Journal of Cleaner Production 141 (2017) 978–988

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

# Evaluation of biogas upgrading technologies using a response surface methodology for process simulation

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## ARTICLE INFO

*Article history:*
Received 5 October 2015
Received in revised form
2 August 2016
Accepted 20 September 2016
Available online 21 September 2016

*Keywords:*
Biomethane
CO2 capture
Process simulation
Response surface methodology

## ABSTRACT

Biogas is commonly upgraded to biomethane to produce a better biofuel. The aim of this work is to compare different types of solvents in biogas upgrading while using an absorber-stripper process. A conventional single-loop absorber-stripper process configuration was simulated with ProMax® for three types of solvents: diglycolamine (DGA), dimethyl ethers of polyethylene glycol (DEPG) and water. Absorption temperature, absorption pressure, CO2 concentration, solvent circulation rate and steam rate (only for DGA) were considered as varying parameters. The effects of these parameters on energy consumption, CO2 capture and CH4 recovery were studied by applying response surface methodology (RSM) to the simulations of the processes. The comparison of the processes at the optimum operating conditions for RSM with the three solvents has shown that the process with water is the simplest and most robust of the three, obtaining high levels of CO2 capture and CH4 recovery with the lowest energy consumption.

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## 1. Introduction

Challenges related to energy shortages are increasingly frequent both at the local and global scale. The growing demand for oil and natural gas caused by high consumption levels is one of the current major problems faced by the world population. Therefore, new forms of energy generation must be investigated that would eventually allow the diversification of the present energy matrix, which has an almost 90% dependence on fossil fuels in Argentina (SEN, 2014). Additionally, the harmful effects of releasing fossil fuels into the atmosphere also motivates finding alternative sources of energy to reduce these detrimental environmental effects, i.e., the generation of greenhouse-gas emissions that contribute to global warming absolutely must be reduced.

Biogas is a fuel produced from the anaerobic degradation of organic matter from various sources, e.g., domestic, industrial, agricultural, or sewage waste. The composition of biogas varies depending upon the source of its production, approximately 40–75% CH4, 25–55% CO2, 0–1% H2S, 0–3% N2 and water up to the saturation point (Rasi et al., 2007). Biogas is advantageous for several reasons. Biogas diversifies the energy matrix and solves problems related to contamination produced by biological wastes by lowering methane emissions. In addition, biogas upgrading allows the capture of CO2. The capture and reuse of CO2 is a technology that is currently being widely investigated as an option for mitigating climate change (Abanades et al., 2015). CO2 reuse or disposal should be considered within the biogas purification process to reduce the environmental effects.

Abatzoglou (2009) and Ryckebosch et al. (2011) discussed different methods of biogas upgrading. Furthermore, Tippayawong and Thanompongchart (2010) investigated the abatement of CO2 and H2S using aqueous solutions of salts and amines in a packed column at a pilot scale. In another pilot-scale study, Lombardi et al. (2011) analyzed the feasibility of eliminating CO2 from biogas produced at a landfill site, by employing an absorption column with an aqueous solution of potassium hydroxide. Among the existing biogas upgrading systems, the Binax process developed by Central Plants Inc., California, USA (Henrich, 1983) is notable. This process could be upgraded by redesigning the absorption column thus achieving the removal of siloxanes and halogenated compounds

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http://dx.doi.org/10.1016/j.jclepro.2016.09.167
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(Läntelä et al., 2012). A publication from IEA Bioenergy's Task 37 (Petersson and Wellinger, 2009) reviewed the latest developments in biogas upgrading and presented a list of upgrading plants and upgrading plant providers. In addition, numerous purification plants of natural gas and CO2 capture from flue gases (Rubin et al., 2012), which focus mainly on conventional absorption-desorption systems, are operational.

CO2 is the main component that must be removed from biogas. Because CO2 is present in high proportions in biogas, its removal increases the heating power of biogas and converts biogas into biomethane, which makes biogas equivalent to natural gas (Petersson and Wellinger, 2009). However, when applying different upgrading technologies, the loss of methane should be minimized not only to take advantage of its combustible properties but also to prevent the contribution of methane to global warming. Prior knowledge of natural gas absorber-stripper processes is useful in upgrading biogas (Nielsen and Kohl, 1997; Jenkins and Haws, 2001). Currently, those processes are also being used for CO2 capture from flue gases (Songolzadeh et al., 2014). For these processes, the cooling and heating duty and power requirements must be low in order to obtain the highest net energy. The power requirement is related to the power necessary for the operation of pumps and compressors used in the process. The cooling duty is required for the operation of the chillers. The thermal duty refers to the heat required to regenerate the solvent. For that reasons, is necessary to study these variables in the upgrading processes.

As the composition of biogas depends on its source, the robustness of the different upgrading processes must be assessed in relation with the different operating conditions, particularly, variations in the composition of raw biogas. This assessment serves as a first step in evaluating the feasibility of biogas production in Argentina. A complete evaluation of biogas upgrading involves a life cycle assessment with methane composition, carbon dioxide capture and energy as main variables (Starr et al., 2012; Morero et al., 2015).

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis in applications where a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery and Runger, 2003). Recently, some papers published the application of RSM related with CO2 adsorption (Gil et al., 2013; Serna-Guerrero, 2010) and others works focused on the optimization of anaerobic digestion processes (Tedesco et al., 2014; Rasouli et al., 2015). These authors analyzed especially the methane and biogas yields and production. In addition, there are applications of RSM to the renewable energy field: biodiesel production and assessment of exhaust emission levels (Mumtaz et al., 2014) and investment analysis for photovoltaic power generation plants (Bendato et al., 2015). For the optimization of CO2 capture with aqueous amine, Nuchitprasittichai and Cremaschi (2011, 2013) used RSM and artificial neural network. But until now, there are not papers which used RSM to optimize the operating parameters affecting absorption-desorption biogas upgrading processes that include CO2 capture and H2S elimination.

The aim of this work is to discuss and optimize for water, physical (DEPG) and chemical (DGA[1]) solvents the different operate parameters affecting absorption-desorption biogas upgrading: absorption temperature, absorption pressure, recirculation flow, and steam rate (only for the processes in which regeneration is obtained with vapor). The response surface methodology (RSM) was applied to identify the ideal levels of parameters that result in the best upgrading biogas process.

## 2. Methods

We employed response surface methodology, or RSM,[2] to the simulation to detect interactions between the factors and to model and analyze the response of interest, which is influenced by several variables. The outputs of computer experiments are deterministic (i.e., no random errors), the RSM design adopted is an unreplicated factorial designs. When analyzing data from unreplicated factorial designs, there is no internal estimate of error (or “pure error”).

