



**UNIVERSIDADE FEDERAL DO RIO DE JANEIRO**  
**CENTRO DE TECNOLOGIA**  
**ESCOLA DE QUÍMICA**  
**PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA DE**  
**PROCESSOS QUÍMICOS E BIOQUÍMICOS**

**RENATA CAROLINA CHINDA**

**PROCESS INTENSIFICATION APPLIED TO UREA PRODUCTION PROCESS**

**RIO DE JANEIRO**  
**2019**

**RENATA CAROLINA CHINDA**

**PROCESS INTENSIFICATION APPLIED TO UREA PRODUCTION PROCESS**

Tese de doutorado submetida ao Corpo Docente do Curso de Pós-Graduação em Engenharia de Processos Químicos e Bioquímicos promovido pela Escola de Química da Universidade Federal do Rio de Janeiro, como requisito parcial à obtenção do título de Doutor em Ciências.

Orientadores: Fernando Luiz Pellegrini Pessoa, D. Sc. (UFRJ)  
Carlos Itsuo Yamamoto, D. Sc. (UFPR)  
Tito Lívio Moitinho Alves, D. Sc. (UFRJ)

**RIO DE JANEIRO**

**2019**

## CIP - Catalogação na Publicação

C539p CHINDA, RENATA CAROLINA  
PROCESS INTENSIFICATION APPLIED TO UREA  
PRODUCTION PROCESS / RENATA CAROLINA CHINDA. -- Rio  
de Janeiro, 2019.  
124 f.

Orientador: FERNANDO LUIZ PELLEGRINI PESSOA.  
Coorientador: TITO LIVIO MOITINHO.  
Tese (doutorado) - Universidade Federal do Rio  
de Janeiro, Escola de Química, Programa de Pós  
Graduação em Engenharia de Processos Químicos e  
Bioquímicos, 2019.

1. INDUSTRIAL SCALE. 2. PROCESS INTENSIFICATION  
. 3. UREA PRODUCTION. I. PESSOA, FERNANDO LUIZ  
PELLEGRINI, orient. II. MOITINHO, TITO LIVIO,  
coorient. III. Título.

Tese de Doutorado :

Process intensification applied to urea production process

Autor:

Renata Carolina Chinda

Orientadores: Fernando L. P. Pessoa, Tito L. Moitinho e Carlos 1. Yamamoto

Data da defesa: 01 de Novembro de 2019

Aprovada por:

---

Fernando Luiz Pellegrini Pessoa, D.Sc. EQ/UFRJ

---

Tito Livio Moitinho Alves, D.Sc. PEQ/UFRJ

---

Carlos Itsuo Yamamoto, D.Sc. EQ/UFPR

---

Karen Signori Pereira, D.Sc. EQ/UFRJ

---

Marisa Fernandes Mendes, D.Sc. EQ/UFRRJ

---

Paulo Henrique de Souza Picciani, D.Sc. IMA/UFRJ

---

Priscilla Filomena Fonseca Amaral, D.Sc. EQ/UFRJ

## ACKNOWLEDGMENTS

I would like to thank the angels I have as parents, Ana Helena Brasil Soares and Renato Chinda, for all they have taught me about strength and perseverance.

To my advisors Prof Dr Fernando Pellegrini and Prof Dr Carlos Yamamoto, for the friendship and technical support. To Daniel Falleiros, urea process engineer from FAFEN-PR for all the conversations related to the idea of innovation in urea process. To Prof Dr Saul Lemkowitz from Delft University of Technology for being so friendly since my first studies on urea production.

To Prof<sup>a</sup> Dr<sup>a</sup> Sonia Lyra, the greatest supporter in all my projects. To Jair Lisboa and Maria do Carmo Czaikowski for the gentleness and kindness with me during my PhD studies. To Jytte Olga Morgenstjerne for being my lovely Danish grandma.

To UFPR and LACAUT<sub>ets</sub> for all the infrastructure support. To DTU and CAPES for the great opportunity to work without boundaries and borders and for the financial support for my PhD internship.

To UFRJ and to EPQB, especially Prof<sup>a</sup> Dr<sup>a</sup> Veronica, for the opportunity to develop my professional and personal skills.

A special thanks to all my friends in this journey - from UFRJ, UFPR and DTU.

