

Use of Recycle for H₂S Removal by MDEA Scrubbing in IGCC Systems

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This work focuses on the analysis of the H₂S removal section of an Acid Gas Removal (AGR) station in an Integrated Gasification Combined Cycle (IGCC) plant.

The AGR station is composed of one absorption section for H₂S and one absorption section for CO₂. The first section aims at removing most of the hydrogen sulfide from the syngas in order to obtain, in the following unit for the CO₂ removal, a CO₂-rich stream containing less than 200 ppmv of H₂S on a dry basis. The H₂S-rich stream obtained from the regeneration and exiting the H₂S removal section is sent for sulfur recovery in a Claus plant, which needs a minimum content of H₂S in the feed.

The acid gas removal is performed by using an aqueous solution of MethylDiEthanolAmine (MDEA). Although it selectively absorbs hydrogen sulfide, part of carbon dioxide is co-absorbed with H₂S, and the minimum content in H₂S required for feeding the Claus plant may be not achieved. A recycle of the H₂S-rich stream exiting the regeneration to the absorption section is not usually employed in these systems, but it has been considered for increasing the amount of hydrogen sulfide absorbed and therefore present in the H₂S-rich stream at the outlet.

A sensitivity assessment has been performed in this work to determine the influence of the recycle stream on the overall absorption process and the minimum amount of the flowrate necessary to accomplish the required specifications.

1. Introduction

Several technologies are available and currently studied for industrial applications to meet greenhouse gas emissions reduction targets. Possible strategies may be the enhancement of energy efficiency, the use of clean coal technologies, as well as carbon capture and storage (CCS).

In the context of studies for reduction of emissions, application of CCS to IGCC power plants may be considered. The coal-derived fuel is pre-treated before combustion for power production, both for H₂S and for CO₂ removal. The purification can be performed by chemical absorption with amine aqueous solutions, for which many studies mainly focused on post-combustion capture (Nagy et al., 2017), involving the modelling (Austgen, 1989; Derks, 2006; Dugas, 2006; Hillard, 2004; Pacheco, 1998; Plaza, 2012) and the simulation of process schemes (Cousins et al., 2011a; Cousins et al., 2011b; Nagy and Mizsey, 2015), can be found in the literature.

Among several types of amines, MethylDiEthanolAmine (MDEA) is characterized by different reaction rates of hydrogen sulphide and of carbon dioxide in the solution: those of H₂S are instantaneous, while those of CO₂ are finite and slow with respect to the mass transfer rate (Kohl and Nielsen, 1997). This difference in the reaction rate makes the MDEA absorption system kinetically selective towards hydrogen sulphide, so it is used for purification of several gaseous streams, in particular when both the two acid gases are present, as in the case of pre-combustion purification of the sour syngas, as considered in this work.

A CO₂-rich stream with characteristics suitable for CO₂ compression, with very low amount of hydrogen sulfide can then be recovered. Two different streams of acid gas can be obtained from the AGR removal plant, as reported also in previous papers (Giuffrida et al., 2016; Moioli et al., 2016).

2. Simulation

The IGCC plant has been simulated by means of the code GS, a proprietary simulation tool developed by the GECOS group of Politecnico di Milano, which has proved to yield highly accurate results for several power plant configurations (Giuffrida et al., 2010; Giuffrida et al., 2011; Giuffrida et al., 2013a,b; Giuffrida and Bonalumi, 2016).

The acid gas removal plant has been simulated in ASPEN Plus[®], which has been customized for the representation of the process. In particular, proper thermodynamic parameters for the Electrolyte-NRTL model have been used (Langé et al., 2013; Pellegrini et al., 2013) and a Fortran external subroutine, developed and linked (Moioli and Pellegrini, 2015a) to the process simulator by the GASP group of Politecnico di Milano has been employed. More information about the methodology can be found elsewhere (Langé et al., 2015; Moioli et al., 2017a; Moioli and Pellegrini, 2015b, 2016).

