

Biogas Upgrading: Analysis and Comparison between Water and Chemical Scrubbings

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Biomethane is a renewable energy source that can be used, e.g., for transportation or injection in the natural gas grids. It is obtained from proper biogas treatment. Biogas is a mixture of mainly methane and CO₂ that can be produced from livestock effluents, municipal and industrial sewage sludge, energy crops, agro-industrial wastes, MSW landfills (in this case the gas is commonly called "landfill gas") etc. In order to obtain biomethane, CO₂ and other compounds must be removed from biogas. The type and the amount of pollutants depend upon the biogas source and determine which cleaning and upgrading techniques are the most suitable for gas purification. "Cleaning" is referred to as the pretreatment that allows the removal of all pollutants but carbon dioxide, while "upgrading" is the treatment for CO₂ removal.

Since there are no clear guidelines for choosing among different upgrading techniques, this work analyzes two of the most commonly used processes: the water scrubbing and the chemical scrubbing (using amine solutions). By means of process simulation with commercial packages (such as Aspen Plus®), a comparison among the performances of the two techniques is made.

1. Introduction

The Directive 2009/28/EC of the European Parliament and of the Council of 23rd April 2009 says "*In the light of the positions taken by the European Parliament, the Council and the Commission, it is appropriate to establish mandatory national targets consistent with a 20 % share of energy from renewable sources and a 10 % share of energy from renewable sources in transport in Community energy consumption by 2020*" (Eur-Lex, 2009). This law perfectly agrees with the common feelings of the public opinion that, nowadays, are calling for an ever increasing attention to the environment. Obviously, taking care of environmental issues and developing technologies for renewable energy utilization are of worldwide interest and besides the European Union, also USA and China invest in alternative energies (Perkowski, 2012; US DoE, 2013). Among renewable resources, biogas is a readily available one and though its worldwide production is unknown (Petersson and Wellinger, 2009), it is used in several countries for heat and power production, as vehicle fuel or as a substitute for natural gas by injection in gas grids - in these two last cases after the upgrading to biomethane (American Biogas Council, 2013; Petersson and Wellinger, 2009; Tricase and Lombardi, 2009).

Biomethane can be obtained from proper biogas treatment. Biogas is a mixture of mainly methane and CO₂ that can be produced from livestock effluents, municipal and industrial sewage sludge, energy crops, agro-industrial wastes, MSW landfills (in this case the gas is commonly called "landfill gas") etc. In order to obtain biomethane, CO₂ and other compounds must be removed from biogas. The type and the amount of pollutants depend upon the biogas source and determine which cleaning and upgrading techniques are the most suitable for gas purification. "Cleaning" is referred to as the pretreatment that allows the removal of all pollutants but carbon dioxide, while "upgrading" is the treatment for CO₂ removal (Petersson and Wellinger, 2009).

In this work, the attention is focused on the upgrading of biogas coming from municipal sewage sludge in order to compare two of the most commonly used processes: the water scrubbing and the chemical scrubbing (using MEA). The aim is to highlight, by means of process simulation with commercial packages

(Aspen Plus[®], 2011), some of the key parameters of the two processes such as solvent requirement and methane recovery for a given biomethane purity.

2. Water and chemical scrubbing processes: basis for simulation and comparison

At the best of our knowledge, scarce detailed technical specifications for biogas upgrading processes are publicly available. It is easier to find some general information about plant capacity (in term of treated raw gas) and obtained biogas purity.

It has been taken as a reference, for what concerns capacity, the King County South Treatment Plant (Renton, Washington). In this wastewater treatment plant, biogas is produced from sludge in four anaerobic digesters as byproduct of the biosolid stabilization process. Total biogas production is about 1.2 million standard cubic feet per day (Stewart, 1995). Biogas is upgraded using water scrubbing - Binax system (Kohl and Riesenfeld, 1985) - at relatively high pressure (300 psi) with no water regeneration step. The final effluent of the water treatment plant is used for carbon dioxide absorption and the water that leaves the absorption towers is returned to the treatment plant. From plant pictures it seems that all the produced biogas is treated in two absorption towers (Krich et al., 2005; Van Holde and Butler, 2008). No details are available about column diameter, height and type but, typically, water scrubbing is performed in packed columns using a high-surface-area plastic media (Krich et al., 2005).