To the Universe for the synchronicities of life.

*Tanze nun auf tausend Rücken  
Wellen-Rücken, Welle-Tücken-  
Heil, wer neue Tänze schafft!  
Tanzen wir in tausend Weisen,  
Frei - sei unsre Kunst geheissen,  
Fröhlich - unsre Wissenschaft!*

*“Dança agora sobre mil dorsos  
Dorsos de ondas, malícias de ondas  
Salve quem novas danças cria!  
Dancemos de mil maneiras  
Livre - seja chamada a nossa arte  
E gaia - a nossa ciência!”*

*Friedrich Nietzsche*

CHINDA, Renata Carolina. Intensificação de Processos Aplicada ao Processo de Produção de Ureia. Orientador: Fernando Pellegrini Pessoa, Carlos Itsuo Yamamoto e Tito Lívio Moitinho. (Tese de Doutorado Engenharia de Processos Química e Bioquímica – Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2019).

## **RESUMO**

Devido a um crescente gama de aplicações, há um constante aumento da demanda por ureia e conseqüentemente o seu processo de produção torna-se um significativo tópico de pesquisa. Os desenvolvimentos tecnológicos até então propostos foram capazes de solucionar os principais problemas enfrentados no processo e novos estudos têm levado em consideração somente as constantes químicas. No atual cenário, estudos para solucionar desafios industriais e a busca por um design de processo mais sustentável tornam-se significativos. Através de uma abordagem tarefa-fenômeno para intensificação de processos este trabalho propõe identificar, analisar e solucionar gargalos de processo presentes na produção industrial de ureia. Para tanto, dados industriais da maior unidade fabril da América Latina foram utilizados. A simulação foi validada com mais de 30 parâmetros industriais. Desvios inferiores a 6% foram obtidos para composição mássica e inferiores a 8% para outras variáveis consideradas. Análises econômica, de sustentabilidade e de ciclo de vida foram realizadas e indicaram o consumo de utilidades na seção de evaporação como o maior gerador de custos. Através de estudos de intensificação de processos uma unidade de membrana para pervaporação é proposta, trazendo um design mais sustentável e inovatividade para o processo, além de ser um ponto-chave para estudos de retrofit.

## **PALAVRAS-CHAVES**

Escala industrial; intensificação de processos; produção de ureia.

CHINDA, Renata Carolina. Process Intensification Applied To Urea Production Process. Advisors: Fernando Pellegrini Pessoa, Carlos Itsuo Yamamoto e Tito Lívio Moitinho. PhD Thesis (Engineering of Chemical and Biochemical Process – Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, 2019).

## **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. Technological developments have solved many of the major issues, while new enhancements typically deal with the chemical constraints of the process. In the current climate however, studies for solving industrial challenges and the search for a more sustainable process design are required. Through a task and phenomena process intensification method, this thesis proposes to identify, analyze and overcome industrial hotspots in urea process, in order to obtain a more sustainable design to the current process production. 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. Economic, sustainability and life cycle Assessment analyses were performed and indicated utilities consumption in evaporation section as the main cost driver. Through process intensification studies, a pervaporation membrane unit is proposed as a new and more sustainable process design for evaporation section and a key point for retrofit studies

## **KEY-WORDS**

Industrial scale; process intensification; urea production.



## LISTA DE FIGURAS

Figure 2.1 - Simplified block diagram for industrial urea production.....	24
Figure 2.2 – Plant size reduction into Urea 200plus™ technology .....	27
Figure 2.3 – THESE synthesis layout.....	28
Figure 2.4 – Main employed technologies for worldwide urea production process.....	29
Figure 2.5 – Published patents correlation according to licensors.....	30
Figure 2.6 – Patents deposits concerning about process innovation.....	31
Figure 3.1 - Framework for base case building, analysis and intensification.....	33
Figure 3.2 –Schematic concept of phenomena-based process intensification.....	39
Figure 4.1 – Range of operational conditions for producing urea.....	43
Figure 4.2 - Process flowsheet and data point collection for Synthesis, Recirculation and Hydrolysis & Desorption sections.....	44
Figure 4.3 - Process flowsheet and data point collection for Evaporation section.....	45
Figure 4.4 – Percentage of utility costs and carbon footprint with respect to each unit operation.....	51
Figure 4.5 - Open- and closed-paths for industrial urea production.....	53
Figure 4.6 - Unit operation flowsheet for Recirculation and Evaporation.....	56
Figure 4.7- Task based flowsheet for recirculation and evaporation sections.....	56
Figure 4.8 - Phenomena based flowsheet for urea production process, focusing on recirculation and evaporation sections.....	57
Figure 4.9- Flowsheet alternative D: Pervaporation membrane unit for the separation of H <sub>2</sub> O/Urea.....	66
Figure 4.10 - Flowsheet alternative E: Vapor-permeation membrane unit for the separation of NH <sub>3</sub> , CO <sub>2</sub> /H <sub>2</sub> O.....	68
Figure 4.11 - Economic and LCA improvements relative to the base case design.....	69

