CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci

 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124046

Design of an Acidic Natural Gas Purification Plant by means of a Process Simulator

Laura A. Pellegrini[1,*], Stefania Moioli[1], Barbara Picutti[2], Paolo Vergani[2], Simone Gamba[1]

[1]Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano
Piazza Leonardo da Vinci 32, I-20133 Milano, Italy
laura.pellegrini@polimi.it
[2]Tecnimont S.p.A., Italy

One of the most used techniques for gas purification from CO_2 and H_2S is chemical absorption by means of an amine solution. This technique is energy-demanding and requires an accurate design of the removal-regeneration system which usually consists of an absorber followed by a distillation unit.
Processes for the combined removal of CO_2 and H_2S have two main fields of application: natural gas (NG) plants and refinery gas purification units.
The paper is mainly focused on the design, using commercially available process simulators, of a purification unit with methyldiethanolamine (MDEA) in a large size NG plant of the Emirates from the point of view of an engineering company. Emphasis is given to the way an engineering company approaches the design task with the constraint of the different types of guarantees that the customer requires.

1. Introduction

Acidic gas treatment processes have two main practical industrial application fields: NG plants and refinery gas purification units. NG purification plants are typically characterized by very high flow rates and relatively low H_2S and CO_2 concentration, as well as high pressures. Moreover the guaranteed values are stringent because the clean gas is the final product of the plant, and the large quantities of gas to be treated have an influence on the overall utilities consumptions. In the case of refinery gas purification, on the other hand, the flow rates are lower but with higher H_2S concentration, although the concentration values on the clean gas are less stringent, because this gas will not be introduced into the distribution pipe network.
Acidic gas removal processes have been widely used for many years in the industrial field and many licensed processes are available, but, since they are of common utilization, there are also many plants that use traditional and "open art" processes. It is therefore not infrequent that an EPC (Engineering, Procurement, Construction) contractor can be involved directly in the plant process design without having a third-party licensing company that provides all process information and relevant guarantees about plant performance according to the client requirements.

Please cite this article as: Pellegrini L.A., Moioli S., Picutti B., Vergani P. and Gamba S., 2011, Design of an acidic natural gas purification plant by means of a process simulator, Chemical Engineering Transactions, 24, 271-276
DOI: 10.3303/CET1124046

In addition, normally, an EPC contractor could not have the sensitivity necessary to evaluate the requested data but it must take the responsibility of the results because the guaranteed product specifications become part of its scope of work.
Some of the problems that must be solved by the EPC contractor when the purification process falls into its scope of work are the following: (1) the impact of some hydrocarbon by-products like COS, aromatics, mercaptans, that could potentially modify the absorption behavior of the amine solution in comparison with H_2S and CO_2. This behavior is not as well known as expected but some parameters are requested by the Client as a guaranteed value: for instance BTX (Benzene, Toluene, Xylenes) concentration on acidic gas; (2) H_2S and CO_2 specification on the clean gas must be fulfilled but it is at the same time important not to exceed also the quantity absorbed into the amine solution in case the rich gas is then sent to a SRU (Sulphur Recovery Unit) because it can exceed the design values of that plant, not always under the control of the same engineering company; (3) since the Clients want to minimize the production costs of the plant, in general they tend to impose some other constraints like, for instance, the maximum steam consumption of the rich amine solution regeneration column and the recirculation flow rate of the amine from the regenerator to the absorber. In this way the safety margins available to cover the uncertainties of the system (namely process units over sizing) are drastically reduced and the risks of the engineering company are consequently increased.
The typical approach to this problem is to simulate the plant using commercial process simulator software, possibly with two different tools, so to check if the required specification values can be achieved and which are the changes to be applied when it is requested to endorse a preliminary project prepared and received from another company.
As highlighted, it is very important that such tools give “each other consistent” and “safe” results but unfortunately this is not what happens in the real life: most of the times the results of the simulations are not in line with each other and, depending on the software used for the simulation, it is possible to have results that are much or less close to the guaranteed values. Being not completely confident in the simulation results, it is not possible for the EPC contractor to know whether the imposed size of the equipment will allow the fulfillment of the performance guarantees.
In order to cover all the possible process design risks, it is really important to know well where and which the limits and the reliability of these tools are.

2. Simulation of a Natural Gas Purification Unit

2.1 Modeling

Thermodynamics, kinetics and mass transfer influence the chemical absorption process. Vapor-liquid equilibrium (VLE) modeling must be properly approached (Gamba et al., 2009; Pellegrini et al., 2010a; Pellegrini et al, 2010b): acidic gases and amines are weak electrolytes, which partially dissociate in the aqueous phase. For the VLE description of these systems, commercial process simulators (Aspen Plus®, 2009; Aspen HYSYS®, 2009; ProMax®, 2009) employ a γ/ϕ method.

