 3	
Chlorine mg m <sup>-3</sup>	53 ± 6	0.24 ± 0.07	< 1	

\*Methane number is calculated according to Annex A of standard method EN 16,726:2015.

effects of HPC towards secondary contaminants of biogas. Specifically, it can be observed a reduction of several water-soluble components such as hydrogen sulphide, ammonia, chlorine and fluorine. Indeed, in industrial scale plants, water-soluble interferents are mostly removed in the cleaning module, but traces of these compounds can reach the upgrading unit. In this case study, their concentration in biomethane is lower than in the inlet biogas, mainly due to two processes. Acidic and volatile interferents are absorbed in the K<sub>2</sub>CO<sub>3</sub> solution and then desorbed in the regeneration column, where pressure is reduced and temperature and pH increase. Low-volatile compounds can be absorbed and then be involved in precipitation processes, and the formed suspension is removed in the filter of the solution pump. In all cases, no accumulation was observed and the absorption solution did not show any turbidity during all the monitoring period.

As a consequence, co-capture of CO<sub>2</sub> and H<sub>2</sub>S could be performed, thanks to the solubility of both compounds in alkaline water solutions. However, regeneration of aqueous solutions from H<sub>2</sub>S requires high energy consumption. For these reasons, it is generally preferable to remove H<sub>2</sub>S in the biogas cleaning module using carbon filters or iron oxides. Some researches have proven the feasibility of a simultaneous biogas cleaning and upgrading, i.e. a removal of both H<sub>2</sub>S and CO<sub>2</sub> in a single step (Paolini et al., 2016): however, most of these researches are related to laboratory scale tests. Most of the industrial scale plants consist of a cleaning module and an upgrading module (Andriani et al., 2014; Bauer et al., 2013): this separation allows to reduce the maintenance costs of the upgrading module. Hence, the use of a cleaning unit before the upgrading step was used also in this study.

### 3.2. Methane slip

The following Table 3 shows the results of off-gas analysis. When compared with the values obtained from other available technologies (Table 1), it is noted that the off-gas methane content is particularly low. It is also worth mentioning that one of the measured values differs from the others in a statistically significant manner: by carrying out a Grubb test on the measurement of May 31, it is observed that the value

**Table 3**  
Off-gas composition (late spring).

Date	CH <sub>4</sub> %v/v	Methane slip
May 29th 2017 (PM)	0.14	0.092%
May 30th 2017 (AM)	0.13	0.085%
May 31 <sup>st</sup> 2017 (AM)	0.45	0.295%
June 5th 2017 (PM)	0.11	0.072%
June 6th 2017 (PM)	< 0.1	0.033%
June 7th 2017 (AM)	0.15	0.098%
June 20th 2017 (PM)	< 0.1	0.033%
June 21st 2017 (AM)	0.14	0.092%
June 21st 2017 (PM)	< 0.1	0.033%
June 22nd 2017 (AM)	< 0.1	0.033%

is to be considered an outlier, with a  $p < 0.05$ . The presence of a single measurement that differs from the others in a statistically significant manner can be attributed to various phenomena related to the management of the plant and the process of analysis. If this datum was excluded from subsequent processing, the average concentration of biomethane would be <0.1%v/v.

Results from a second monitoring campaign performed in October 2017 are reported in Table 4. It can be observed that no significant changes occurred in the process performance. On average, a methane slip of 0.078% can be calculated.

The experimental results, compared with performances of other technologies resumed in Table 1, show that the HPC process has by far the lowest methane losses. As a general consideration, for upgrading methods based on absorption, the only way by which CH<sub>4</sub> can slip from the biomethane product is through its solubilization in the washing solution during the CO<sub>2</sub> absorption process. In the specific case of HPC, a lower methane slip (<0.1%) is observed, thanks to a further reduction in the physical solubility of methane in the K<sub>2</sub>CO<sub>3</sub> solution.

