

Industrial Urea Process – Simulation and Validation

Renata Chinda¹, Carlos Yamamoto², Daniel Lima³ and Fernando Pessoa⁴

¹Engenharia de Processos Químicos e Bioquímicos, Universidade Federal do Rio de Janeiro, Brazil.

Email: chinda@eq.ufrj.br

²LACAUT, Universidade Federal do Paraná, Brasil

Email: ciyama@ufpr.br

³Araucária Nitrogenados S.A.

Email: falleiros@petrobras.com.br

⁴SENAI CIMATEC, Brazil.

Email: fernando.pessoa@fieb.org.br

Abstract— Due to a variety of applications, there is an ever-increasing demand for urea and subsequently its production process remains a popular research topic. In the current climate however, studies for solving industrial challenges and the search for a more sustainable process design are required. Previous works concerning simulation of industrial scale production have been developed, however almost none of them are reproducible nor consider urea quality parameters. The severe process operating conditions and the lack of biuret information are the main challenges in modeling and simulating such complex process. This paper proposes a systematic approach for simulation and validation of the current urea production process. Industrial data from the largest operational urea facility in Latin America are used. Simulation is validated against more than 30 industrial parameters. Deviation of less than 6% is obtained for mass composition and less than 8% for other variables considered. This work is a key point for retrofit studies and design of new processes models.

Keywords— industrial data validation, industrial process simulation, urea process.

I. INTRODUCTION

Demand for urea is constantly increasing. Widely used as nitrogen-based fertilizer, additive in animal feed and in cosmetic industries, urea has recently taken a leading role reducing NO_x emissions for diesel engines [1].

There are a number of reported studies ([2]; [3]; [4]; [5]; [6]; [7]; [8]; [9]; [10]; [11] and [12]) on mathematical modeling and/or simulation synthesis section - the reaction section. Nevertheless, there is still a range of restrictions for simulating such a complex process.

A mathematical model for synthesis section was developed by [6]. The thermodynamic framework was based on Wilson and ideal gas equations. Inlet and outlet temperatures and mass fractions in the reactor and Scrubber outlet were compared to industrial data and varied from -6.9% to 2.6%. Zhang et al. (2005) simulated also the high synthesis loop. Extended electrolytic UNIQUAC equation and perturbed-hard-sphere were employed for thermodynamic modeling. Reactor and stripper outlet mass fractions varied from 2.7% to 9.7% when compared to industrial data. Rasheed (2011)

simulated the urea reactor applying SR-POLAR equation for thermodynamic modelling and proposed a power law kinetic for ammonium carbamate and urea formation. Deviations from industrial data were reported as less than 5.0% for liquid composition in the reactor outlet. Zendejboudi et al. (2014) proposed a mathematical model for urea reactor based in a UNIQUAC approach. When compared to industrial data, deviation less than 2.3% for the liquid outlet stream is obtained. Edrisi et al. (2016) simulated the entire urea plant using SR-POLAR for thermodynamic modeling. Industrial data deviation and biuret reaction were not reported. Chinda et al. (2017) simulated the synthesis loop through SR-POLAR basis and proposed a power law kinetic model for ammonium carbamate, urea and biuret formation. Deviations from industrial data were less than 6%. Jeenchay et al. (2018) simulated urea process using NRTL for thermodynamic approach and no validation was presented.

The main difficulty in simulating urea process is still the availability of physical-chemical data in the range of conditions observed along the entire process. An important quality parameter for urea as final product, the

biuret content, is lacking in available data at relevant process conditions. Just Hamidipour et al. (2005), Zendejboudi et al. (2014) and Chinda et al. (2017) had considered biuret reaction in synthesis section. Besides this, further studies using the developed simulation as basis are only presented in [12], as an economic analysis of the process. A validated simulation is a reliable way to identify industrial bottlenecks in the current urea process and a key point for studies aiming in promoting innovation and technology breakthroughs for industries.

This paper proposes a systematic approach for simulating and validating urea process. For this, industrial data from the largest operational urea facility in Latin America and biuret reaction are considered. Employed methodology is presented in three steps: *Step 1 - Industrial data collection*; *Step 2 - Process Simulation*, *Step 3 - Process validation*.