## LISTA DE TABELAS

Table 3.1 - Translation of economic ( $\alpha$ ), sustainability ( $\beta$ ) and LCA ( $\gamma$ ) analysis into process Hotspots.....	37
Table 3.2 - Identified design targets from the identified process hot-spot.....	38
Table 4.1 - Model library from AspenPlus.....	47
Table 4.2 - Statistical Analyses with capacity plant data.....	47
Table 4.3 - Absolute average deviation for evaluated points.....	48
Table 4.4 – Costs related to utilities, raw material and product.....	49
Table 4.5- Parameters considered for economic analyses.....	50
Table 4.6- Paths in the base case with highest improvement potential.....	51
Table 4.7 - Sustainability metrics for the base case design.....	52
Table 4.8 - Main potential improvement points with respect to sustainability, economic and LCA analysis.....	54
Table 4.9 - Identified process hotspots for urea production process.....	54
Table 4.10 – Pure compound properties.....	58
Table 4.11 - Binary ratio matrix for a set of selected properties.....	58
Table 4.12 - List of selected desirable PBBs linked to the identified tasks V – vapour, L – liquid, LL – liquid–liquid, MSA – mass separating agent.....	59
Table 4.13 - List of feasible SPBs.....	60
Table 4.14 - Generation of hybrid/intensified unit operations from combination of PBB.....	64
Table 4.15 – Works concerning about membranes capable of doing the required task.....	67
Table 4.16 - Performance metrics and LCA analysis for the base case and the two flowsheet alternatives generated.....	68

## ABBREVIATIONS AND NOMENCLATURE

2phM	2-phase mixing
AF	Accumulation factor
Carb	Ammonium carbamate
C	Compressor
D	Dividing
EWC	Energy waste cost
GWP	Global warming potential
HTPI	Human toxicity potential by ingestion
H/C	Heating/Cooling
L	Liquid
LCA	Life cycle assessment
M	Mixing
MVA	Material value added
MW	Molecular weight
PBBs	Phenomena building blocks
PC	Phase contact
PI	Process intensification
PT	Phase transition
PS	Phase separation
P	Pump
R	Reaction
RG	Radius of gyration
RM	Raw materials
SolPar	Solubility parameter
SPBs	Simultaneous phenomena building blocks
TVA	Total value added
V	Vapor
T	Tower or column
eq.	Equivalent
NSPBmax	Total number of possible SPBs
nPBB	Total number of phenomena building blocks
nPBB <sub>D</sub>	Total number of dividing phenomena
nPBB <sub>E</sub>	Total number of energy transfer phenomena
nPBB <sub>M</sub>	Total number of mixing phenomena
R	Reactor
Rc	Reactor-condenser
Tb	Boiling temperature
Tm	Melting temperature
VdW	Van der Waals volume
VM	Molar volume
VP	Vapor pressure