Kinetics and mass transfer can be described using two different approaches: the "equilibrium-based stage efficiency" model or the "rate-based" one. The "equilibrium-based stage efficiency" approach corrects the performance of a theoretical stage by a factor called "stage efficiency". It takes into account mass transfer and non equilibrium chemical reactions for all species (Aspen HYSYS®) or only mass transfer for non reactive species, when kinetics is considered (ProMax®).
The "rate-based" model analyses the mass and heat transfer phenomena that occur on a real tray or actual packing height, avoiding the approximation of efficiency. In Aspen Plus® the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman (1924) and proper kinetic expressions are implemented.

2.2 The case study
The steady increase in the use of natural gas (Zucca et al., 2005) makes necessary an up to date analysis and optimization of the consolidated processes for gas purification especially for what concerns the removal of acid gases. The case studied in this work regards a gas sweetening unit with MDEA in a large size NG plant (Figure 1).

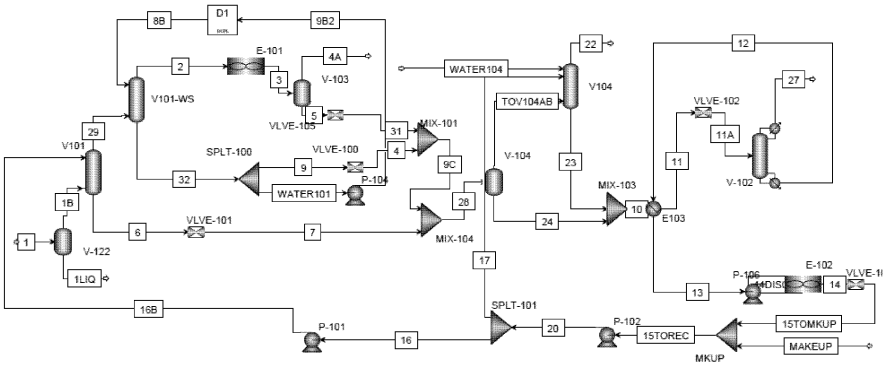

Figure 1: Scheme of the simulated plant (as from Aspen Plus ®).

It consists of an absorption section followed by a regeneration one. The acidic gas stream entering the system has a temperature of 37°C, a pressure of 61.5 bar, and a flow rate of about 32000 kmol/h; its composition is reported in Table 1.
The purification is obtained using an aqueous solution of MDEA (45% w/w), whose acidic gases rich loading should not exceed 0.45 mol/mol, according to customer requirements.
The absorption section consists of two columns (Table 2). The first column, performs a bulk acid gas removal while the second one has the aim of reducing the amount of both H_2S and CO_2 to low levels.
The exhaust solvent is preheated to 107°C and fed to the regeneration column where CO_2 and H_2S are removed from the amine solution. The obtained gas, rich in hydrogen sulfide, is fed it to a SRU.

Table 1: Characteristics of the stream entering the purification system

compound	%mol	compound	%mol
H_2S	4.3313	n-Hexane	0.2414
CO_2	5.1515	n-Heptane	0.0681
H_2O	0.1	n-Octane	0.013
Nitrogen	0.2301	n-Nonane	0.0019
Methane	70.6804	n-Decane	0.0002
Ethane	9.3927	Benzene	0.0193
Propane	5.6016	Toluene	0.0095
i-Butane	1.0203	Methyl Mercaptan	0.0048
n-Butane	2.0706	Ethyl Mercaptan	0.0085
i-Pentane	0.5101	COS	0.0045
n-Pentane	0.5402	MDEA	0

Table 2: Characteristics of the two columns of the absorption section

parameter	high pressure column	low pressure column
diameter [m]	6.2	0.9
type of column	tray column	packing column
packing / tray type	Nutter float valve	Pall ring 1in
packing height [m]/number of trays	32	9
pressure [bar]	60.4	9.48

3. Results and Discussion

The first absorber (lean amine solution flow rate of 55460 kmol/h at 60°C) of the purification plant described in the previous section has been simulated by means of different commercial softwares.

Results from the different process simulators are not in agreement.

Removal of carbon dioxide in Aspen Plus® is higher than in the other process simulators (Figure 2): the first column removes most of the CO_2 from the natural gas stream, with no selectivity toward H_2S. The upper part of the column is useless: design with Aspen Plus® requires a lower number of trays than with the other simulators.

Differences in acidic gas removal correspond to differences in temperature profile (Figure 3). The bulge is located at the bottom of the column, as usual for this system (Kohl and Nielsen, 1997), but the value of the maximum temperature in the absorber varies of about 15°C, leading to different temperatures at the bottom of the column and of the liquid outlet stream.

The differences obtained in the simulation results suggest that the calculation approach ("rate-based" or "equilibrium-based stage efficiency") as well as the thermodynamic, kinetic and mass transfer correlations must be carefully checked and chosen.