In order to guarantee reproducibility for other urea industrial cases, all steps are performed using commercial software and the main simulation parameters are presented.

II. METHODOLOGY

The methodology presented here is hierarchical and is composed of three steps. Each step can be used independently given that information from previous step is available.

Step 1.1. Industrial Data Collection

At this step, all industrial data (flows, compositions, temperatures and pressures) are collected. The intention of this step is to obtain enough information to model the process and validate the simulation. Industries usually have their own agenda for collecting data concerning stream compositions depending on the analytical equipment used and the laboratory procedures and schedules.

It is important to collect data from all available composition analyzers and flowmeters in the plant in order to validate the mass balance of the simulation. In order to validate the energy balance, it is necessary to collect data from pressure and temperature indicators. It is convenient to have these data from points as close as possible to the composition analyzers, such that flow rates can be estimated where necessary.

Step 2. Process Simulation

The steady state simulation proposed for urea process is built in AspenPlus®. Ammonium carbamate, urea and biuret reactions are considered, given that urea is formed only in liquid phase. Industrial data do not consider the

ammonium carbamate mass fraction. Therefore, it was assumed that 99.0% of CO₂ reacts to form ammonium carbamate, according to [8] and [13].

Thermodynamic modeling is based on SR-POLAR equation, recommended for highly non-ideal systems at high temperatures and pressures and for both non-polar and high polar components, according to [14], [15] and [16]. Kinetic equations are taken from [10].

Pure component data and binary interaction parameters of NH₃, CO₂, H₂O, urea, ammonium carbamate, N₂, O₂ and H₂ are taken from the AspenPlus database. Biuret pure component data is obtained from NIST (National Institute of Standards and Technology) and DECHEMA (Gesellschaft für Chemische Technik und Biotechnologie) database. In terms of vapor pressure and binary interaction parameters, biuret is assigned the same parameters as urea. This step results in detailed mass and energy balance data and the properties of all streams in the flowsheet.

Step 3. Process Validation

The main objective of this step is to perform the validation of the simulation using the data collected in Step 1. Thus, it is necessary to process all the industrial data in order to evaluate which data can be used to validate the simulation, since industrial data may present some fluctuation during operation. All the plant data collection, performed in Step 1, should be taken at the same time or, at least, on the same day. This is a point to be highlighted, given that inter-connected industrial plants do not operate at steady-state and it is important to ensure stable operating points are used in the data treatment. In a urea production complex, it is possible for example that the ammonia unit is shut-down before the urea plant experiences deviations due to upstream process e.g. natural gas/residue asphaltic processing. It is less important to understand the nature of the up-streams deviations, as long as it is possible to identify deviations in the given process data in order to rule them out of validation process. For this, an analysis with the variation coefficient is performed with the capacity data taken each 4 hours. Coefficient of variation with values less than 1.5% are considered to represent data that are not varying significantly [10] and, therefore, indicate a steady-state condition in the process. These two procedures can guarantee that data used for validation correspond to a stable and continuous operation. Finally, the validation process can be performed calculating the deviation between industrial experimental data and data obtained from the simulation. Thus, this step can be described as: (a) from the processed data from Step 1, select only those

ones that were taken on the same day. (b) collect production capacity data. (c) calculate arithmetic means, sample standard deviation and coefficient of variation using the production capacity data. (d) eliminate data with variation coefficient greater than 1.5%. (e) evaluate the deviation between industrial experimental data and data obtained from the simulation.

III. RESULTS AND DISCUSSION

The process unit analyzed produces 2000 ton/day of urea through Stamicarbon technology and can be divided into five blocks: synthesis, evaporation, prilling, desorption & hydrolysis and recirculation. A simple block diagram of the process can be seen in Fig. 1.

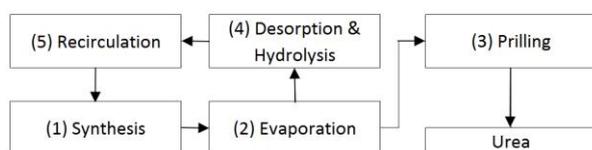


Fig.1 - Simplified block diagram for industrial urea production.