## CONTENTS

<b>1. INTRODUCTION .....</b>	<b>13</b>
1.1 PROJECT MOTIVATION AND OBJECTIVE.....	14
1.2 STRUCTURE OF THE THESIS.....	14
<b>2. LITERATURE REVIEW .....</b>	<b>16</b>
2.1 UREA PRODUCTION PROCESS .....	16
2.2 MODELING AND SIMULATING UREA PRODUCTION PROCESS.....	17
2.3 STATE OF ART: PROCESS INTENSIFICATION APPLIED TO UREA PRODUCTION .....	18
2.4 CONCLUSION.....	24
<b>3. METHODOLOGY .....</b>	<b>25</b>
3.1 LEVEL 1 - BASE CASE BUILDING AND VALIDATION.....	25
3.1.1 <i>Step 1.1. Industrial Data Collection</i> .....	25
3.1.2 <i>Step 1.2. Process Simulation</i> .....	26
3.1.3 <i>Step 1.3. Process Validation</i> .....	26
3.2 LEVEL 2 - BASE CASE ANALISES .....	27
3.2.1 <i>Step 2.1. Economic, Sustainability &amp; Life Cycle Assessment Analysis</i> .....	27
3.2.2 <i>Step 2.2. Hot-Spots Identification</i> .....	28
3.3 LEVEL 3 - SUSTAINABLE DESIGN / INNOVATION .....	31
3.3.1 <i>Step 3.1. Process Analysis</i> .....	32
3.3.2 <i>Step 3.2. Identification of desirable tasks &amp; phenomena</i> .....	32
3.3.3 <i>Step 3.3 Generation of flowsheet alternatives</i> .....	33
3.3.4 <i>Step 3.4. Comparison and selection of the best flowsheet alternatives</i> ....	33
<b>4. RESULTS AND DISCUSSION .....</b>	<b>35</b>
4.1 LEVEL 1 - BASE CASE BUILDING AND VALIDATION.....	35
4.1.1 <i>Step 1.1. Industrial data collection</i> .....	35
4.1.2 <i>Step 1.2. Process simulation</i> .....	38
4.1.3 <i>Step 1.3. Process Validation</i> .....	39
4.2 LEVEL 2 - BASE CASE DESIGN ANALYSIS .....	41
4.2.1 <i>Step 2.1. Economic, Sustainability and LCA Analysis</i> .....	41
4.2.2 <i>Step 2.2. Hot-Spots Identification</i> .....	46
4.3 LEVEL 3 - SUSTAINABLE DESIGN / INNOVATION .....	47

4.3.1 Step 3.1. Process Analysis .....	47
4.3.2 Step 3.2. Identification of desirable tasks and phenomena .....	51
4.3.3 Step 3.3. Generation of flowsheet alternatives .....	52
4.3.4 Step 3.4. Comparison and selection of the best flowsheet alternatives....	60
<b>5. CONCLUSIONS AND FUTURE PERSPECTIVE .....</b>	<b>62</b>
<b>6. REFERENCES.....</b>	<b>65</b>
<b>APPENDIX A.....</b>	<b>69</b>
<b>APPENDIX B.....</b>	<b>72</b>
<b>APPENDIX C .....</b>	<b>76</b>
<b>APPENDIX D.....</b>	<b>77</b>
<b>APPENDIX E .....</b>	<b>78</b>
<b>APPENDIX F .....</b>	<b>94</b>
<b>APPENDIX G.....</b>	<b>109</b>
<b>APPENDIX H.....</b>	<b>123</b>

## 1. 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<sub>x</sub> emissions for diesel engines (BROUWER, 2010).

Process intensification (PI) offers significant improvements in chemical and bio-chemical manufacturing and processing, resulting in substantially decreased equipment volume, energy consumption, or waste formation, and ultimately leading to cheaper, safer and sustainable technologies (STANKIEWICZ, 2003).

Retrofit is a fundamental concept in PI and can be defined as the improvement of an existing plant by substituting or improving some of its unit operations while fitting the rest of the plant and some of the process variables (LUTZE, GANI, & WOODLEY, 2010).

In petrochemical industries, like urea plants, energy represents a relevant part of the total delivered product cost, significantly affecting economy and sustainability productions. Given their large size and the highly competitive market, it is worthwhile combining reliability and predictability in order to achieve a decrease in costs (CURCIO, 2007). In this context, PI may play an important role either in reducing energy costs or in lowering capital requirements for investments, keeping safety and process reliability at the levels required. PI aims at promoting innovation and creating technology breakthroughs for industries (HARMSEN, 2010).