The responses considered were CO2 capture, efficiency in the recovery of CH4, power required, cooling duty, reboiler duty and stripper pressure (these latter two parameters were analyzed only for DGA) all variables detected as important. To simulate the process for each solvent, the commercial simulator ProMax (ProMax®, 2013) with TSWEET® and PROSIM® was employed. The program has proved to be reliable in natural gas sweetening unit design with amines, and the ProMax capacities have been previously described by several authors (Gao et al., 2014; Luo et al., 2009). The simulator was previously calibrated with literature data (see Appendix). The Design Expert software (Design Expert, 2013) was employed for the RSM.

The biogas incoming stream into the purification process was comprised of the following: 58.4% CH4, 37.3% CO2, 1% N2, 0.1% H2S, 3.2% H2O at atmospheric pressure and room temperature. The biogas circulation rate was 250 m3/h. In the simulation analysis, CO2 and CH4 concentrations varied, but the concentrations of the other compounds were maintained.

### 2.1. Water upgrading process simulation

To purify the biogas with water, a conventional absorption/desorption system was simulated (Fig. 1a), in which the regenerated water was reutilized in the process. Regeneration occurred at low pressures in the desorption tower (71 kPa). To decrease methane losses, a low pressure tank (HP flash) was implemented (operating at 400 kPa) to return a fraction of the stream to the bottom of the absorber to recover methane. The pump efficiencies were 65%, the compressor efficiencies were 90%, and we considered 3 ideal trays.

The thermodynamic model used the Peng-Robinson equation of state (PR) to calculate the vapor phase fugacity and the Wilson model to calculate the activity coefficients of the liquid phase (Prausnitz et al., 2001). The model calibration was previously performed with data obtained from the literature (see Appendix).

### 2.2. DEPG upgrading process simulation

DEPG was selected among the physical solvents commercially used for natural gas treatment. This solvent allows the simultaneous abatement of H2S and CO2. Additionally, DEPG has a low vapor pressure, has a low absorption capacity for methane and has been used for biogas upgrading (Epps, 1992; Barzagli et al., 2014). Fig. 1b shows a diagram of the process. Two low pressure tanks (HP flash and LP flash) were placed between the absorber and the desorber, the first (HP flash) operating at 500 kPa (with solvent recirculation into the absorber to minimize the methane losses) and the second (LP flash) at atmospheric pressure. Solvent regeneration was performed at a low pressure (71.32 kPa). The pump efficiencies were 65%, and the compressor efficiencies were 90%. We considered 7 ideal trays, and the minimum end approach temperature in heat recovery was 3.33 K. The equation of state

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[1] DGA: diglycolamine.

[2] RSM: response surface methodology.

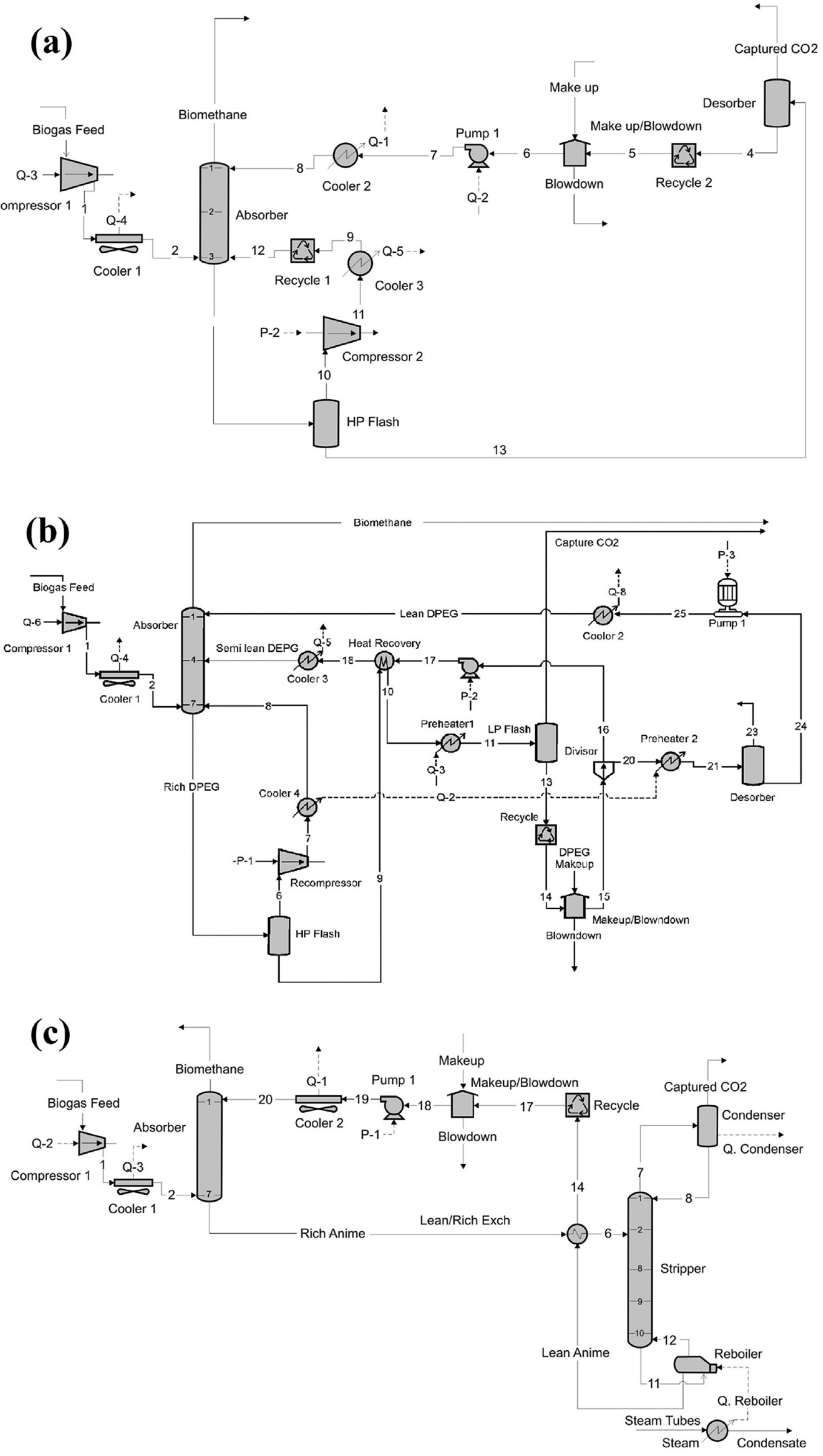

**Fig. 1.** Flow diagram of the biogas upgrading process with (a) water; (b) DEPG and (c) DGA.

selected to evaluate the thermodynamic behavior was the Soave-Redlich-Kwong (SRK) equation (Reid et al., 1977), which was previously validated with solubility data available in the literature (see Appendix).