3. Description of the Plant

3.1 The IGCC Plant

The IGCC system considered in this work is the one investigated in a previous paper (Giuffrida et al., 2016) and consists of an advanced plant based on air-blown coal gasification with CO₂ capture. Reference to Giuffrida et al. (2016) for a detailed description of the IGCC is here made for the sake of brevity.

The syngas stream obtained from the gasification section, after water-gas shift reaction and cooling, has a flowrate of 269.42 kg/s and is available at 35 °C and 24.11 bar. The mixture is composed of 0.527 % Ar, 0.505 % CH₄, 0.816 % CO, 26.995 % CO₂, 26.526 % H₂, 0.233 % H₂O, 0.042 % H₂S and 44.356 % N₂.

3.2 The AGR Section

The Acid Gas Removal (AGR) station is composed of one absorption section for H₂S and one absorption section for CO₂. The first section aims at removing most of the hydrogen sulfide from the syngas in order to obtain, in the following unit for the CO₂ removal, a CO₂-rich stream containing less than 200 ppmv of H₂S on a dry basis according to the EBTF guidelines (EBTF, 2011). The H₂S-rich stream from the regeneration and exiting the H₂S removal section is sent to a Claus plant, which needs a minimum content of H₂S in the feed of 20 % (mole basis) (Kohl and Nielsen, 1997).

In the absorption column for the removal of hydrogen sulfide, some carbon dioxide may react with the aqueous amine solution and be co-absorbed with H₂S. However, the co-absorption of carbon dioxide can be accepted if the overall stream exiting the top of the regeneration section is able to fulfill the specifications required for feeding a Claus plant for sulfur recovery.

In the case of the sour gaseous stream considered, the minimum content in H₂S required for feeding the Claus plant may be not achieved, because of the lower amount of hydrogen sulfide present in the system. Thus, a recycle of the H₂S-rich stream exiting the regeneration to the absorption section has been taken into account. It is not usually employed in these systems, but it can help in increasing the amount of hydrogen sulfide absorbed and therefore to increase the H₂S-to-CO₂ ratio in the H₂S-rich stream at the outlet.

A detailed description of the H₂S removal section, on which the paper is focused, is reported in the following. Both the scheme without recycle and the one with recycle have been taken into account.

H₂S removal: scheme without recycle

The H₂S removal section is composed of two parallel trains, each one treating half of the overall gas flowrate. Figure 1 shows one train. The sour syngas (1) is fed to the absorber, together with a recycle of gases unreacted in the Claus plant (assumed to be 4 % of the fed hydrogen sulfide and 100 % of the fed carbon dioxide), and exits this unit purified from H₂S. The solvent, exiting the bottom of the same unit, is rich in H₂S and in co-absorbed CO₂. It is sent to a flash unit, operated at atmospheric pressure, for partial regeneration. The flash unit is included to remove most of the co-absorbed carbon dioxide, which shows a lower bond with the MDEA solution in the liquid phase if compared to hydrogen sulfide, and tends to transfer to the vapor phase more than H₂S. The vapor stream (8) exiting the flash vessel is sent to the CO₂ removal section together with stream (5), and, after compression, is mixed with it for feeding the CO₂ absorber. Reference to Giuffrida et al. (2016) is here made for a detailed description of the CO₂ removal section. The liquid stream (9) is heated by a countercurrent heat exchanger with the hot lean amine (12) exiting the reboiler and is fed to the regeneration column, where acid gases are removed and exit the top of the column as stream (11) for being fed to a Claus plant.

Results from simulations of this scheme in Figure 2 show that for any solvent flowrate chosen, the column is not able to perform the desired separation. H₂S is absorbed, so that the H₂S content in the CO₂-rich stream exiting the regeneration section of the following CO₂ removal section remains below 200 ppm (left axis of

Figure 2), but too much carbon dioxide is co-absorbed, and the specifications for feeding a Claus plant are not satisfied (right axis of Figure 2).