Based upon the above-mentioned data the following simulation basis for water scrubbing has been chosen: 30.03 kmol/h of gas has to be treated in one packed column (packing: plastic Pall rings) at 20 bar with pure water at 25 °C to obtain 98 % v/v methane (Petersson and Wellinger, 2009) on a dry basis. The inlet gas composition is 60 % v/v CH₄ and 40 % v/v CO₂, a typical composition of biogas coming from municipal wastewater treatment plant sludge digestion (Osorio and Torres, 2009; Van Holde and Butler, 2008). Other components have been neglected. Packing height has been set to 10.0 m and column diameter has been set to 1 m. Column dimensions have been arbitrarily chosen since unavailable and since the aim of this work is to reasonably compare water and chemical scrubbing and not to achieve a detailed process design.

For what concerns chemical scrubbing, a 30 % w/w and a 15 % w/w MEA aqueous solutions have been used for the absorption. The column retains the same dimensions as in the case of water scrubbing as well as the specifications for the separation. The only differences lie in the packing material (metal instead of plastic (Rennie, 2006)) and in the absorption pressure (atmospheric pressure (Petersson and Wellinger, 2009) instead of 20 bar).

2.1 Absorption modelling

Both water scrubbing and chemical absorption have been simulated in Aspen Plus[®] by means of a rate-based approach.

As for the physical absorption by water, the VLE has been described using the Henry constant for the CO₂ solubility in water and the SRK EoS (Soave, 1972) for the vapour phase. Since the correct description of the VLE conditions is a requirement for a reliable process simulation (Gamba et al., 2009; Pellegrini et al., 2010), the performances of the chosen thermodynamic model have been verified by comparison with VLE experimental data. Data sources are reported in Table 1.

Table 1: Experimental data sources for the VLE of the CO₂-H₂O system

Source	T [K]	P [bar]
Novák et al. (1961)	284.59-342.07	0.13-0.97
Zawisza and Malesinska (1981)	323.14	1.57-24.15
Valtz et al. (2004)	298.28-318.23	4.98-49.88

From Figure 1 and Figure 2 the suitability of the thermodynamic model can be inferred. Moreover, the CO₂ Henry constant of the Aspen Plus[®] database has been compared with that published by Carroll et al. (1991), relevant to low pressure CO₂ solubilities. The dependence on temperature of the two constants agrees each other. Ionization of CO₂ in water has been neglected as also made by Carroll et al. (1991).

For what concerns heat and mass transfer, the built-in correlations of Aspen Plus[®] has been used (film theory by Lewis and Whitman (1924) plus Onda et al. (1968) correlation).

As for the chemical absorption with amines, the modelling approach comes from previous works in the field of gas purification (Moioli et al., 2012; Pellegrini et al., 2011a; Pellegrini et al., 2011b). Details about modelling the CO₂ absorption with MEA can be found in Pellegrini et al. (2011a), where the calibration of the thermodynamic model (based on the Electrolyte-NRTL theory developed by Chen et al. (1979), Chen

et al. (1982) and Chen and Evans (1986) for aqueous systems and subsequently extended by Mock et al. (1986) to mixed solvent electrolyte systems) is also presented.