The main equipment in the synthesis section are: pool condenser, reactor, scrubber and stripper. This section is responsible for ammonium carbamate and urea production. After leaving the synthesis section, the liquid product from the stripper is sent to recirculation. This section is responsible for removing the ammonium carbamate present in the solution through its decomposition in NH_3 and CO_2 , besides condensing NH_3 and CO_2 into ammonium carbamate and recycle them back to the synthesis section. The recirculation section consists in: rectifying column and its respective heaters, condensers and an atmospheric flash tank. The production from the recirculation section is fed to the evaporation section in order to concentrate up the urea solution before it is prilled. This section operates under vacuum, which means a big part of water, ammonia and carbon dioxide are removed from the solution. The evaporation section consists mainly of three evaporators and its respective heaters. The last section is called desorption and hydrolysis and consists in an adsorber and two desorber units. The main function of this section is to recovery NH_3 , CO_2 and urea present in the water that comes from the Evaporation section.

Step 1. Industrial data collection

Industrial data collection was performed as described at Step 1. Thus, mass composition analyzers and flowmeters were identified in the industrial flowsheet. Further, pressure and temperature indicators closest to mass composition analyzers were also identified. Process

flowsheet and data point collection can be seen in Fig. 2 and Fig. 3. Mass composition analyzers are indicated in blue, flowmeters in green, pressure indicators in yellow and temperature indicators in red. In order to facilitate the sequence of processing units, TAG order is based on section unit (S-Synthesis; E- Evaporation; P-Prilling; D&H-Desorption & Hydrolysis; R-Recirculation) and flow streams (numerical sequence).

Step 2. Process simulation

Process simulation was performed as described in Step 2. From AspenPlus model library: urea reactor was modeled as a sequence of CSTRs in series; pool condenser using R-Stoic; stripper, scrubber, rectifying column, absorber, desorbers and hydrolyzers as RadFrac columns; main heat exchangers, condenser and evaporator T-5 were modeled as Heat-X; evaporators T-6 and T-7 were modeled as V-drum. List of the main equipment and the correspondent AspenPlus model library used for simulation can be seen in Table 1.

Table 1 - Model library from AspenPlus.

TAG	Unit	Model	TAG	Unit	Model
S-2	Stripper	RadFrac	R-7	Rectifying	RadFrac
S-4	Pool	R-Stoic	R-8	Condenser	Heat-X
S-5	Reactor	RCSTR	R-12	Absorber	RadFrac
S-6	Scrubber	RadFrac	H&D-17	Desorber1	RadFrac
E-24	Condenser	Heat-X	H&D-18	Hydrolyzer	RadFrac
E-25	Evaporator	V-drum	H&D-19	Desorber2	RadFrac
E-26	Absorber	RadFrac			

Step 3. Process Validation

Data from a total of 270 operational days were provided by an industrial urea plant for validating the simulation. As described at Step 3(a), in order to guarantee consistency to the analysis, all the experimental points should be taken in the same operational condition. Only 32 operational data points (days) met this criterion. (b) Production capacity from this data was taken in intervals of 4 hours. (c) Arithmetic mean (AM), sample standard deviation (SSD) and variation coefficient (VC) were calculated. (d) Production capacity data with coefficient of variation with values lower than 1.5% were selected. Table 2 presents the data used and obtained at this step for points with VC lower than 1.5%. The production capacity range varied from 86.45% to 98.21%. (e) Validation of the simulation was performed calculating the difference between industrial and simulated data and dividing it per industrial data.