H₂S removal: scheme with recycle

As shown in Figure 2, the determination of the liquid rate for the selective absorption of hydrogen sulfide is complicated by the co-absorption of carbon dioxide. For the base scheme treating the syngas stream with the composition reported in Section 3.1, a minimum amount of solvent flowrate able to satisfy all the required specifications for the H₂S absorption section cannot be determined, so the use of the recycle has been introduced.

The modifications are shown in Figure 3. The H₂S-rich stream (12) is split into stream (13), sent to the Claus plant, and into stream (14), which is recycled back to the absorber, after mixing with stream (2) and compression to the operating pressure of the absorber. Stream (2), as in Figure 1, contains the amount of species unreacted in the Claus plant and it is recycled back for processing into the absorber.

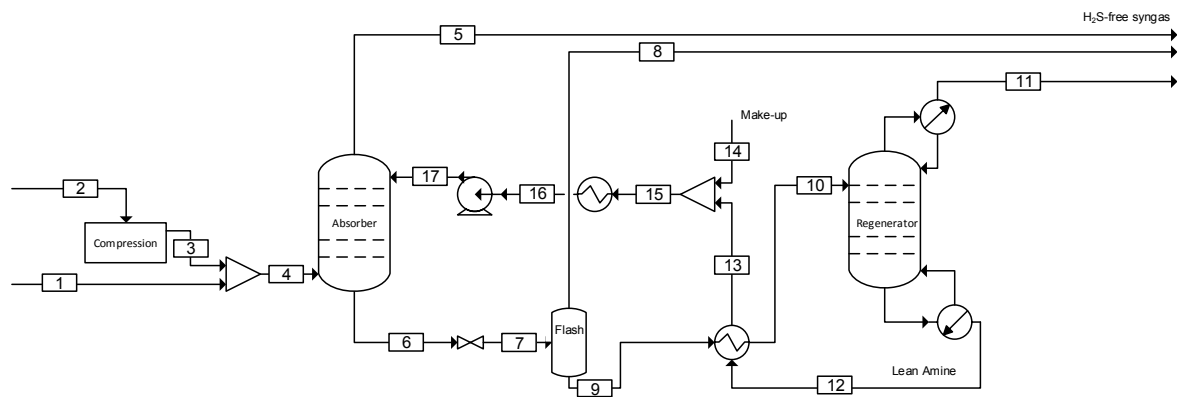


Figure 1: Scheme of the H₂S removal section without recycle.

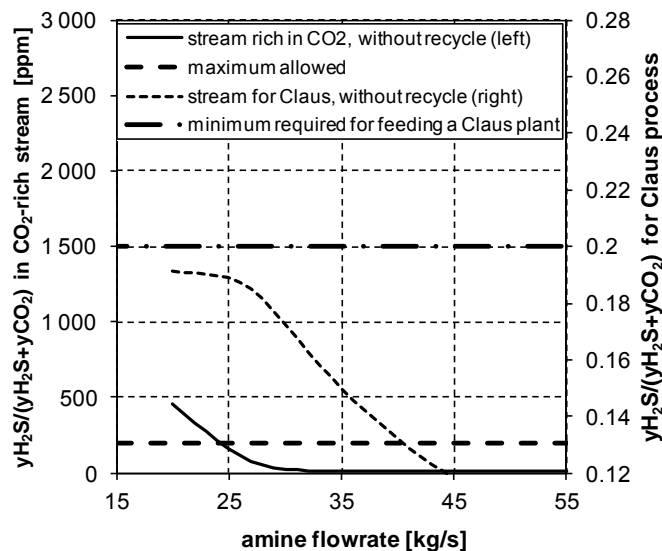


Figure 2: H₂S content in the CO₂-rich stream sent to compression (left) and in the acid gas rich stream exiting the top of the regeneration column (right) by varying the solvent flowrate for the scheme without recycle.