### 2.3. DGA upgrading process simulation

The biogas upgrading process diagram with chemical solvents is shown in Fig. 1c. The selected amine was DGA because it was the best option in previous studies (Morero, and Campanella, 2013). In the ProMax® (with TSWEET® and PROSIM®) simulated absorption/desorption process, the low vapor pressure of H2S and CO2 over amine solutions was calculated using the Extended Long Range (ELR) electrolytic model (see Appendix). This model obtains the liquid phase activity coefficients with the Pitzer-Debye-Hückel model (Pitzer and Kim, 1974). A kinetic model in the absorber (TSWEET Kinetics) predicts the effects of residence time, temperature, solution concentration, pressure and amine type on the CO2 absorption velocity. The weight of the circulating solution was 50%, and we considered 7 ideal trays in the absorber and 10 ideal trays in the stripper. The residence time for each ideal tray was set at 2.5 s. The pump efficiencies were 65%, and the compressor efficiencies were 90%. The minimum end approach temperature in the reboiler was 31.98 K and was 5.49 K in the Lean/Rich exchange (see Fig. 1c).

### 2.4. Analysis of simulations

RSM are usually used in experiments in which various factors intervene and in which their combined effects on the response must be studied to find out the interactions between variables (Montgomery and Runger, 2003). For biogas upgrading with different solvents, the factors to be considered for the analysis change as a function of the solvent employed as discussed in Introduction. Table 1 shows the factors considered in each case and their respective levels.

The responses analyzed for the three solvents were: power requirement (W) cooling duty (W), recovered CH4 (%), captured CO2 (%), and in the case of DGA and DEPG, in which regeneration is performed with vapor, reboiler duty (W).

Once the experiment design for simulation was created, all simulations were performed using ProMax with the characteristics previously explained for each process. After the responses for each solvent were obtained, the Design Expert software was used for the ANOVA analysis (Analysis of Variance) and for the RSM, where a central composite design was employed. The optimization module in Design-Expert searches for a combination of the factors that simultaneously satisfy the requirements placed on each of the responses and factors. Design Expert uses a method developed by Myers et al. (2009), which describe a multiple response method called desirability. The method makes use of an objective function (desirability function) which reflects the desirable ranges for each response (0 least desirable, 1 most desirable). The numerical optimization provided by Design Expert was applied to the dataset of RSM for the best level of factors that maximizes the desirability function. The desirability function is comprised of the four studied responses and must satisfy the following conditions:

- Minimize Power Requirement (R1)
- Minimize Cooling Duty Requirement (R2)
- Maximize CH4 Recovered Efficiency (R3)
- Maximize CO2 Captured Efficiency (R4)
- Minimize Reboiler Duty Requirement (R5) (only for DGA and DEPG)

## 3. Results and discussion

### 3.1. Analysis of the simulations of the water upgrading process

Design Expert software provides various settings for the response and indicates which of the adjustment proposes are the best option for the answer studied. The adjustment can be polynomial type (quadratic, cubic, etc) or factorial type 2-factor interaction (2FI, 3FI, etc.). A factorial model is composed of a list of coefficients multiplied by associated factor levels. For polynomial models some of the factors within a term may raised to a power. The statistical software was used to generate the ANOVA (see Table 2) and the response plots. The ANOVA analysis indicates that the 2FI model is significant for the responses R1 and R2; and the quadratic model is significant for the responses R3 and R4. The regression models, which describe each response, are the following:

**R1: Power requirement (W)** $= +76783.34 + 49159.26 * A + 33009.96 * B + 25702.65 * AB$
**R2: Cooling duty (W)** $= +80574.82 + 50957.43 * A + 32256.25 * B - 4235.73 * C + 25293.69 * AB$
**R3: Recovered CH4 (%)** $= +97.40 - 3.87{*}B + 2.32{*}C - 0.35{*}D + 2.10{*}BC + 0.65{*}CD$

**Table 1**
Factors analyzed in the processes of biogas upgrading.

| Description | Level | | |
|---|---|---|---|
| | −1 | 0 | 1 |
| Solvent: water | | | |
| A: Absorption pressure, kPa | 500 | 2250 | 4000 |
| B: Solvent circulation rate, m3/h (Stream 8 in Fig. 1a) | 10 | 42.5 | 75 |
| C: Absorption temperature, K | 278.15 | 295.65 | 313.15 |
| D: Biogas feed CO2 concentration, % | 25 | 40 | 55 |
| Solvent: DEPG | | | |
| A: Absorption pressure, kPa | 500 | 1750 | 3000 |
| B: Solvent circulation rate, m3/h (Stream 15 in Fig. 1b) | 15 | 38.50 | 62 |
| C: Absorption temperature, K | 278.15 | 295.65 | 313.15 |
| D: Biogas feed CO2 concentration, % | 25 | 40 | 55 |
| Solvent: DGA | | | |
| A: Absorption pressure, kPa | 414 | 689 | 965 |
| B: Solvent circulation rate, m3/h (Stream 20 in Fig. 1c) | 1.36 | 2.95 | 4.54 |
| C: Absorption temperature, K | 288.71 | 316.48 | 338.71 |
| D: Biogas feed CO2 concentration, % | 25 | 40 | 55 |
| E: Steam rate, kg/m3 | 83.88 | 131.81 | 179.74 |
| F: Stripper pressure, kPa | 103.42 | 293.03 | 482.63 |

**Table 2**
ANOVA for (a) R1: Power requirement and (b) R2: cooling duty. (c) R3: CH4 recovered and (d) R4: CO2 Captured in the water upgrading process.