Such a solubility reduction can be attributed to the synergy of the following three effects: the high absorption temperature, a low liquid/gas ratio and presence of electrolytes. First of all, a specific advantage of the considered technology is that absorption can be performed at relatively high temperature (60–90 °C), compared to other absorption methods. As a consequence, CH<sub>4</sub> solubility is further reduced, according to the Henry constant (K<sub>H</sub>) dependence upon temperature (Sander, 2015; Gevantman, 2019). The second contribution to the reduction in CH<sub>4</sub> solubility is related to mass effect: indeed, the chemical reaction (2) requires a low liquid/gas ratio in the absorber, i.e. 0.02 m<sup>3</sup> of liquid per Nm<sup>3</sup> of gas, which is about 75% lower than water scrubbing. This contributes to decrease the CH<sub>4</sub> solubilization, by reducing its residence time in the absorption column thanks to the low solution flowrate (Giacopini and Costantino, 2017). Finally, the K<sub>H</sub> of CH<sub>4</sub> in carbonate solutions is higher than its K<sub>H</sub> in pure water. Indeed, the solubility reduction of CH<sub>4</sub> in the presence of an electrolyte is a widely known phenomenon (Hermann et al., 1995): of course, this effect can be observed not only in HPC, but also in the absorption with alkaline solutions (Ryckebosch et al., 2011).

Finally, it is worth mentioning that a further technical guard to minimize the methane slip is the flash tank in the solution stream coming from the absorber (Fig. 2): thanks to a pressure reduction, the eventual traces of methane entrapped in the solution are released and recy-

**Table 4**  
Off-gas composition (autumn).

Date	CH <sub>4</sub> %v/v	Methane slip
October 9th 2017 (AM)	0.12	0.079%
October 9th 2017 (PM)	< 0.1	0.033%
October 10th 2017 (AM)	< 0.1	0.033%
October 10th 2017 (PM)	0.14	0.092%
October 11th 2017 (AM)	0.11	0.072%

cluded back to the absorber, while the solution is fed to the stripper column almost free of methane.

### 3.3. Energy consumption

The following Table 5 shows the electricity consumption of the system during the monitoring period (column A). During this period the plant was fed with an average biogas flow rate of  $150 \text{ Nm}^3 \text{ h}^{-1}$ . The same data are also reported for a colder period (column B). In addition, in column C, consumption is shown for the flow rate of  $200 \text{ Nm}^3 \text{ h}^{-1}$  of biogas: indeed, this is the optimal flow rate for which the system has been sized and for which the maximum efficiency is therefore obtained. In all 3 cases the biomethane is produced at a pressure of 800 kPa.

For the time period of column A (average outdoor temperature  $21^\circ \text{C}$ ), heat consumption is also available. Data are based on direct measurements of heat consumption of the monitored pilot plant. Heat consumption is  $0.424 \text{ kWh Nm}^{-3}$ , and heat recovery is  $0.365 \text{ kWh Nm}^{-3}$ . Obviously, heat consumption is mainly related to the regeneration of the solution.

### 3.4. Process costs

Table 6 reports the investment and operational costs of a plant based on HPC absorption, with a flow rate of  $1000 \text{ m}^3 \text{ h}^{-1}$  of biogas inlet. It is assumed that the plant operates for 20 years, with a discount rate of 5% and an inflation of 1%. Electricity and heat costs are assumed to be 0.16 and 0.03 euro/kWh, respectively.

No investment is foreseen for off-gas post treatments (e.g. burner to remove methane), due to the low concentration of methane in this gas

**Table 5**  
Electricity consumption.

	A	B	C
Date	May 29th - June 1st June 5th -June 6th June 20th - June 22th	February 21st - April 14th	April 27th - April 29th
Biogas (BG) flow rate $\text{Nm}^3 \text{ h}^{-1}$	148.76	149.3	195.9
Average outdoor temperature $^\circ \text{C}$	21	13	13
Specific consumption for upgrading $\text{kWh Nm}^{-3} \text{ BG}$	0.064	0.057	0.050
Specific consumption for gas compressor $\text{kWh Nm}^{-3} \text{ BG}$	0.165	0.147	0.149
Specific consumption for upgrading and gas compressor $\text{kWh Nm}^{-3} \text{ BG}$	0.229	0.204	0.199
Specific consumption for pretreatment $\text{kWh Nm}^{-3} \text{ BG}$	0.038	0.030	0.039