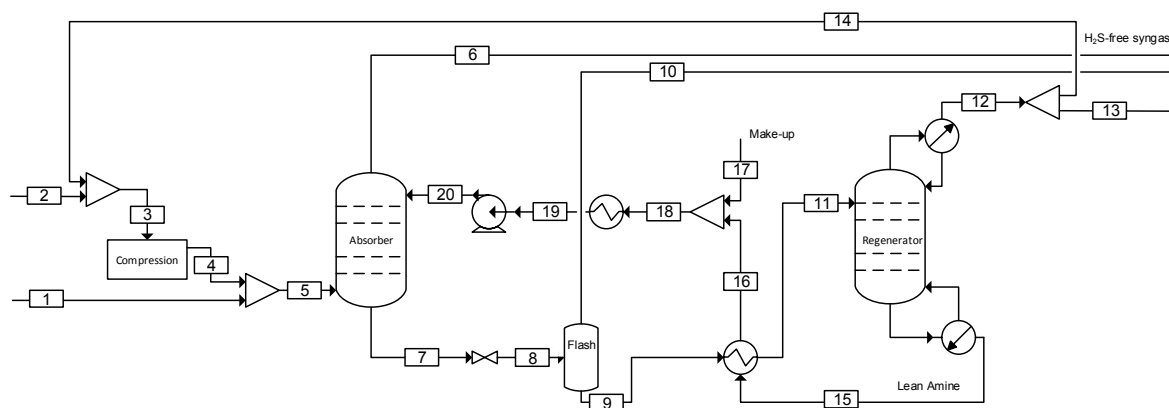


Figure 3: Scheme of the H₂S removal section with recycle.

The flowrates in stream (13) and stream (14) have been chosen on the basis of the sensitivity analysis described in Section 4.

4. Sensitivity Analysis

A sensitivity analysis on the ratio of flowrates of stream (13) and of stream (14) in Figure 3 has been carried out in order to determine the minimum flowrate for the recycle stream (14) able to perform the desired separation. The specifications to be satisfied are:

1. H₂S content in CO₂-rich stream exiting the CO₂ removal section and sent to compression lower than 200 ppmv, according to the EBTF guidelines (EBTF, 2011);
2. H₂S content in the H₂S-rich stream exiting the H₂S removal section and sent to the Claus plant higher than 20 % (mole basis), according to Kohl and Nielsen (Kohl and Nielsen, 1997).

The analysis has been done based on values for the split fraction of stream (12) into stream (14) equal to 10 %, 20 %, 30 %, 40 % and 50 %. The complementary % split fraction is considered for stream (13).

For each split fraction, the solvent flowrate has been varied to check whether the required specifications are matched. For high removal of hydrogen sulfide, the first specification may be satisfied, while a co-removal of carbon dioxide may cause the second specification not to be fulfilled.

Determining the possible flowrate (if present for a given recycle % split fraction) results therefore fundamental for achieving the desired composition of all the products in this system.

5. Results

Figure 4 and Figure 5 show the results of the sensitivity analysis.

For a split fraction lower than 30 %, the desired specifications cannot be achieved. In case of a split fraction of 20 %, for instance, the specification on the CO₂-rich stream sent to compression is fulfilled for flowrates of the amine solvent larger than 29 kg/s. However, a hydrogen sulfide content higher than 20 % in the acid gas stream to be sent to the Claus plant is not obtained for any considered flowrate.

A very tiny range of possible operation is available if a split fraction equal to 30 % is chosen. The overall flowrate of the amine solution should be at minimum equal to 30 kg/s in order to achieve 200 ppmv of H₂S in the CO₂-rich stream, but should not be higher than 31 kg/s to fulfill the specifications for feeding a Claus plant. Recycle split fractions of 40 % and 50 % result better in terms of extension of the range for which the circulating rate of solvent may be chosen.