| Source[a] | SS | df | MS | F Value | p-value | |
|---|---|---|---|---|---|---|
| ANOVA for response surface 2FI model | | | | | | |
| **(a) R1: Power requirement (W)** | | | | | | |
| Model | 7,38E+10 | 10 | 7,38E+09 | 1130,48 | <0,0001 | **Significant** |
| A-Presure (kPa) | 4,35E+10 | 1 | 4,35E+10 | 6667,54 | <0,0001 | |
| B-Flow rate (m3/h) | 1,96E+10 | 1 | 1,96E+10 | 3006,39 | <0,0001 | |
| C-Temperature (K) | 1,82E+06 | 1 | 1,82E+06 | 0,28 | 0,6061 | |
| D-CO2 concentration (%) | 2,75E+07 | 1 | 2,75E+07 | 4,22 | 0,0592 | |
| AB | 1,06E+10 | 1 | 1,06E+10 | 1620,16 | <0,0001 | |
| AC | 3,97E+06 | 1 | 3,97E+06 | 0,61 | 0,4486 | |
| AD | 2,52E+07 | 1 | 2,52E+07 | 3,87 | 0,0694 | |
| BC | 1,09E+07 | 1 | 1,09E+07 | 1,67 | 0,2171 | |
| BD | 1,01E+05 | 1 | 1,01E+05 | 0,02 | 0,9028 | |
| CD | 2,07E+05 | 1 | 2,07E+05 | 0,03 | 0,8613 | |
| Residual | 9,13E+07 | 14 | 6,52E+06 | | | |
| Cor Total | 7,38E+10 | 24 | | | | |
| **(b) R2: Cooling task (W)** | | | | | | |
| Model | 7,62E+10 | 10 | 7,62E+09 | 513,71 | <0,0001 | **Significant** |
| A-Presure (kPa) | 4,67E+10 | 1 | 4,67E+10 | 3152,74 | <0,0001 | |
| B-Flow rate (m3/h) | 1,87E+10 | 1 | 1,87E+10 | 1263,28 | <0,0001 | |
| C-Temperature (K) | 3,23E+08 | 1 | 3,23E+08 | 21,78 | 0,0004 | |
| D-CO2 concentration (%) | 5,38E+07 | 1 | 5,38E+07 | 3,63 | 0,0775 | |
| AB | 1,02E+10 | 1 | 1,02E+10 | 690,47 | <0,0001 | |
| AC | 1,42E+07 | 1 | 1,42E+07 | 0,96 | 0,3449 | |
| AD | 3,77E+07 | 1 | 3,77E+07 | 2,54 | 0,133 | |
| BC | 1,97E+07 | 1 | 1,97E+07 | 1,33 | 0,2686 | |
| BD | 6,73E+04 | 1 | 6,73E+04 | 0,00 | 0,9472 | |
| CD | 4,64E+06 | 1 | 4,64E+06 | 0,31 | 0,5847 | |
| Residual | 2,08E+08 | 14 | 1,48E+07 | | | |
| Cor total | 7,64E+10 | 24 | | | | |
| ANOVA for response surface quadratic model | | | | | | |
| **c) R3: Recovered CH4 (%)** | | | | | | |
| Model | 469,01 | 14 | 33,50 | 29,77 | <0,0001 | **Significant** |
| A-Presure (kPa) | 4,31 | 1 | 4,31 | 3,83 | 0,0788 | |
| B-Flow rate (m3/h) | 269,80 | 1 | 269,80 | 239,75 | <0,0001 | |
| C-Temperature (K) | 96,62 | 1 | 96,62 | 85,86 | <0,0001 | |
| D-CO2 concentration (%) | 2,17 | 1 | 2,17 | 1,93 | 0,1949 | |
| AB | 0,11 | 1 | 0,11 | 0,09 | 0,7648 | |
| AC | 0,09 | 1 | 0,09 | 0,08 | 0,7786 | |
| AD | 0,28 | 1 | 0,28 | 0,25 | 0,6271 | |
| BC | 70,45 | 1 | 70,45 | 62,60 | <0,0001 | |
| BD | 4,28 | 1 | 4,28 | 3,81 | 0,0796 | |
| CD | 6,79 | 1 | 6,79 | 6,03 | 0,0339 | |
| Aˆ2 | 0,74 | 1 | 0,74 | 0,66 | 0,4369 | |
| Bˆ2 | 2,04 | 1 | 2,04 | 1,81 | 0,2078 | |
| Cˆ2 | 1,03 | 1 | 1,03 | 0,91 | 0,3614 | |
| Dˆ2 | 0,07 | 1 | 0,07 | 0,06 | 0,8125 | |
| Residual | 11,25 | 10 | 1,13 | | | |
| Cor Total | 480,26 | 24 | | | | |
| **(d) R4: Captured CO2 (%)** | | | | | | |
| Model | 23950,38 | 14 | 1710,74 | 17,63 | <0,0001 | **Significant** |
| A-Presure (kPa) | 3317,83 | 1 | 3317,83 | 34,18 | 0,0002 | |
| B-Flow rate (m3/h) | 13258,31 | 1 | 13258,31 | 136,60 | <0,0001 | |
| C-Temperature (K) | 1495,49 | 1 | 1495,49 | 15,41 | 0,0028 | |
| D-CO2 concentration (%) | 9,34 | 1 | 9,34 | 0,10 | 0,7628 | |
| AB | 7,47 | 1 | 7,47 | 0,08 | 0,7871 | |
| AC | 2,11 | 1 | 2,11 | 0,02 | 0,8858 | |
| AD | 330,06 | 1 | 330,06 | 3,40 | 0,095 | |
| BC | 297,23 | 1 | 297,23 | 3,06 | 0,1107 | |
| BD | 403,09 | 1 | 403,09 | 4,15 | 0,0689 | |
| CD | 1,30 | 1 | 1,30 | 0,01 | 0,91 | |
| Aˆ2 | 421,66 | 1 | 421,66 | 4,34 | 0,0637 | |
| Bˆ2 | 1380,40 | 1 | 1380,40 | 14,22 | 0,0037 | |
| Cˆ2 | 1,69 | 1 | 1,69 | 0,02 | 0,8975 | |
| Dˆ2 | 32,84 | 1 | 32,84 | 0,34 | 0,5737 | |
| Residual | 970,62 | 10 | 97,06 | | | |
| Cor Total | 24921,01 | 24 | | | | |

[a] SS: Sum of Squares; df: degree of freedom; MS: Mean Square; p-value: Prob > F.

**R4: Captured CO2 (%)** = + 89.62 + 13.58*A + 27.14*B - 9.11*C - 23.28*Bˆ2

Where A, B, C and D are the factors of Table 1.

Table 3 exposes the correlation coefficients value (r2). As can be seen, the values of r2, adjusted-r2 and predicted-r2 are close to 1 and so indicate that the adopted model is adequate. The achieved adequate precision is $\gg 4$, which indicates good model

**Table 3**
Correlation coefficients value for the different responses in water upgrading process.

| | Response 1 | Response 2 | Response 3 | Response 4 |
|---|---|---|---|---|
| r2 | 0.999 | 0.997 | 0.977 | 0.961 |
| Adjusted- r2 | 0.998 | 0.995 | 0.944 | 0.907 |
| Predicted- r2 | 0.995 | 0.989 | 0.818 | 0.689 |
| Adequate precision | 98.89 | 69.83 | 19.42 | 13.25 |

discrimination. Externally studentized residuals are reasonably close to the normal probability diagonal, so the developed models are adequate and fit the data with a normal distribution of probability.