**Table 6**  
Costs (euro) of a  $1000 \text{ m}^3 \text{ h}^{-1}$  HPC plant.

		CHP available	CHP not available
Capital expenditure	Investment for biogas upgrading	1,700,000	1,700,000
	Investment for off-gas post treatment	0	0
Operating expense	Methane loss	55,000	55,000
	Energy consumption	2,780,000	4,985,000
	Consumables	875,000	875,000
	Maintenance	1,105,000	1,105,000
Life cycle cost		6,515,000	8,720,000

stream, as reported in paragraph 3.2. Operational costs include methane loss, because of the high economic value of this biofuel (currently ca  $0.8 \text{ euro/m}^3$ ). Energy consumption comprises both electricity (mainly for biogas and biomethane compression) and heat for the regeneration of the absorbing solution: this latter cost is reported in Table 6 both in the case in which heat is available from a CHP unit, and in the worst case where no heat from CHP is available. Consumables consist in activated carbon and other adsorbents for the removal of  $\text{H}_2\text{S}$  and volatile organic compounds, while the HPC does not need other chemicals for  $\text{CO}_2$  absorption.

A detailed comparison is given with one specific upgrading technology. The selected technology to be compared with HPC is membrane separation, which is currently the most common technology among the newly installed upgrading plants, both in Europe and in the Italian case study (Anon., 2019a). In the Italian case study, the average investment cost for the construction of a membrane upgrading plant is 1,500,000 Euros, but a post-treatment unit for off-gas is necessary (350,000 Euros); regarding consumables and maintenance, an average annual cost of 80,000 and 50,000 Euros is assumed for plant maintenance and membrane substitution, respectively (Pastori et al., 2018). According to literature cited in Table 1, the following parameters are assumed for a membrane upgrading plant: methane slip 1% (average in 20 years), electricity consumption  $0.29 \text{ kWh m}^{-3}$ , no heat consumption. Based on these assumptions, Table 7 reports capital expenditure and operating expense of a typical upgrading plant based on membrane separation, with a flow rate of  $1000 \text{ m}^3 \text{ h}^{-1}$ , for 20 years of operation with a discount rate of 5% and an inflation of 1%. Data are provided both in the case in which heat is available from CHP unit, and in the worst case where no heat from CHP is available. For both cases, Table 8 also reports the difference (in revenue) with HPC from previous Table 7.

Capital expenditure for membrane separation and HPC are quite similar, since the lower cost of membrane upgrading (1.5 MEuros versus 1.7 MEuros) is balanced by the off-gas post-treatment (350,000 Euros), which is necessary only for membrane plants, whose methane slip is higher than 0.2% (HPC's methane slip  $< 0.1\%$ ). Overall, the capital expenditure is slightly lower for HPC (1.7 MEuros instead of 1.85 MEuros).

On the other hand, significant differences can be observed for operating expense. Indeed, the high methane slip of membrane separation results in high costs due to methane loss. Another major contribution to operating expense is the energy consumption: while membrane separation requires no thermal energy, it still requires more electricity ( $0.29 \text{ kWh m}^{-3}$ ) than HPC ( $0.22 \text{ kWh m}^{-3}$ ) based on the same biomethane pressure (12 barg). Operating expense associated to energy consumption increases if no CHP is available. Finally, higher maintenance and consumable costs are related to membrane substitution and biogas pretreatment (mainly higher consumption of activated carbon to preserve membranes). The sum of these factors leads to a significantly higher operating expense for membrane reactor, compared to HPC.