Because of the higher circulating solvent, the resulting reboiler duty with recycle 50 % is about 20 % higher than the one with recycle 40 %. However, the total amount for the H₂S section is limited (Giuffrida et al., 2016) and it does not significantly affect the overall energy requirement of the acid gas removal station, being the one of the CO₂ removal section one order of magnitude higher (Giuffrida et al., 2016). The section for carbon dioxide purification is the one for which studies about possible energy saving solutions need to be performed (Moioli et al., 2017b).

A 50 % split flow ratio has the advantage of a higher operating range (if flexibility is needed) and of presenting a higher total liquid flowrate, which is a benefit for the considered absorption column, because of the

large diameter and the very low liquid-to-gas ratio (L/G). Moreover, since stream (13) and stream (14) have the same composition, if the flowrates are equal (as in the case of 50 % split fraction), an indirect further advantage may be obtained by the purchase and the installation of identical pipelines. According to these considerations, the scheme with recycle of 50 % can be chosen for the H₂S removal section.

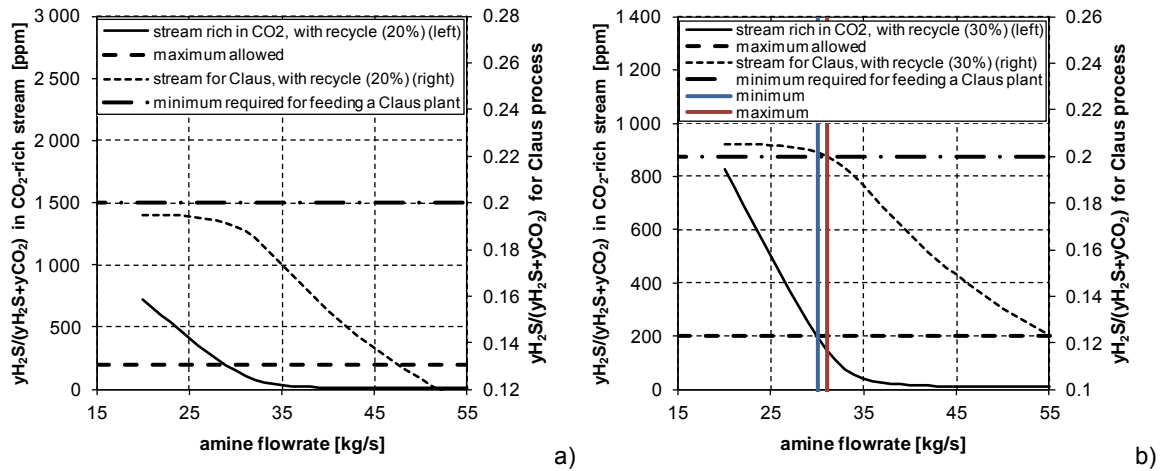


Figure 4: H₂S content in the CO₂-rich stream sent to compression (left) and in the acid gas rich stream exiting the top of the regeneration column (right) by varying the solvent flowrate for the scheme a) with recycle 20 % and b) with recycle 30 % (“minimum”, the vertical line on the left, and “maximum”, the vertical line on the right, indicate the lower and the higher limits of the acceptable operating range, when present).