The optimized numerical factors that were obtained are summarized in Table 4, which also shows the responses obtained by the ProMax simulation. The numerical optimization selected (desirability value nearest to 1) is the better set of conditions that met all the goals. The effect of factors (process variables) on the response is presented in two types of graphs: a perturbation plot and an interaction plot. The perturbation plot compares the effect of all the factors at a particular point in the design space. The response is plotted by changing only one factor over its range while holding of the other factors constant. By default, Design-Expert sets the reference point at the midpoint of all the factors. A steep slope or curvature in a factor shows that the response is sensitive to that factor. An interaction occurs when the response is different depending on the settings of two factors. Plots make it easy to interpret two factor interactions. They will appear with two non-parallel lines, indicating that the effect of one factor depends on the level of the other. The graphs belonging to the water upgrading process are showed in Fig. 2 (perturbation plot) and Fig. 3 (interaction plot). The graphs for the other processes could be found in the Supplementary material. A notable aspect of the RSM analysis was the change in the desirability region when the parameters varied within the selected ranges through graphical optimization in Design-Expert (Fig. 4). This type of study is useful in defining the optimum operating parameters according to the conditions originally imposed in the analysis and according to the desired gas purification levels. The overlay plot shows regions of desirable response by superimposing critical response contours on a contour plot and permit search for the best option.

The absorption pressure (curve A in Fig. 2) and water circulation rate (curve B in Fig. 2) are the main factors affecting the power requirement and the cooling duty. A significant interaction between these variables is observed, indicating that when the circulation rate is high, an important increase occurs in both responses when absorption pressure increases. This is not as noticeable when the circulation rate is low. This is shown in Fig. 3a for power requirement and in Fig. 3b for cooling water. The temperature is also an important factor affecting the cooling duty response. The analysis of variance summarized in Table 2 confirms these findings (p-value less than 0.05 indicates the significant model terms).

Analyses also showed that the circulation rate has the highest effect on the amount of CH4 recovered. A significant interaction between the circulation rate and the temperature was also detected. The interaction shows that when the temperature is high, increasing the flow does not significantly influence the amount of CH4 recovered. However, when the temperature is low (which favors the solubility of methane in water) an increase in the circulation rate reduces CH4 recovery. For the CO2 captured response, no significant interactions between the analyzed factors were observed. However, the circulation rate and absorption pressure are the factors that most affected the CO2 capture; an increase in both factors improves CO2 capture. The temperature is also an important factor affecting this response; a decrease in temperature factor improves CO2 capture. Fig. 4 show the response surfaces of the main factors which impact on the objective function (maintained the other factors in the midpoint) for the different response of the water upgrading process, and summarize the effect of the main factors as discussed.

The RSM analysis shown in Fig. 5a reveals that to satisfy the initial proposed conditions, the pressure must be above 1500 kPa, and the circulation rate must exceed 35 m3/h. At low temperatures (278.15 K), the desirable zone that satisfies both constraints (methane concentration > 90% and CO2 capture > 95%) is larger than when the temperature is high (313.15 K; limited by restricting CO2 capture > 95%) (Fig. 5b).

### 3.2. Analysis of the simulations for the DEPG upgrading process

The results obtained from the analysis of DEPG showed that both the solvent circulation rate and absorption pressure are the main factors that affect the energy requirements in the upgrading process with DEPG. In addition, the solvent circulation rate is the factor that has the highest effect on the recovery of CH4, showing a mild interaction with biogas feed CO2 concentration. The solvent circulation rate is the factor that most affects the CO2 captured

**Table 4**
Comparison of upgrading processes using optimal operating parameters and using the operating parameters (in brackets) to meet natural gas quality specifications.

| Properties | Solvent | | |
|---|---|---|---|
| | Water | DEPG | DGA |
| Factors | | | |
| Absorption pressure (kPa) | 2697 (4000) | 1666 (1666) | 414 (414) |
| Absorption temperature (K) | 285.15 (285.15) | 278.15 (278.15) | 288,15 (288,15) |
| Solvent circulation rate (m3/h) | 38.76 (55.00) | 38.33 (38.33) | 2.81 (2.81) |
| Regeneration pressure (kPa) | 71.32 (71.32) | 71.32 (71.32) | 103.32 (103.32) |
| Steam rate (kg/m3) | | | 83,88 (131.81) |
| Responses obtained by ProMax simulation | | | |
| Power required (kW) | 86.08 (146.34) | 81.28 (81.28) | 50.65 (78.72) |
| Cooling duty requirement (kW) | 90,76 (150.25) | 187.63 (187.63) | 111.40 (194.92) |
| Reboiler duty requirement (kW) | – | 104.48 (104.48) | 138.97 (229.21) |
| Energy demand of the process (%) | 8.65 (14.58) | 11.04 (18.43) | 22.92 (27.26) |
| CO2 capture (%) | 95.90 (97.30) | 99.33 (99.33) | 99.90 (99.98) |
| CH4 losses (%) | 3.54 (6.71) | 4.92 (4.92) | 0.15 (0.20) |
| CO2 content in upgraded biogas (%) | 2.91 (1.93) | 0.34 (0.34) | 0.07 (0.02) |
| CH4 content in upgraded biogas (%) | 95.23 (96.16) | 97.78 (97.78) | 97.6 (96.27) |
| H2S content in upgraded biogas (ppm) | 72.96 (50.69) | 1.93 (1.93) | 0.03 (0.003) |
| H2O content in upgraded biogas (%) | 0.06 (0.04) | 0.01 (0.01) | 0.55 (1.93) |