**Table 7**  
Costs (euro) of a  $1000 \text{ m}^3 \text{ h}^{-1}$  membrane plant.

		CHP available	CHP not available
Capital expenditure	Investment for biogas upgrading	1,500,000	1,500,000
	Investment for off-gas post treatment	350,000	350,000
Operating expense	Methane loss	540,000	540,000
	Energy consumption	3,780,000	5,165,000
	Consumables	1,170,000	1,170,000
	Maintenance	1,925,000	1,930,000
Life cycle cost		9,265,000	8,720,000
Difference with HPC		2,750,000	1,935,000

**Table 8**  
Comparison between upgrading technologies.

	Water scrubbing	Amine absorption	Vacuum/ pressure swing adsorption (PSA/VSA)	Membrane separation	Cryogenic upgrading	Hot Potassium carbonate
Methane slip	High	Low	High	High	Low	Low
Off-gas post-treatment	Yes	No	Yes	Yes	No	No
Investment costs	Medium/low	Medium/high	Medium	Medium/low	High	Medium/low
Electricity consumption	Medium	Low	Medium	High	Very High	Medium/low
Heat consumption	No	Yes	No	No	No	Yes
Use of harmful substances	No	Yes	No	No	No	No
Maintenance and consumables	Low	Medium	Medium	High	High	Low
Suitable for liquefaction	No	No	No	No	Yes	No

In conclusion, the use of HPC in substitution of currently used membrane systems can result in a total Life Cycle Cost reduction of 2,750,000 Euros, if a CHP unit is available. If CHP is not available, the total Life Cycle Cost reduction is 1,935,000 Euros.

### 3.5. Comparison with other technologies

A summary of advantages and disadvantages of the proposed methodology is reported in Table 8. Low methane slip is a major advantage of HPC, when compared to membrane separation, pressure swing adsorption and vacuum swing adsorption (PSA/VSA). Indeed, methane slip for these latter technologies is generally in the range 0.5–2% (see Table 1), while in this study an average methane slip of 0.078% was obtained through HPC. This allows to increase the environmental sustainability of biogas upgrading, avoiding the emission of CH<sub>4</sub> which is a strong greenhouse gas (IPCC, 2013; Paolini et al., 2018a). As discussed in paragraph 3.4, methane slip is also a key parameter in the total revenues of the plant: costs associated to methane loss can decrease from 540,000 to 55,000 euros in 20 years (see Tables 6 and 7).

Off-gas post-treatment is required for plants with high methane slip. This is not the case of HPC, amine absorption and cryogenic upgrading: this advantage results in a slight reduction of capital expenditure.

Investment costs are of course lower for those technologies where no off-gas post-treatment is required. Simpler processes such as water scrubbing also involve lower costs. On the other hand, cryogenic upgrading is generally regarded as the technology involving the higher investment costs.

Energy consumption of other technologies (Table 1) can be compared with data from paragraph 3.3. For HPC, electricity consumption is slightly lower than PSA/VSA and membrane separation. On the other hand, heat consumption is 0.424 kW h Nm<sup>-3</sup> but 0.365 kW h Nm<sup>-3</sup> can be recovered. With this regard, it should be pointed out that electricity has a higher impact than heat on total costs. The consequence of the electricity costs are reported in paragraph 3.4, including a case study comparison with a membrane separation plant: in spite of the heat required, the lower electricity consumption of HPC significantly decreases the energy costs of the plant, from 3,780,000 to 2,780,000 Euros over 20 years, if a combined heat and power (CHP) unit is available. In the worst scenario when no CHP is available, energy costs can decrease from 5,165,000 to 4,985,000 Euros over 20 years using HPC instead of membrane separation (see Tables 6 and 7). As a summary, the need of a thermal energy input can be considered a disadvantage of HPC, but heat costs are negligible compared to electricity costs.

Harmful chemicals are generally not necessary in most kinds of upgrading plants. With this regard, potassium carbonate cannot be considered as a source of chemical hazard (Anon., 2019b). Similar considerations apply to membranes, as well as to zeolites and/or carbon used in PSA/VSA. The only methodology which involves the use of harmful substances is amine absorption: indeed, mono- and di-ethanolamine are

associated to several kinds of chemical hazard, as discussed and referenced in the Introduction (Anon., 2010a; Elder, 1983; Kamijo et al., 2009; Arutyunyan et al., 1987; Savonius et al., 1994; Bello et al., 2009; Anon., 1996, 2010b; Anon., 2013).