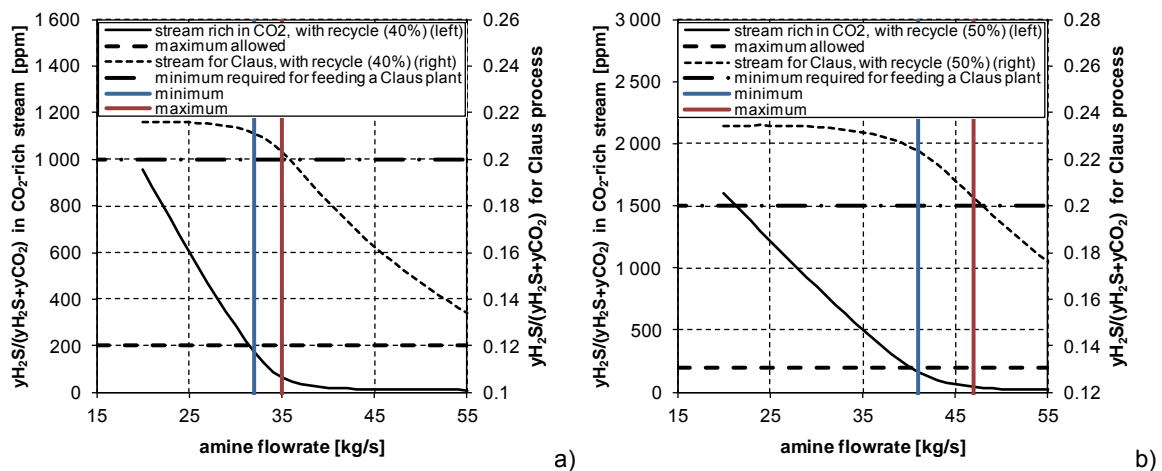


Figure 5: H₂S content in the CO₂-rich stream sent to compression (left) and in the acid gas rich stream exiting the top of the regeneration column (right) by varying the solvent flowrate for the scheme a) with recycle 40 % and b) with recycle 50 % (“minimum”, the vertical line on the left, and “maximum”, the vertical line on the right, indicate the lower and the higher limits of the acceptable operating range).

6. Conclusions

The acid gas removal in an IGCC plant is performed by using an aqueous solution of MethylDiEthanolAmine (MDEA). Although it selectively absorbs hydrogen sulfide, part of carbon dioxide is co-absorbed with H₂S, and the minimum content in H₂S required for feeding the Claus plant may be not achieved. A recycle of the H₂S-rich stream exiting the regeneration to the absorption section is not usually employed in these systems, but it has been considered for increasing the amount of hydrogen sulfide absorbed and therefore present in the outlet H₂S-rich stream. A sensitivity assessment has been performed to determine the influence of the recycle stream on the overall absorption process and the minimum amount of its flowrate needed to accomplish the required specifications. A split ratio of 50 % (50 % recycle stream, 50 % H₂S-rich product stream) has been found to be the best process solution.