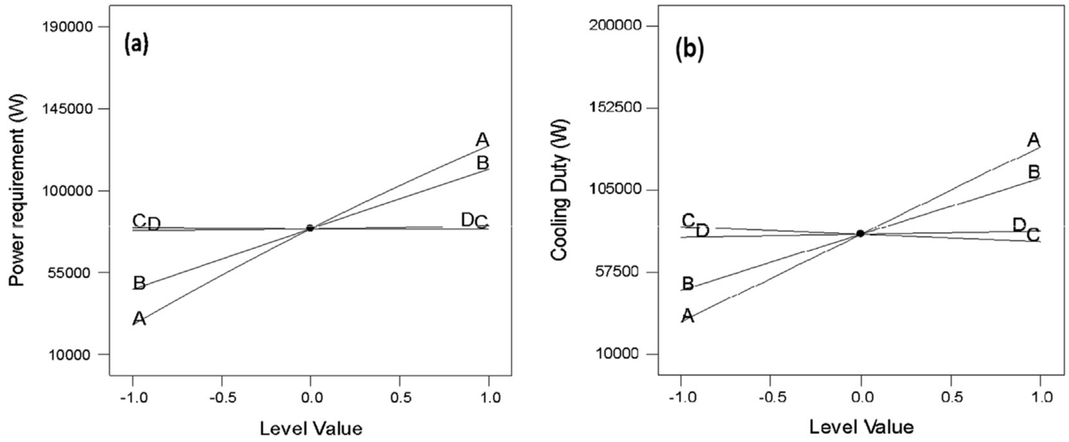

**Fig. 2.** Perturbation plot showing the effect of factors (process variables of Table 1) on the (a) power requirement; and (b) on the cooling duty in the water upgrading process.

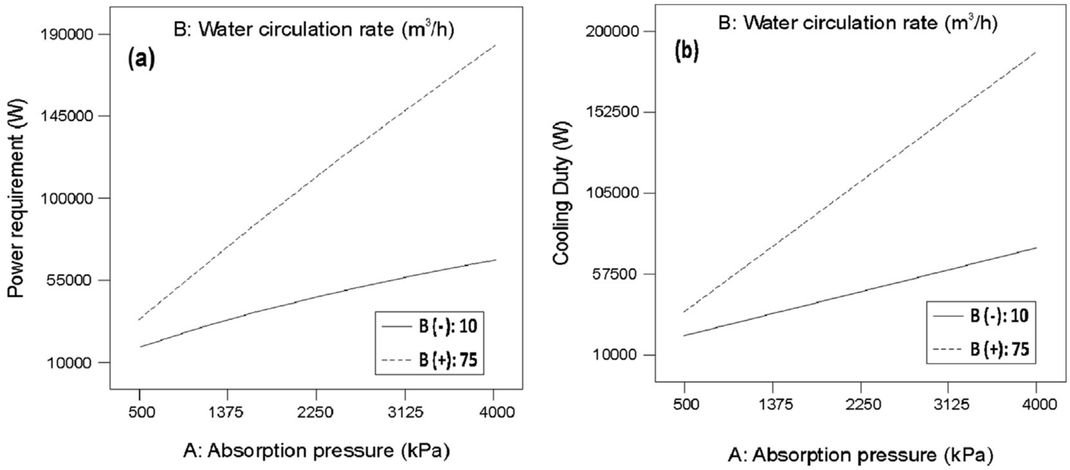

**Fig. 3.** Interaction plot showing the interaction between the absorption pressure (A) and water circulation rate (B) on the (a) power requirement; and (b) on the cooling duty in the water upgrading process.

response and a significant absorption pressure effect is also observed. These two factors are influenced by the CO2 concentration. The circulation rate must increase and work at higher absorption pressures when the CO2 concentration is high (55%).

The RSM analysis showed different desirable areas depending on the values adopted for each parameter. The analysis revealed that the temperature can be used in any of the values within the proposed range; although at 278.15 K the desirable zone is larger, and the process can work at lower pressures. Moreover, the results show that the pressure must be above 600 kPa to obtain a CO2 capture above 95%; this pressure is met only at low temperatures (<283.15 K) and high circulation rates (>45 m3/h). At high pressures (3000 kPa), the operational range covers the range of temperatures and a wide range of circulation rates (between 34 and 60 m3/h). The circulation rate must exceed 34 m3/h (to comply with restrictions on CO2 capture) and must be below 60 m3/h (to achieve a methane recovery above 90%).

### 3.3. *Analysis of simulations of DGA upgrading process*

The solvent circulation rate, stripper pressure and steam rate are the main factors affecting the power requirement and cooling duty. Increasing the circulation rate increases the power requirement; these consumptions are further stressed when the steam rate is high. When the steam rate and the circulation rate increase, the power consumption increases. This increase is even more marked when the stripper pressure is low. The cooling duty also increases with increases in the vapor and circulation rates, however in contrast to power consumption, the increase is more significant when the regeneration pressure is higher.

The reboiler duty response does not present interactions between factors. However, the steam and circulation rates are the main factors contributing to the increase of reboiler duty response.

In the analysis of the recovery of methane, several effects and interactions were observed, but the amount of CH4 recovered exceeded 99% in all cases. For that reason, we considered that the influence of the factors in this response was not relevant. The circulation rate, CO2 concentration and steam rate are the factors that most influence the CO2 captured. The interactions between these factors showed that when the initial concentration of CO2 is high, the circulation rate must be increased to achieve high levels of removal. This is related to the number of amine moles present in the solution; the amines react with CO2. When the initial composition of CO2 is low, an increase in the circulation rate does not significantly influence the final amount captured because enough amine is present to ensure the reaction with CO2. Moreover, the interaction between the flow and steam rate shows that when the steam rate is low, the circulation rate must be increased to achieve high levels of CO2 captured. When the steam rate is low, the regeneration of the amine solution is unfavorable. Therefore, to