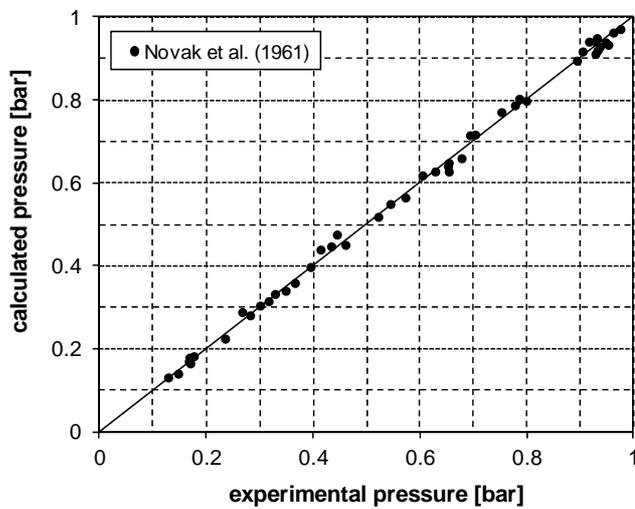


Figure 1: parity plot of the bubble point pressure for $\text{CO}_2\text{-H}_2\text{O}$ mixtures (low pressure data).

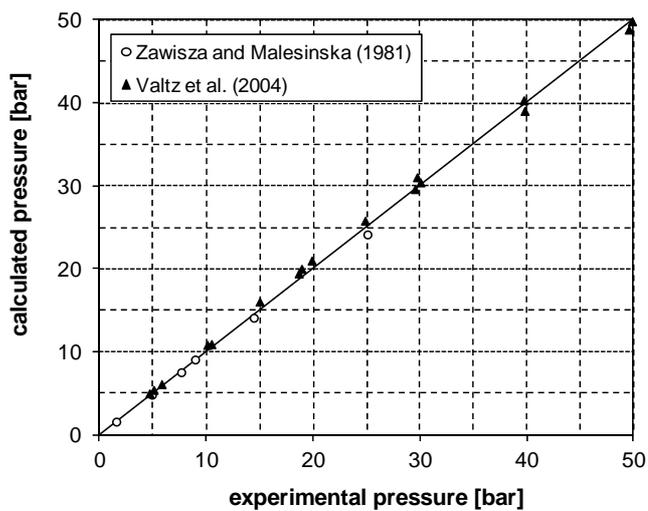


Figure 2: parity plot of the bubble point pressure for $\text{CO}_2\text{-H}_2\text{O}$ mixtures (medium-high pressure data).

3. Results and discussion

Both water scrubbing and chemical absorption have been simulated in order to find the absorbent flowrate needed for obtaining a 98 % v/v biomethane on a dry basis. Moreover the dependence of biomethane purity and methane recovery on the absorbent flowrate has been computed. Results have been reported in Figures 3 and 4 as function of the ratio between the total molar flowrate of the inlet absorbent (L_{in}) and the total molar flow rate of the inlet gas (G_{in}).

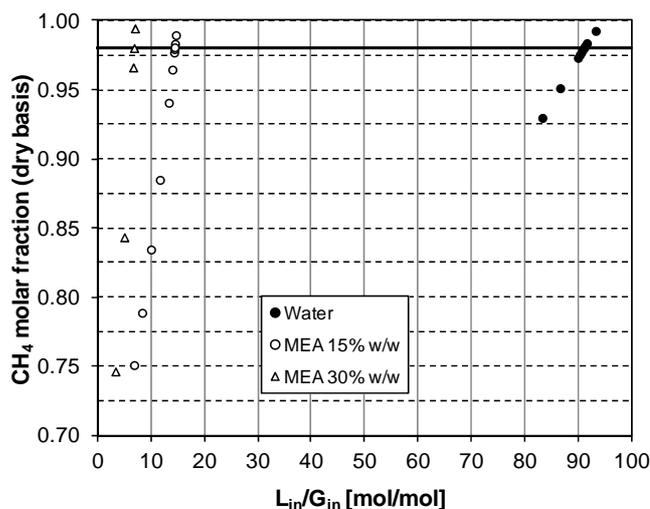


Figure 3: dependence of the molar fraction of methane in the obtained purified gas on the absorbent/gas molar flowrate ratio (the solid line shows the 98 % v/v desired purity) .