Reference

- Austgen, D.M.A., 1989, Model of Vapor-Liquid Equilibria for Acid Gas-Alkanolamine-H₂O Systems. University of Texas, Austin, Texas.
- Cousins, A., Wardhaugh, L.T., Feron, P.H.M., 2011a, Preliminary analysis of process flow sheet modifications for energy efficient CO₂ capture from flue gases using chemical absorption, *Chem. Eng. Res. Des.* 89, 1237-1251.
- Cousins, A., Wardhaugh, L.T., Feron, P.H.M., 2011b, A survey of process flow sheet modifications for energy efficient CO₂ capture from flue gases using chemical absorption, *Int. J. Greenh. Gas Control* 5, 605-619.
- Derks, P.W.J., 2006, Carbon dioxide absorption in piperazine activated N-methyldiethanolamine, University of Twente, Twente.
- Dugas, R.E., 2006, Pilot Plant Study of Carbon Dioxide Capture by Aqueous Monoethanolamine. The University of Texas, Austin, Texas, USA.
- EBTF, 2011. http://caesar.ecn.nl/fileadmin/caesar/user/documents/D_4.9_best_practice_guide.pdf
- Giuffrida, A., Bonalumi, D., 2016, Investigations of an air-blown integrated gasification combined cycle fired with high-sulphur coal with post-combustion carbon capture by aqueous ammonia, *Energy* 117, 439-449.
- Giuffrida, A., Bonalumi, D., Lozza, G., 2013a, Amine-based post-combustion CO₂ capture in air-blown IGCC systems with cold and hot gas clean-up, *Appl. Energy* 110, 44-54.
- Giuffrida, A., Moioli, S., Romano, M.C., Lozza, G., 2016, Lignite-fired air-blown IGCC systems with pre-combustion CO₂ capture, *Int. J. Energ. Res.* 40, 831-845.
- Giuffrida, A., Romano, M.C., Lozza, G., 2013b, Efficiency enhancement in IGCC power plants with air-blown gasification and hot gas clean-up, *Energy* 53, 221-229.
- Giuffrida, A., Romano, M.C., Lozza, G., 2011, Thermodynamic analysis of air-blown gasification for IGCC applications, *Appl. Energy* 88, 3949-3958.
- Giuffrida, A., Romano, M.C., Lozza, G., 2010, Thermodynamic assessment of IGCC power plants with hot fuel gas desulfurization, *Appl. Energy* 87, 3374-3383.
- Hillard, M.G., 2004, Thermodynamics for aqueous piperazine/potassium carbonate/carbon dioxide characterized by the Electrolyte NRTL Model within ASPEN Plus[®]. The University of Texas, Austin, Texas.
- Kohl, A.L., Nielsen, R., 1997, *Gas Purification*, 5th ed. Gulf Publishing Company, Book Division, Houston, Texas, USA.
- Langé, S., Moioli, S., Pellegrini, L.A., 2015, Vapor-Liquid Equilibrium and Enthalpy of Absorption of the CO₂-MEA-H₂O System, *Chemical Engineering Transactions* 43, 1975-1980.
- Langé, S., Pellegrini, L.A., Moioli, S., Picutti, B., Vergani, P., 2013, Influence of Gas Impurities on Thermodynamics of Amine Solutions. 2. Mercaptans, *Ind. Eng. Chem. Res.* 52, 2025-2031.
- Moioli, S., Giuffrida, A., Romano, M.C., Pellegrini, L.A., Lozza, G., 2016, Assessment of MDEA absorption process for sequential H₂S removal and CO₂ capture in air-blown IGCC plants, *Appl. Energy* 183, 1452-1470.
- Moioli, S., Nagy, T., Langé, S., Pellegrini, L.A., Mizsey, P., 2017a, Simulation Model Evaluation of CO₂ Capture by Aqueous MEA Scrubbing for Heat Requirement Analyses, *Energy Procedia*.
- Moioli, S., Pellegrini, L.A., 2015a, Improved rate-based modeling of the process of CO₂ capture with PZ solution, *Chem. Eng. Res. Des.* 93, 611-620.
- Moioli, S., Pellegrini, L.A., 2015b, Physical properties of PZ solution used as a solvent for CO₂ removal, *Chem. Eng. Res. Des.* 93, 720-726.
- Moioli, S., Pellegrini, L.A., 2016, Modeling the methyldiethanolamine-piperazine scrubbing system for CO₂ removal: Thermodynamic analysis, *Front. Chem. Sci. Eng.* 10, 162-175.
- Moioli, S., Pellegrini, L.A., Romano, M.C., Giuffrida, A., 2017b, Pre-combustion CO₂ removal in IGCC plant by MDEA scrubbing: modifications to the process flowsheet for energy saving, *Energy Procedia*.
- Nagy, T., Mizsey, P., 2015, Model verification and analysis of the CO₂-MEA absorber-desorber system, *Int. J. Greenh. Gas Control* 39, 236-244.
- Nagy, T., Moioli, S., Langé, S., Pellegrini, L.A., Mizsey, P., 2017, Improvement of post-combustion carbon capture process in retrofit case, *Energy Procedia*.
- Pacheco, M.A., 1998, Mass Transfer, Kinetics and Rate-Based Modeling of Reactive Absorption. The University of Texas, Austin, Texas.
- Pellegrini, L.A., Langé, S., Moioli, S., Picutti, B., Vergani, P., 2013, Influence of Gas Impurities on Thermodynamics of Amine Solutions. 1. Aromatics, *Ind. Eng. Chem. Res.* 52, 2018-2024.
- Plaza, J.M., 2012, Modeling of Carbon Dioxide Absorption Using Aqueous Monoethanolamine, Piperazine and Promoted Potassium Carbonate. The University of Texas, Austin, Texas.