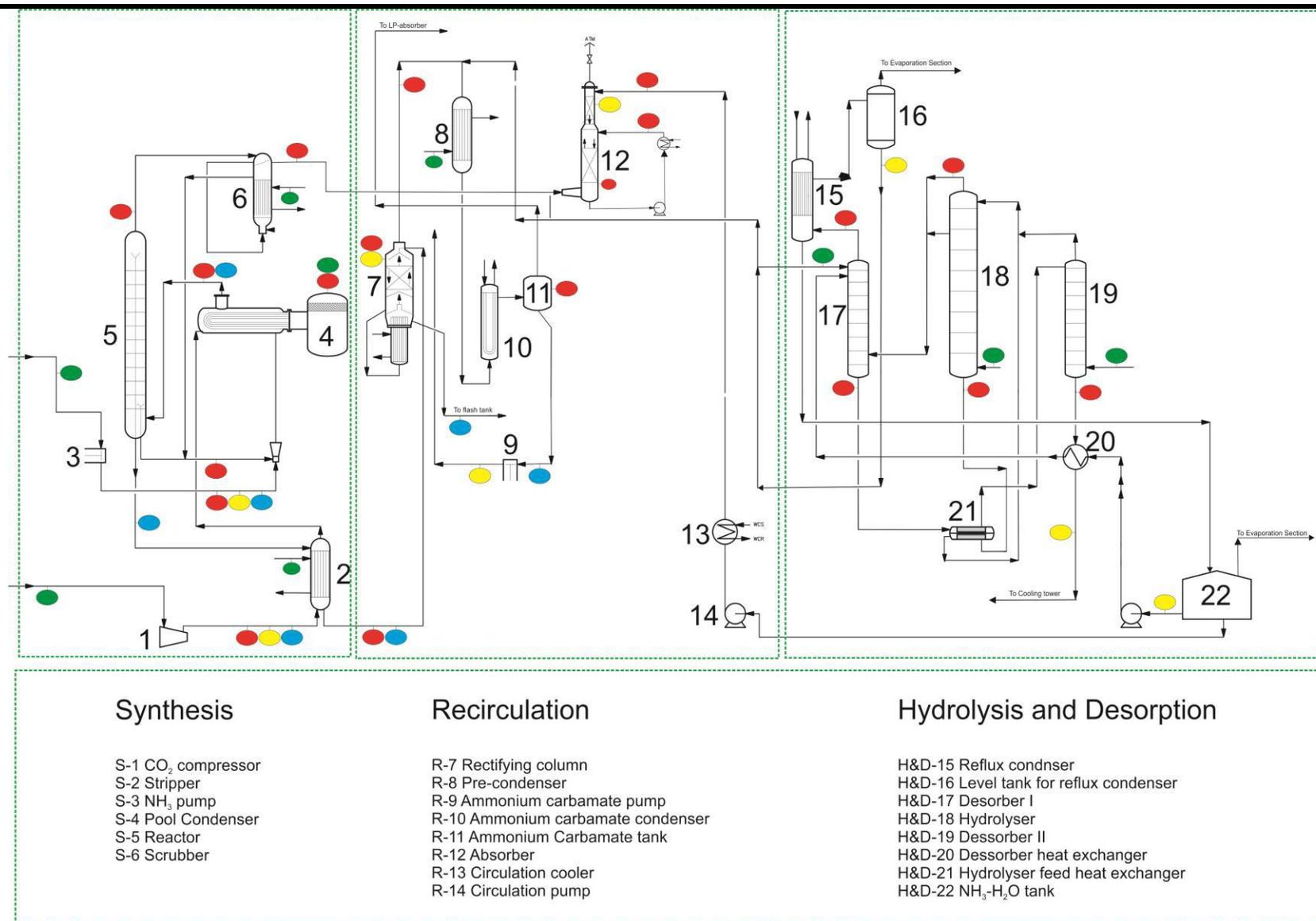
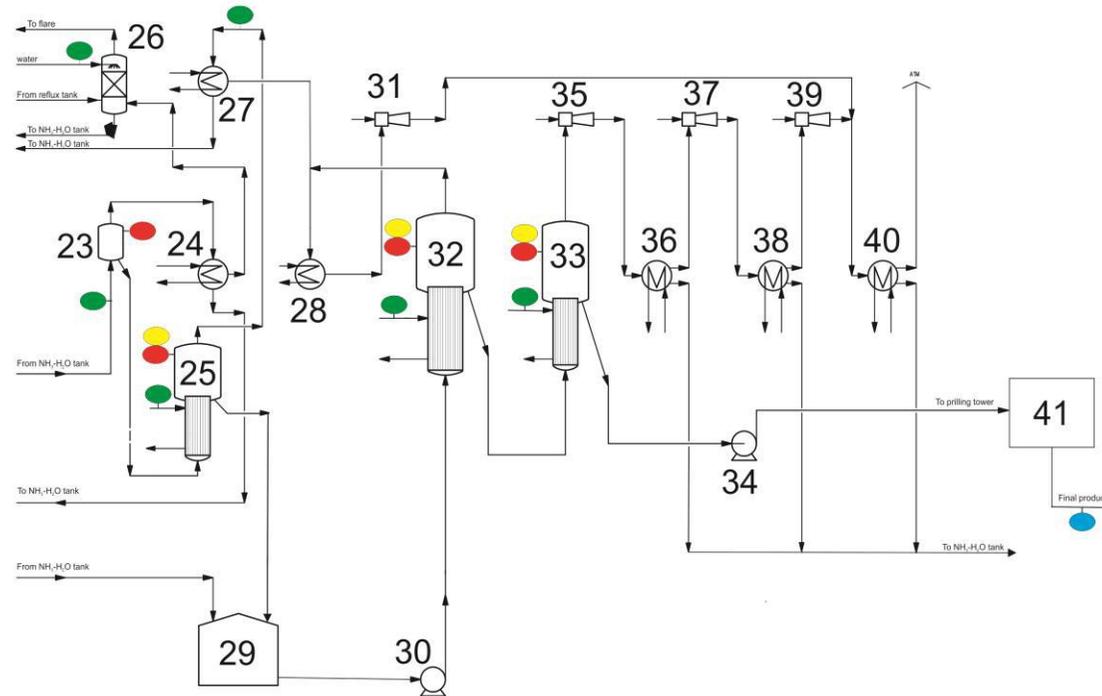