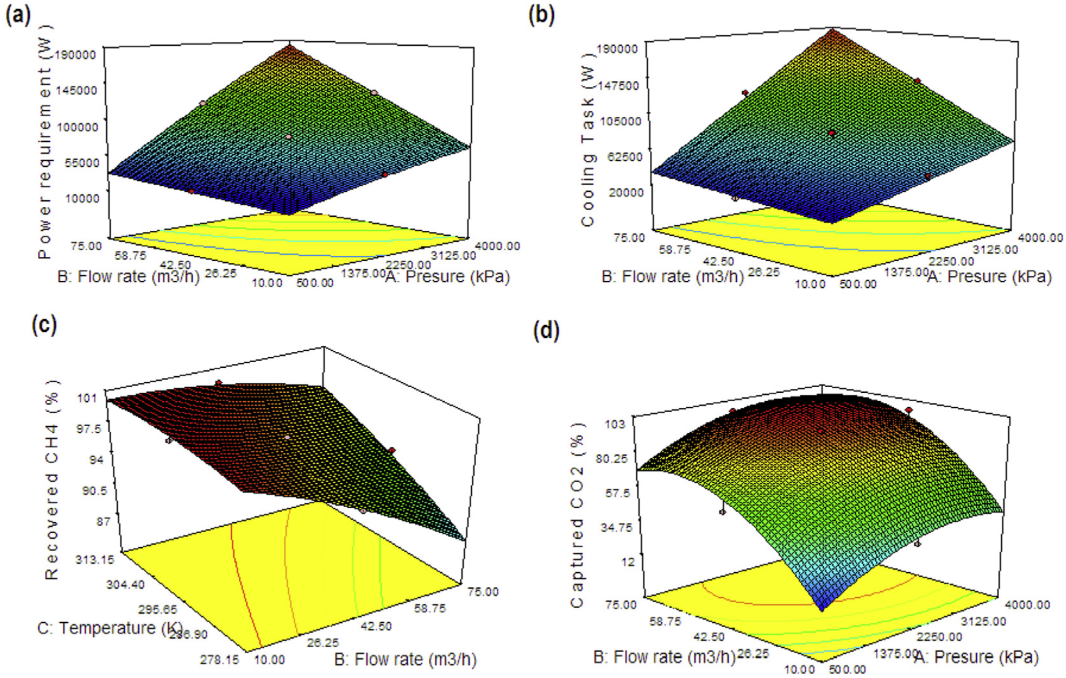

**Fig. 4.** Response surfaces of the main factors which impact on the objective function (maintained the other factors in the midpoint) for (a) power requirement (b) cooling duty (c) CH4 recovered and (d) CO2 Captured, in the water upgrading process.

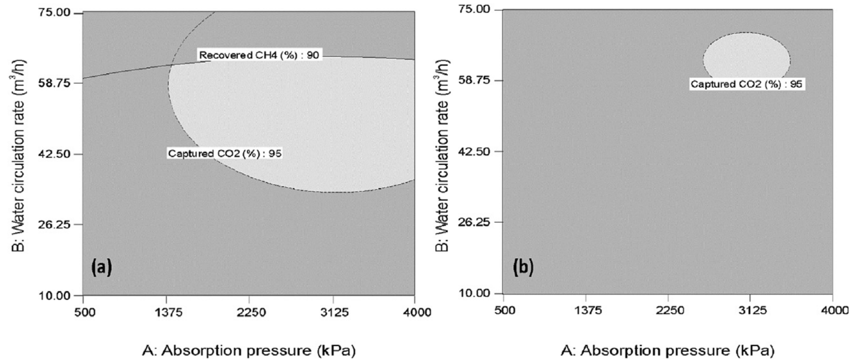

**Fig. 5.** Overlay plot showing the region of an optimal factor (process variables of Table 1) at a CO2 concentration of 40% and absorption temperature of (a) 285.15 K or (b) 313.15 K in the water upgrading process.

achieve certain CO2 removals, the two most important variables to define are the flow and steam rate. However, this analysis shows the lack of robustness in the process for large variations in the initial biogas composition.

The desirable region does not vary significantly when the parameters changed from the minimum to the maximum. This indicates that in the proposed range, the process efficiently captures CO2 and recovers CH4. The variable which conditions the CO2 capture is the circulation rate.

### 3.4. Optimized simulation of the upgrading processes

RSM allows us to identify the effect of the main parameters of the conventional absorption-desorption processes and to observe their influence and the interactions.

In the physical solvent processes (water and DEPG), the circulation rate and absorption pressure are the main parameters influencing the power required and the cooling duty; both the circulation rate and absorption pressure are also responsible for the process efficiency through CO2 capture and CH4 recovery.

In the chemical solvent process (DGA), the circulation rate, the steam rate and the stripper pressure exert a high influence on the power required, on the reboiler duty and on the cooling duty. The amount of CO2 present in the biogas feed also influences the chemical solvent process. Moreover, RSM results have shown that the recirculation rate and steam rate are the key factors in achieving a high efficiency in the CO2 captured. However, the DGA flow rate and the steam rate selected must ensure the maximum rich loadings (0.35 mol of acid gas/mol of amine) and approach the equilibrium method. Because of corrosion problems, these maximums cannot be ignored.

The simulation results with the optimized parameters selected with RSM are shown in Table 4. The operating conditions displayed in the table are consistent with the information available in the literature for each process analyzed. The range of operating pressure for water upgrading is in the literature 600–2200 kPa and the range of operating temperature is 10–25 °C (Hagen and Polman, 2001). In the literature DEPG upgrading process the operating pressure ranges from 1000 to 2500 kPa and the operating temperature from 7 to 35 °C (Epps, 1992; Hagen and Polman, 2001).

While for literature DGA upgrading the operating pressure is between 100 and 200 kPa (Bauer et al., 2013). Typical value of CH4 purity is around 94–98% for water upgrading, between 95 and 98% for DEPG upgrading and between 98 and 99% for amine upgrading (Starr et al., 2012; Hagen and Polman, 2001; Bauer et al., 2013). An advantage to organic solvents, such as DEPG and DGA, is that CO2 is more soluble in them than in water. Therefore, organic solvents can remove higher amounts at lower pressures, and this is reflected in the high efficiency of CO2 capture (>99%). The process that uses DGA as a solvent obtains the highest levels of CO2 capture (99.90%); however, because CH4 is not soluble in DGA, the loss of CH4 is low (0.15%). Considering the amount of water present in the upgraded biogas, the physical processes (water and DEPG) have the lowest amount and, therefore, would not require a subsequent gas drying step. However, in those processes, CH4 losses are high (>3.5%). With regard to H2S removal, the processes with DEPG and amines reduced the H2S concentration. In the case of the amines, the H2S concentration complies with natural gas quality standards; therefore, the amine process requires no extra step to remove this compound. When upgrading with water, a prior step to remove H2S will be required; however this pre-treatment step is also recommended for all upgrading processes to avoid corrosion problems. Corrosion problems could also occur during amine regeneration. Corrosion could be controlled by working at lower temperatures, reducing the concentration of amines in the solution and adjusting the acid gas loading (moles of acid gas/moles of amine). The major advantage observed with the water process is that the process requires less cooling duty than the others processes and additional heat is not necessary. In spite of accomplishing the optimization conditions (CH4 recovery> 90% and CO2 capture> 95%), water upgrading is the process with the lowest amount of CO2 captured (95.90%). Furthermore, the CO2 concentration in biomethane exceeds Argentina natural gas quality standards. To achieve local gas quality standards (CO2 concentration less than 2%) using water as a solvent, this process will require an increase in the circulation rate and absorption pressure because these factors have been shown to be the most influential parameters in the CO2 capture process with water.