Maintenance and consumables can significantly affect total costs. For PSA/VSA, relatively high costs are related to the substitution of the adsorbent (zeolite or activated carbon). Similarly, in membrane separation the maintenance and substitution of membranes can affect total costs, as discussed in full details in previous paragraph 3.4.

Finally, it is worth mentioning that cryogenic upgrading is the sole technology suitable for direct production of liquefied biomethane. Of course, liquefaction might also be performed for biomethane produced with other technologies, but it would strongly increase total costs.

Compared with membrane and PSA/VSA, HPC has the following advantages: lower methane slip which results in a lower capital expenditure (for off-gas post-treatment) and higher revenues; lower operational expense due to lower electricity consumption and lower maintenance and consumable costs. On the other hand, the disadvantage of HPC towards membrane and PSA/VSA is the heat consumption.

Similar considerations can also be made when comparing water scrubbing and HPC.

The HPC has a lot of similarities with amine absorption: low methane slip (and consequently no need of off-gas post-treatment), heat consumption required, low electricity consumption. However, compared to this technology, investment is lower, plant is smaller and no harmful organic substances are involved (Anon., 2010a; Elder, 1983; Kamijo et al., 2009; Arutyunyan et al., 1987; Savonius et al., 1994; Bello et al., 2009; Anon., 1996, 2010b; Anon., 2013).

Advantages of cryogenic upgrading can be resumed in no heat requirement and suitability for liquefaction. The advantage of HPC toward cryogenic upgrading is the lower investment and operational cost, while low methane slip is still achieved with both technologies.

## 4. Conclusions

In this study, a demonstrative plant based on HPC absorption was validated for biogas upgrading to biomethane. Results obtained showed that the investigated methodology can be successfully applied for the production of biomethane for grid injection or for use as automotive fuel, in compliance with current standard requirements.

The main advantage is related to methane slip, which is significantly lower compared to currently used technologies. Specifically, an average methane slip below 0.1% was achieved, while most of commercial plants generally show an average methane slip ranging from 0.5 to 2%, according to Table 1. Another important advantage of HPC is the lower electricity consumption, which results in lower operational expense.

On the other hand, HPC requires thermal energy input but at the same time a high recovery rate (80% of consumption) is possible: with this regard, the performance of the investigated pilot plant might be

compared to amine absorption, but in this case there is not an involvement of harmful organic substances (as discussed in the Introduction with the above mentioned references, (Anon., 2010a; Elder, 1983; Kamijo et al., 2009; Arutyunyan et al., 1987; Savonius et al., 1994; Bello et al., 2009; Anon., 1996, 2010b; Anon., 2013)). By reducing the chemical hazard for operators, the process and plant are simpler.

The use of HPC technology in biomethane production, in substitution of membrane separation, pressured water absorption and PSA/VSA, would lead to a significant methane slip reduction. As a consequence, one of the major sources of CH<sub>4</sub> emissions from biogas industry (Liebetrau et al., 2017; Ravina and Genon, 2015) would be efficiently reduced, thus increasing both economic and environmental sustainability of biomethane production.