Fig.2 - Process flowsheet and data point collection for Synthesis, Recirculation and Hydrolysis & Desorption sections.



Evaporation

- E-23 Flash tank
- E-24 Condenser flash tank
- E-25 Pre evaporator
- E-26 Atmospheric absorber
- E-27 Pre evaporation condenser
- E-28 Condenser 1st stage evaporator
- E-29 Urea tank
- E-30 Urea solution pump
- E-31 Ejector 1st stage

- E-32 1st stage evaporator
- E-33 2nd stage evaporator
- E-34 Concentrated urea pump
- E-35 Booster
- E-36 1st condenser from 2nd stage evaporator
- E-37 1st ejector 2nd stage
- E-38 2nd condenser from 2nd stage evaporator
- E-39 2nd ejector 2nd stage
- E-40 After condenser
- E-41 Prilling tower

Fig.3 - Process flowsheet and data point collection for Evaporation section.

Table 2 - Statistical Analyses with capacity planta data.

Point	AM (%)	SS D	VC (%)	Point	AM (%)	SS D	VC (%)
A	86.45	0.39	0.45	G	95.66	0.14	0.15
B	86.70	0.39	0.45	H	95.87	0.29	0.30
C	87.06	1.05	1.21	I	96.62	0.63	0.65
D	87.33	0.07	0.08	J	98.13	0.11	0.11
E	87.37	0.52	0.60	K	98.21	0.49	0.42
F	87.41	0.10	0.11				

Equations used for process validation step, can be seen in Table A Appendix A. Fig. 4 shows the comparison of mass fraction for each component in the outlet of the reactor (R) and the stripper (S). As it can be seen there is a great accordance between industrial (IND) and simulation (SIM) results.

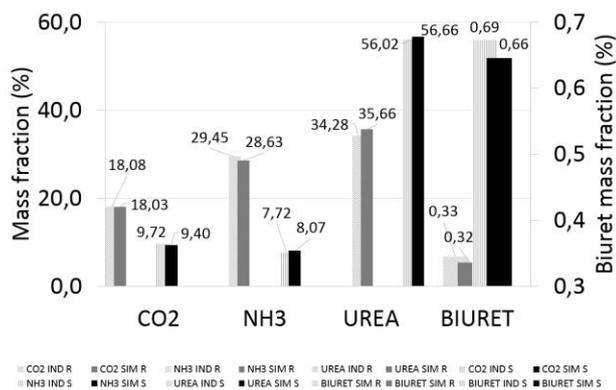


Fig.4 - Comparison between mass fraction composition in the outlet of the reactor and the liquid outlet of stripper.