Taking into account the considerations above, operating conditions were modified. In the water process, the absorption pressure was increased to 4000 kPa, and the circulation rate was increased to 55 m3/h to comply with natural gas quality requirements. The amine process was modified to ensure maximum rich amine loadings (0.35 mol of acid gas/mol of amine) and to approach the equilibrium method. Therefore, the steam rate was increased to 131.81 kg/m3 to reduce the maximum load at 0.344 mol acid gas/mol amine. Table 4 also shows a comparison of the three processes at these new conditions (numbers in brackets). This new comparison shows that the water process significantly increases the power required because of the rise in the absorption pressure and circulation rate. However, this process demanded less cooling duty and did not require heat.

The use of water as an absorbent presents several advantages over the other two processes, such as the simple design of the plant in which, in contrast to what happens with DGA, it is not necessary to use a vaporizer for the regeneration of the solvent or to add two low pressure tanks, as is the case with DEPG. Moreover, this solvent is easily available at low costs and does not react with certain trace compounds (COS, $O_2$) which may be present in the biogas from sanitary landfills. When compared with amines, water has the advantage of not including nitrogenated solvent vapors in the gas stream (Nielsen and Kohl, 1997). However, the removal of H2S in a previous stage is recommended in this particular process because, when dissolved in water, H2S can produce corrosion problems in equipment. In addition to, CO2 dissolving into water can acidify the solution and also produce corrosion. Working at low temperatures is favorable with respect to corrosion, and the absence of heat exchangers reduces the amount of exposed corrodible metal. The CH4 losses are higher for water. The losses of methane displayed in Table 4 is the CH4 present in the captured stream of CO2 and it is only a part of the “methane split” that includes additional methane losses due to problematic equipment. Beside lower profit, methane losses are significant because methane, as a greenhouse gas, is 21 times more harmful than CO2. However, its environmental impact would depend of the final disposal of the captures CO2 stream.

The amines absorption is the least robust of the three compared processes. In the RSM analysis, the CO2 concentration of crude biogas influences the CO2 capture. This influence is not so marked in the physical processes. One disadvantage of using amines is that they consume a high amount of energy in the recovery stage of the solvent, causing the thermal duty to increase significantly to meet the amine maximum load to prevent corrosion. However, the amine process employs the lowest power requirement of the three processes (78.72 kW) because of low circulation rates and absorption pressures, as reported in the literature (Starr et al., 2012; Hagen and Polman, 2001). However, the cooling task remains the highest of the three compared technologies.

By comparing the energy consumption in terms of an equivalent unit, the most energy efficient process of the three options can be determined. To obtain these values, the different types of energy (power, heating and cooling) were converted into tonnes of oil equivalent (toe). As shown in Table 4, upgrading with water is the process with the lowest energy demand (%) of the three solvents analyzed.

## 4. Conclusions

The methodology employed (RSM) is useful to understand, from a wide point of view, the main factors that influence some chemical processes and allow us to detect the most sensitive parameters affecting the process. In the physical solvent processes (water and DEPG), the circulation rate and absorption pressure are the main parameters influencing the power required and the cooling duty; both the circulation rate and absorption pressure are also responsible for the process efficiency through CO2 capture and CH4 recovery. In the chemical solvent process (DGA), the circulation rate, the steam rate and the stripper pressure exert a high influence on the power required, on the reboiler duty and on the cooling duty. The amount of CO2 present in the biogas feed also influences the chemical solvent process. Moreover, RSM results have shown that the recirculation rate and steam rate are the key factors in achieving a high efficiency in the CO2 captured. The response surface methodology (RSM) was applied to identify the ideal levels of parameters that result in the best upgrading biogas process. Using RSM, we detect the desirable response zone for the capture of CO2, recovery of methane, power, cooling and reboiler duty requirements. The highest CO2 capture and the lowest CH4 loss were obtained with DGA absorption. It also has the advantage of removing H2S to acceptable levels in biogas. The main disadvantages of the amine include requiring a large amount of steam. An advantage of the physical solvent processes is the low concentration of water in the upgraded biogas (no additional step to dry the gas is required). Finally, the process using water is the simplest with the lowest energy consumption. The response surface methodology (RSM) can be applicable to others upgrading processes, where different parameters affect its optimum performance.

## Acknowledgments

The authors acknowledge the financial support received from the Universidad Nacional del Litoral (UNL)(Project Nº 50120110100269LI) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

## Appendix A. Thermodynamic model calibration

### A.1. Biogas-water model

To calibrate the equilibrium model in ProMax simulator, the binary systems (CH4-H2O, H2S-H2O, CO2-H2O) were analyzed and compared with data available in the literature (Chapoy et al., 2004; Valtz et al., 2004; Chapoy et al., 2005a, b). Calculations were performed within the range of interest for the purification of biogas (283–313 K) for different pressures. It was considered the solubility of each compound in water and the water content in CH4, H2S and CO2. In all cases standard deviations ranging from 1 to 10% were obtained, except for the solubility of CO2 in water where the deviation was 25%. Then a pilot plant obtained from the literature (Läntelä et al., 2012) was simulated. The thermodynamic model used the Peng-Robinson equation of state (PR) to calculate the vapor phase fugacity and three models to describe the condensed aqueous phase were compared (Peng Robinson, Wilson and the electrolytic equation Extended Long Range). The model Wilson-PR scored low deviation in the values of CH4 losses and CO2 reduction. The model PR scored the lowest values of deviation in CO2 reduction, but the deviation in the CH4 losses was very high to consider it a good choice. Furthermore, from these simulations it was concluded that the design of the absorption column gives 3 theoretical plates.

### A.2. Biogas-DEPG model

In the literature there is scarce solubility data of the gases present in biogas in DEPG (Burr and Lyddon, 2008). Nevertheless, the data compared (at 25 °C and 1 atm) showed very good results with standard deviations ranging between 1 and 13%.

### A.3. Biogas-amine model

To calibrate the thermodynamic model, the experimental and calculated partial pressure of CO2, H2S and CH4 in aqueous solutions of MDEA and MEA were compared (Kuranov et al., 1996; Carroll et al., 1998), to temperatures ranging from 313 to 413 K and pressure between 0 and 10 MPa. Simultaneous solubility of CO2 and H2S was also simulated in an aqueous solution of MDEA, with methane as inert compound (Huttenhuis et al., 2009). The simulation was done at a temperature of 298 K and pressures between 6.9 and 69 bar. The simulator fits well the experimental and calculated data, with deviations between 3 and 20%. The highest deviation was observed in the CO2. From the information available in the literature it was concluded that the design of the absorber column contain 7 theoretical plates and the regenerator contain 10 theoretical plates.

## Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2016.09.167.

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