Through a task and phenomena based PI method, this work proposes to identify, analyze and overcome hotspots (bottlenecks) in industrial urea process, in order to obtain a more sustainable process compared to the current urea process production. For this, using industrial data from the largest operational urea facility in Latin America and considering biuret reaction, a systematic approach leads to the simulation, validation and identification of hotspots. Employed methodology is presented in three levels: Level 1- Base Case Building and Validation, in which industrial data is collected and simulation and validation are performed; Level 2 - Base Case Design Analysis, in which economic, sustainability and life cycle assessment analyses are performed and the process hotspots are identified. Level 3 – Sustainable Design / Innovation, in which alternatives that match the established targets for process improvements are generated and evaluated.

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

## 1.1 Project Motivation and Objective

Urea production process has been developed since the 1950s. However, some process bottlenecks have not been overcome until now. The most advanced technologies propose minor modifications in unit operations and equipment that end up being applicable only in new facilities or, if possible, in existing units, but with adaptations.

Thus, it is highly significant a process innovation that can be applied directly to units already in operation and that can be able, if not to increase, at least keep the same production capacity and product quality at the same time in which is able to reduce costs and waste. Along these lines the main objective of this thesis can be described as:

*Through process intensification methodology, achieve improvements in energy consumption, by-product generation and operating costs for urea production process taking into account sustainable LCA metrics.*

Thus, the specific objectives are:

- 1) Model, simulate and validate the urea production unit
- 2) Identify hot-spots through economic, sustainability and life cycle assessment analyses
- 3) Propose a new flowsheet for the process in order to overcome the identified hot-spots

## 1.2 Structure of the Thesis

This thesis consists of 5 main chapters and has the following sequence outline.

In Chapter 1 an introduction of theme is presented. Project motivation, the main and the specific objectives are shown.

In Chapter 2 an overview of the current urea production process is presented. Modeling and simulation works concerning about urea process are reviewed as well as the state of art for process intensification applied to urea production.

In Chapter 3, methodology employed is explained in three different levels: Level1: Base Case Building and Validation, in which industrial data is collected and processes simulation and validation are performed; Level 2: Base Case Analyses, in which process hot-spots are identified through economic, sustainability and life cycle assessment analyses; Level 3: Sustainable Design / Innovation, in which the process intensification methodology is performed in order to overcome the previously identified process hot-spots.

In Chapter 4 results obtained for the urea industrial process and discussions concerning the feasibility of the new proposals are presented.

In Chapter 5 an overview of what has been developed in this thesis and the conclusion of the entire thesis are presented. Finally, the future perspectives concerning innovation in urea process are also presented.

Appendix A to E present the tables necessary to perform some Steps in hot spots identification and process intensification. In Appendix F, G and H publications generated from this thesis can be seen.



## 2. LITERATURE REVIEW

### 2.1 Urea production process

CO<sub>2</sub> Stripping process – Stamicarbon licensed - is the production route here studied, due to a partnership with Fábrica de Fertilizantes Nitrogenados-PR. The process unit analyzed produces 2000 ton/day 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. 2.1.

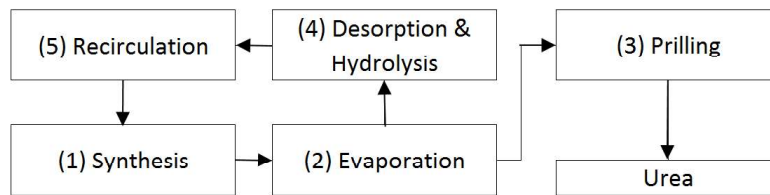
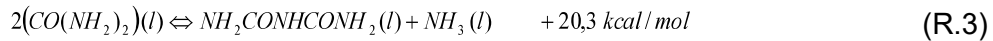
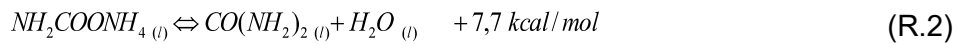


Figure 2.1 - Simplified block diagram for industrial urea production.

The main reactions present in this process are: ammonium carbamate formation (R.1), urea formation (R.2) and biuret formation (R.3).



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.

Recirculation section is responsible for removing the ammonium carbamate present in the solution through its decomposition in NH<sub>3</sub> and CO<sub>2</sub>, besides converting and condensing NH<sub>3</sub> and CO<sub>2</sub> 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 the 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  $\text{NH}_3$ ,  $\text{CO}_2$  and urea present in the water that comes from the Evaporation section.