A total of 37 different process parameters were evaluated, among them stream temperature, steam generation, mass fraction for CO₂, NH₃, urea, H₂O and biuret, CO₂ conversion in the reactor and stripper efficiency. For all mass fractions evaluated, the deviation between the value predicted by the simulation and the real value obtained from industrial data were less than 6%, while for steam generation and stream temperatures the deviation was less than 8%. A selected list of variables and the comparative deviations with other similar works are given in Table 3. As it can be seen for reactor and stripper results were very close to reported data from literature.

Table 3 - Absolute average deviation for evaluated points.

Equipment	Parameter	This work	Lite-rature	Ref.
Pool Condenser	LP steam flow	7.56%	-	-
	Urea MF	0.89%	-	-
Reactor	CO ₂ MF	5.95%	8.84%	[6]
	NH ₃ MF	4.33%	9.76%	[24]
	Urea MF	3.38%	2.65%	[5]
	H ₂ O MF	4.38%	2.71%	[24]
	Biuret content	4.96%	-	-
	CO ₂ conversion	2.41%	0.44%	[3]
	N/C ratio	4.83%	6.90%	[5]
Scrubber	H ₂ O /urea ratio	6.18%	-	-
	T of the liquid outlet	4.77%	-	-
	CO ₂ MF	5.00%	5.10%	[24]
	NH ₃ MF	6.12%	4.14%	[24]
	urea MF	2.93%	0.20%	[4]
	H ₂ O MF	4.32%	4.96%	[24]
	Biuret content	4.96%	-	-
Stripper	Efficiency	2.53%	-	-
	N/C	2.42%	-	-
	H/urea	6.50%	-	-
	Steam flow	4.27%	-	-
	T of liq outlet	6.16%	-	-
	Urea production	3.56%	-	-
	Urea MF	1.52%	-	-
Rectifying column	H ₂ O MF	3.04%	-	-
	Biuret content	3.18%	-	-
Urea tank	Urea MF	4.17%	-	-
	H ₂ O MF	4.83%	-	-
Final product	Biuret content	3.82%	-	-
	H ₂ O MF	6.91%	-	-
Reflux condensate tank	Biuret content	5.73%	-	-
	CO ₂ MF	4.34%	-	-
	NH ₃ MF	4.89%	-	-
Ammonia water tank	urea MF	2.58%	-	-
	CO ₂ MF	4.31%	-	-
	NH ₃ MF	4.55%	-	-
Ammonia water tank	Urea MF	3.49%	-	-
	H ₂ O MF	0.34%	-	-

IV. CONCLUSION

A simulation for all sections of urea production is developed and validated against more than 30 industrial parameters using a total of 32 processed daily operations data. Good consistency between simulation results and industrial data is presented, being that a deviation of less than 6% is obtained for mass composition and less than 8% for other variables considered. Reproducibility of other industrial urea plants is therefore possible and permits using it for reliable retrofit studies and design of new processes models

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APPENDIX A

Table A - Equations used in validation step.

Simple Arithmetic Average	$\bar{x} = \sum_{i=1}^n x_i$
Sample Standard Deviation	$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$
Coefficient Of Variation	$Cv = \frac{s}{\bar{x}}$
Deviation between simulated and industrial data	$deviation(\%) = \frac{industrialdata - simulationdata}{industrialdata} \times 100$
CO ₂ conversion	$\chi_{CO_2} = \frac{urea}{urea + 1,365 \times CO_2}$
N/C relation	$\frac{NH_3}{CO_2} = \frac{2 \times urea + 3,53 \times NH_3}{urea + 1,365 \times CO_2}$
H/U relation	$\frac{H_2O}{urea} = \frac{H_2O \times 3,33}{urea}$
Stripper efficiency	$\eta = \frac{urea}{urea + 1,765 \times NH_3}$
Biuret content	$biuretcontent = \frac{biuretmass}{biuretmass + ureamass} \left[\frac{kg}{kg} \right]$