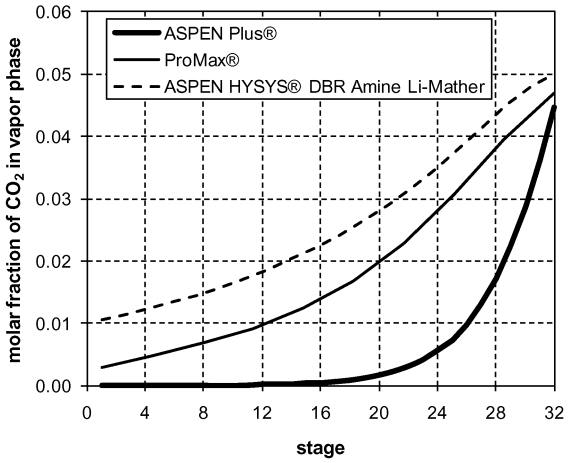

Figure 2: Molar fraction profile of CO_2 in vapor phase along the high pressure absorption column obtained with different process simulators.

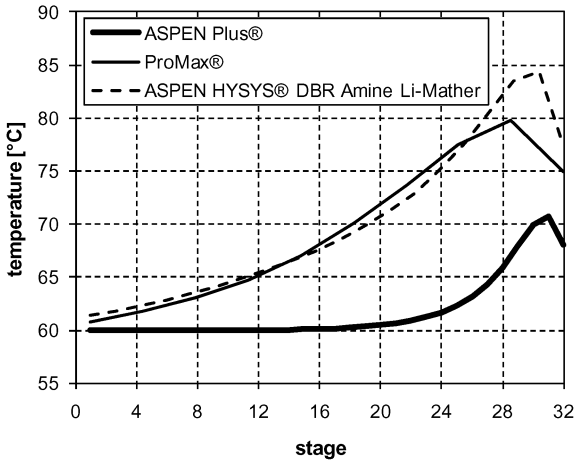

Figure 3: Temperature profile along the high pressure absorption column obtained with different process simulators.

Simulations of a pilot-scale plant whose data are available (Daviet et al., 1984) will be carried out in order to verify the agreement between calculated and experimental plant performances. In the case a satisfactory agreement will not be achieved a work similar to that already carried out for a MEA-based process (Pellegrini et al., 2010b) will be necessary in order to establish a reliable base for the process simulation. In particular: (1) proper kinetic and equilibrium constant correlations will be retrieved from the open literature; (2) thermodynamic model parameters will be checked and, if necessary, regressed from available experimental data; (3) mass transfer correlations will be

properly chosen. From this point of view, it is very important that it is possible for the user to control and possibly change the default correlations/parameters of the process simulator.

4. Conclusions

In order to reduce uncertainties in plant design and to be sure to fulfill the more and more stringent customer guarantees, it is a common and advisable practice of engineering companies to compare simulation results from different process simulators. Taking as case study a large NG plant under construction in the Emirates, the reliability of simulation results has been checked using a "rate-based" model as well as "equilibrium-based stage efficiency" approaches. The obtained results show significant differences, suggesting that a deeper insight of the theories on which the models are based and of the way such models are implemented in the simulators is advisable.

References

Aspen HYSYS®, V7.0, 2009, Aspen HYSYS Simulation Basis; Aspen HYSYS User's Guide, in: AspenONEV7.0 Documentation, AspenTechnology, Inc., Burlington, Massachusetts.

Aspen Plus®, V7.0, 2009, Aspen Physical Property System: Physical Property Methods, Physical Property Models; Aspen Plus Input Language Guide, in: AspenONEV7.0 Documentation, AspenTechnology, Inc., Burlington, Massachusetts.

Daviet G.R., Donnelly S.T. and Bullin J.A., 1984, Dome's North Caroline plant successful conversion to MDEA, Proceedings of the Sixty-Third GPA Annual Convention, Tulsa, Oklahoma, Gas Processors Association, 75–79.

Gamba S., Soave G.S. and Pellegrini L.A., 2009, Use of normal boiling point correlations for predicting critical parameters of paraffins for vapour-liquid equilibrium calculations with the SRK equation of state, Fluid Phase Equilibria, 276, 133–141.

Kohl A. and Nielsen R., 1997, Gas Purification, fifth ed., Gulf Publishing Company, Huston, Texas.

Lewis W.K. and Whitman W.G., 1924, Principles of gas absorption, Industrial & Engineering Chemistry, 16, 1215–1220.

Pellegrini L.A., Gamba S. and Moioli S., 2010a, Using an adaptive parameter method for process simulation of nonideal systems, Industrial & Engineering Chemistry Research, 49, 4923–4932.

Pellegrini L.A., Moioli S. and Gamba S., 2010b, Energy saving in a CO_2 capture plant by MEA scrubbing, Chemical Engineering Research and Design, doi: 10.1016/j.cherd.2010.09.024.

ProMax® with Tsweet® & Prosim® Process Simulation Software, 2009, Bryan Research & Engineering, Inc., Bryan, Texas.

Zucca T., Pellegrini L.A., Nava C., Bellasio R. and Bianconi R., 2005, Reduction of the flare system in the installations of natural gas, Chemical Engineering Transactions, 6, 629–634.