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## References

- Abdeen, F.R.H., Mel, M., Jami, M.S., Ihsan, S.I., Ismail, A.F., 2016. A review of chemical absorption of carbon dioxide for biogas upgrading. *Chin. J. Chem. Eng.* 24 (6), 693–702.
- Andriani, D., Wresta, A., Atmaja, T.D., Saepudin, A., 2014. A review on optimization production and upgrading biogas through CO<sub>2</sub> removal using various techniques. *Appl. Biochem. Biotechnol.* 172 (4), 1909–1928.
- Anon, 1996. Occupational Safety and Health Administration (OSHA). Occupational Safety and Health Guideline for Ethanolamine. [Online]. Available: [http://www.osha.gov/dts/chemicalsampling/data/CH\\_239000.html](http://www.osha.gov/dts/chemicalsampling/data/CH_239000.html).
- Anon, 2010. Letter to the Environmental Protection Agency Reporting an Actue Inhalaton Toxicity Studies of a Formulation Containing DEA. 8EHQ-0610-17981A.
- Anon, 2010b. National Institute for Occupational Safety and Health (NIOSH). Pocket Guide to Chemical Hazards: Ethanolamine. [Online]. Available: <http://www.cdc.gov/niosh/npg/ngpd0256.html>.
- Anon, 2013. IARC (International Agency of Research on Cancer) monographs 77 and 101; Year.
- Anon, 2019. "EBA European Biogas Association, Statistical Report 2017. Available at <http://european-biogas.eu/wp-content/uploads/2017/12/Statistical-report-of-the-European-Biogas-Association-web.pdf> Last Access January 2019.
- Anon, 2019. PubChem Open Chemistry Database. Laboratory Chemical Safety Summary for Potassium Carbonate. Available at: [https://pubchem.ncbi.nlm.nih.gov/compound/potassium\\_carbonate#datasheet=lc&section=Top](https://pubchem.ncbi.nlm.nih.gov/compound/potassium_carbonate#datasheet=lc&section=Top) Last Access January 2019.
- Arshad, M., Wukovits, W., Friedl, A., 2014. Simulation of CO<sub>2</sub> absorption using the system K<sub>2</sub>CO<sub>3</sub>-piperazine. *Chem. Eng.* 39, 577–582.
- Arutyunyan, R., Zalinyan, R., Mugnetsyan, E., LA, G., 1987. Mutagenic action of latex polymerization stabilizers in different test systems. *Tsitol. Genet.* 21, 450–456.
- Bachmann, N., 2015. Sustainable Biogas Production In Municipal Wastewater Treatment Plants. IEA Bioenergy Report ISBN 978-1-910154-22-9 Available at: [http://task37.ieabioenergy.com/files/daten-redaktion/download/Technical%20Brochures/Wastewater\\_biogas\\_grey\\_web-1.pdf](http://task37.ieabioenergy.com/files/daten-redaktion/download/Technical%20Brochures/Wastewater_biogas_grey_web-1.pdf) Last acc IEA Bioenergy, pp. 1–20, 2015.
- Batstone, D.J., Hülsen, T., Mehta, C.M., Keller, J., 2015. Platforms for energy and nutrient recovery from domestic wastewater: a review. *Chemosphere* 140, 2–11.
- Bauer, F., Hultberg, C., Persson, T., Tamm, D., 2013. "Biogas Upgrading – Review of Commercial Technologies. Swedish Gas Center Report SGC 2013:270. Available at [http://vav.griffel.net/filer/C\\_SGC2013-270.pdf](http://vav.griffel.net/filer/C_SGC2013-270.pdf) Last Access August 2017.
- Bekkering, J., Hengeveld, E.J., van Gemert, W.J.T., Broekhuis, A.A., 2015. Will implementation of green gas into the gas supply be feasible in the future?. *Appl. Energy* 140, 409–417.
- Bello, A., Mm, Q., Mj, P., Dk, M., 2009. Characterization of occupational exposures to cleaning products used for common cleaning tasks - a pilot study of hospital cleaners. *Env. Heal.* 27, 8–9.
- CEN, 2016. "European Committee for Standardization, Standard EN 16726:2016 Gas Infrastructure - Gas Quality - Group H. In: <https://www.cen.eu/Pages/default.aspx>.