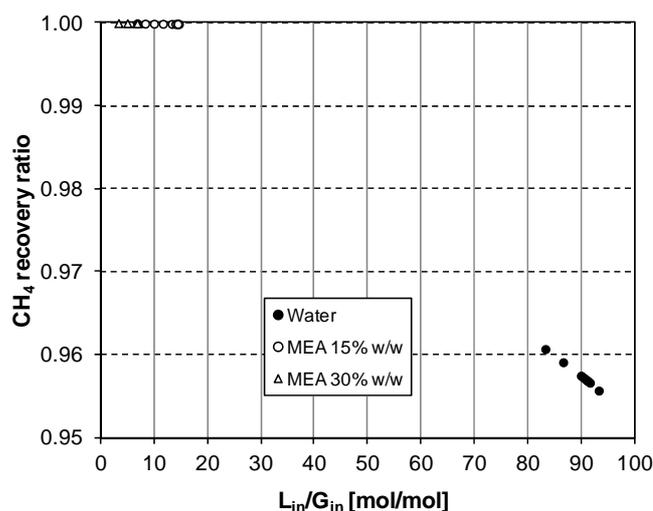


Figure 4: dependence of the methane recovery ratio on the absorbent/gas molar flowrate ratio.

Figure 3 clearly outlines the different solvent requirements between water scrubbing and chemical absorption. For the case analyzed in this study, the water requirement for a 20 bar pressure absorption is about 13 times the MEA 30 % w/w solution requirement and about 6 times the MEA 15 % w/w solution requirement for an atmospheric pressure chemical absorption. Moreover the chemical absorption ensures a total methane recovery while the water scrubbing is characterized by higher methane losses which exhibit a stronger dependence on the solvent flowrate than in the case of chemical absorption (Figure 4). The two advantages of the chemical absorption here highlighted present a drawback: due to the lower pressure and the higher temperature reached in the absorber, the purified gas coming from a chemical absorption is characterized by higher water content than that obtained from the water scrubbing. Among the MEA 30 % w/w solution and the MEA 15 % w/w solution, the last one ensures lower water content in the gas due to the lower absorption temperature.

Besides the above-mentioned key factors, several other aspects must be taken into consideration in order to decide when water scrubbing should be preferred over the chemical scrubbing and vice versa. For the sake of completeness they are highlighted in the following.

In a wastewater treatment plant, water is readily available for the physical absorption and no regeneration is needed since the CO₂-water mixture can be sent back to the treatment plant (Van Holde and Butler, 2008). On the other hand non-negligible compression work is needed.

Amine scrubbing, in any case, requires regeneration and an exhaustive technical-economic analysis should take into account whether heating sources at no or moderate costs are available for this purpose or not, and, in case, quantify the revenue losses if a fraction of the produced biogas is used for the amine regeneration. Furthermore the water content of the purified gas impacts on the subsequent gas drying facilities and, if chemical scrubbing is used, the absorption pressure could be slightly increased in order to obtain an acceptable compromise between the drying costs and the costs due to the gas compression work.

Finally, the pumping work for the solvent circulation must be taken into account. Thus lots of different factors must be considered when deciding what biogas upgrading purification must be preferred (also depending on the biogas source which, as in the case of biogas from municipal wastewater treatment plant sludge, could be linked to the absorbent source), but the correct calculation of the performances of the techniques to be potentially chosen is a necessary starting point.

4. Conclusions

In this work a comparison between water and MEA scrubbing for biogas purification has been made. The reliability of the thermodynamic model chosen for simulating the water scrubbing has been tested as well. The comparison has been based on key factors such as solvent requirement and methane recovery. This comparison is the necessary starting point for any other consideration to be made when deciding what upgrading technique must be chosen for biogas. These considerations will be developed in future works where the possible presence of H₂S in the biogas to be scrubbed will be considered along with the solvent regeneration (if necessary) and economic considerations.

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