- Colling Klein, B., Bonomi, A., Maciel Filho, R., 2017. Integration of microalgae production with industrial biofuel facilities: a critical review. *Renew. Sustain. Energy Rev.* 82 (June), 1376–1392, 2018.
- Demirbas, A., Taylan, O., Kaya, D., 2016. Biogas production from municipal sewage sludge (MSS). *Energy Sources Part A Recover. Util. Environ. Eff.* 38 (20), 3027–3033.
- EEA, 2016. European Environment Agency, EMEP/EEA Air Pollutant Emission Inventory Guidebook 2016 Section 1.A.3.b Passenger Cars, Light Commercial Trucks, Heavy-duty Vehicles Including Buses and Motor cycles.
- Elder, R.E., 1983. "Final report on the safety assessment of triethanolamine, diethanolamine, and monoethanolamine. *J. Am. Coll. Toxicol.* 2 (7).
- Gevantman, L.H., 2019. CRC Handbook of Chemistry and Physics, 91th Edition.
- Giacopini, W., Costantino, M., 2017. An innovative approach for biogas upgrading to biomethane. *Procedia Environ. Sci. Eng. Manag.* 4 (1), 49–52.
- Hermann, C., Dewes, I., Schumpe, A., 1995. The estimation of gas solubilities in salt solutions. *Chem. Eng. Sci.* 50 (May (10)), 1673–1675.
- Hetland, J., Christensen, T., 2008. Assessment of a fully integrated SARGAS process operating on coal with near zero emissions. *Appl. Therm. Eng.* 28 (no. 16), 2030–2038.
- Hoyer, K., Hultberg, C., Svensson, M., Jenberg, J., Nørregård, J., 2016. Biogas up-grading: a technical review. Report 2016, 275, Energiforsk.
- Imle, M., Kumelan, J., Speyer, D., McCann, N., Maurer, G., Hasse, H., 2013. Solubility of carbon dioxide in activated potash solutions in the low and high gas loading regions. *Ind. Eng. Chem. Res.* 52 (37), 13477–13489.
- IPCC, 2013. "IPCC (Intergovernmental Panel on Climate Change) Contribution of Working Group I to the Fifth Assessment Report ISBN 978-1-107-05799-1."
- ISO, 2016. International Standard Organization Standard Method ISO 6976:2016 Natural Gas -- Calculation of Calorific Values, Density, Relative Density and Wobbe Indices From Composition. In: <https://www.iso.org/standard/55842.html>, Last access August 2017.
- Kamijo et al., 2009 Y. Kamijo, I. Hayashi, A. Ide, K. Yoshimura, K. Soma, M. Majima, Effects of inhaled monoethanolamine on bronchoconstriction, *J. Appl. Toxicol.* 29 (1) (2009) 15–19.
- Kamps, A.P.S., Meyer, E., Rumpf, B., Maurer, G., 2007. Solubility of CO<sub>2</sub> in aqueous solutions of KCl and in aqueous solutions of K<sub>2</sub>CO<sub>3</sub>. *J. Chem. Eng. Data* 52 (3), 817–832.
- Kim, Y.E., Choi, J.H., Yun, S.H., Nam, S.C., Il Yoon, Y., 2016. CO<sub>2</sub> capture using aqueous solutions of K<sub>2</sub>CO<sub>3</sub> + 2-methylpiperazine and monoethanolamine: Specific heat capacity and heat of absorption. *Korean J. Chem. Eng.* 33 (12), 3465–3472.
- Li, S., Jin, H., Gao, L., Mumford, K.A., Smith, K., Stevens, G., 2014. Energy and exergy analyses of an integrated gasification combined cycle power plant with CO<sub>2</sub> capture using hot potassium carbonate solvent. *Environ. Sci. Technol.* 48 (24), 14814–14821.
- Liebetrau, J., Reinelt, T., Agostini, A., Linke, B., 2017. IEA International Energy Agency Task 37. Methane Emissions From Biogas Plants - Methods for Measurement, Result and Effect on Greenhouse Gas Balance of Electricity Produced. ISBN 9781910154359.
- Mahmoodi, L., Darvishi, P., 2017. Mathematical modeling and optimization of carbon dioxide stripping tower in an industrial ammonia plant. *Int. J. Greenh. Gas Control* 58, 42–51.
- Munoz, R., Meier, L., Diaz, I., Jeison, D., 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Rev. Environ. Sci. Biotechnol.* 14 (4), 727–759.
- Paolini, V., Petracchini, F., Guerriero, E., Bencini, A., Drigo, S., 2016. Biogas cleaning and upgrading with natural zeolites from tuffs. *Environ. Technol. (United Kingdom)* 37 (11), 1418–1427.
- Paolini, V., Petracchini, F., Segreto, M., Tomassetti, L., Naja, N., Cecinato, A., 2018. Environmental impact of biogas: a short review of current knowledge. *J. Environ. Sci. Heal. Part A*
- Paolini, V., et al., 2018. Characterisation and cleaning of biogas from sewage sludge for biomethane production. *J. Environ. Manage.* 217, 288–296.
- Pastori, M., Giacopini, W., Paolini, V., Segreto, M., Torre, M., 2018. LCC e methane slip nel biogas upgrading: 2 parametri chiave nella scelta della tecnologia. *Ecomondo 2018, XX Conference on Composting and Anaerobic Digestion.*
- Patterson, T., Esteves, S., Dinsdale, R., Guwy, A., 2011. An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. *Energy Policy* 39 (3), 1806–1816.
- Petracchini, F., et al., 2017. A novel pilot scale multistage semidry anaerobic digestion reactor to treat food waste and cow manure. *Int. J. Environ. Sci. Technol.*
- Ravina, M., Genon, G., 2015. Global and local emissions of a biogas plant considering the production of biomethane as an alternative end-use solution. *J. Clean. Prod.* 102 (2015), 115–126.
- Ryckebosch, E., Drouillon, M., Vervaeren, H., 2011. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy* 35 (5), 1633–1645.
- Sander, R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.* 15, 4399–4981.
- Sanyal, D., Vasishtha, N., Saraf, D.N., 1988. Modeling of carbon dioxide absorber using hot carbonate process. *Ind. Eng. Chem. Res.* 27 (11), 2149–2156.
- Savonius, B., Keskinen, H., Tuppurainen, M., Kanerva, L., 1994. Occupational asthma caused by ethanolamines. *Allergy* 49, 877–881.
- Semple, S., Apsley, A., Wushishi, A., Smith, J., 2014. Commentary: switching to biogas - what effect could it have on indoor air quality and human health?. *Biomass Bioenergy* 70, 125–129.
- Singhal, S., Agarwal, S., Arora, S., Sharma, P., Singhal, N., 2017. Upgrading techniques for transformation of biogas to bio-CNG: a review. *Int. J. Energy Res.* (March).
- Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., Yu, X., 2015. Selection of appropriate biogas upgrading technology - a review of biogas cleaning, upgrading and utilisation. *Renew. Sustain. Energy Rev.* 51, 521–532.
- Thee, H., et al., 2012. A kinetic and process modeling study of CO<sub>2</sub> capture with MEA-promoted potassium carbonate solutions. *Chem. Eng. J.* 210, 271–279.
- Urech, J., Tock, L., Harkin, T., Hoadley, A., Maréchal, F., 2014. An assessment of different solvent-based capture technologies within an IGCC e CCS power plant. *Energy* 64, 268–276.
- Wesley Awe, O., Zhao, Y., Nzihou, A., Minh, D.P., Lyczko, N., 2017. A review of biogas utilisation, purification and upgrading technologies. *Waste Biomass Valorization* 8 (2), 267–283.

- Yang, L., Ge, X., Wan, C., Yu, F., Li, Y., 2014. Progress and perspectives in converting biogas to transportation fuels. *Renew. Sustain. Energy Rev.* 40, 1133–1152.
- Zhang, L., Gai, X., Yang, R., Qi, Q., Cheng, Y., Sun, J., 2017. Kinetic study of absorption of carbon dioxide in biogas using hot potassium carbonate solution process in a dual-driver reactor. *Huanjing Kexue Xuebao/Acta Sci. Circumstantiae* 37 (7), 2490–2497.

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