Flowsheet of the process can be seen in Fig. 4.2 and 4.3.

## 2.2 Modeling and simulating urea production process

There are a number of reported studies ((DENTE, PIERUCCI, & SOGARO, 1988); (DENTE et al, 1992); (ISLA, IRAZOQUI, & GENOUD, 1993); (SATYRO et al, 2002); (HAMIDIPOUR et al, 2005); (c); (RASHEED, 2011); (ZENDEHBOUDI et al., 2014); (CHINDA et al, 2015); (EDRISI, MANSOORI, & DABIR, 2016) and (JEENCHAY & SIEMANOND, 2018)) on mathematical modeling and/or simulating synthesis section, which means, the reaction section. Nevertheless, there is still a range of restrictions for simulating such a complex process.

HAMIDIPOUR et al.,(2005) developed a mathematical model for the synthesis section. The thermodynamic framework was based on Wilson and ideal gas equations. Inlet and outlet temperature and mass fraction in the reactor and outlet temperature of the scrubber were compared to industrial data and varied from -6.90% to 2.65%.

ZHANG at al. (2005) simulated also the high synthesis loop. Extended electrolytic UNIQUAC equation and perturbed-hard-sphere were employed as thermodynamic models. Outlet mass fraction data from reactor and stripper varied from 2.71% to 9.76% 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.

ZENDEHBOUDI et al., (2014) proposed a mathematical model only for the reactor based in a UNIQUAC approach. When compared to industrial data, deviation less than 2.35% for the liquid outlet stream is reached.

EDRISI et al., (2016) simulated the entire urea plant using SR-POLAR for thermodynamic description. Authors did not report industrial data deviation, do not considered biuret reaction and simulated recirculation section with a Gibbs reactor approach.

CHINDA et.al. (2017) simulated the synthesis loop, proposed a power law kinetic model for ammonium carbamate, urea and biuret formation, thermodynamic model was SR-POLAR based. Deviations from industrial data were less than 6%.

JEENCHAY & SIEMANOND (2018) simulated the entire process using NRTL for thermodynamic approach, but did not perform validation data against industrial parameters.

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 reaction, is lacking in available data at relevant process conditions. Just (HAMIDIPOUR et al., 2005), (ZENDEHBOUDI et al., 2014) and (CHINDA et al., 2017) had considered the biuret reaction in synthesis section. Besides this, further studies using the developed simulation as basis are only presented in (JEENCHAY & SIEMANOND, 2018), as an economic analysis of the process.

### **2.3 State of Art: process intensification applied to urea production**

According to HARMSSEN, (2010), PI technologies like reactive distillation, dividing wall column distillation and reverse flow combustors have been implemented many times in the petrochemical industry. The main drivers for innovation in process industry are feedstock efficiency increase, lower capital cost, lower safety risks, energy saving and carbon dioxide emission reduction.

PI comprises a set of often innovative approaches in process engineering and equipment design that results in substantially smaller, more selective and more energy-efficient processing plants. In essence, PI involves breaking apart complex process problems into the underlying fundamentals to find solutions beyond conventional unit operations (PEREIRA, 2019).

Worldwide trends in urea process technologies evolves (a) larger plants, (b) lower elevation and (c) submerged condensation in synthesis section, and (d) higher alloy materials for corrosion resistance, as pointed in EIJKENBOOM & BROUWER (2015) . Quickly associated with efforts in process intensification studies, items (b), (c) are both related to synthesis section.

Development of Stamicarbon urea synthesis passed through the oxygen-passivated plant, CO<sub>2</sub> Stripping process, pool condenser implementation and, later, Urea 2000plus™ technology. The main equipment in synthesis section – stripper, scrubber, reactor and condenser – were positioned above each other in the old process. After improvements, an advanced approach combined stripper and reactor in one unit: the horizontal pool reactor. The layout of the new plant had a height reduction by a factor of 3 and also the number of units has been decreased. (MOULIJN & STANKIEWICZ, 2004)

According to MOULIJN & STANKIEWICZ (2004), all these modifications are results of process intensification (PI) studies applied to urea Synthesis section. A schematic drawing of this evolution can be seen in Fig 2.2.

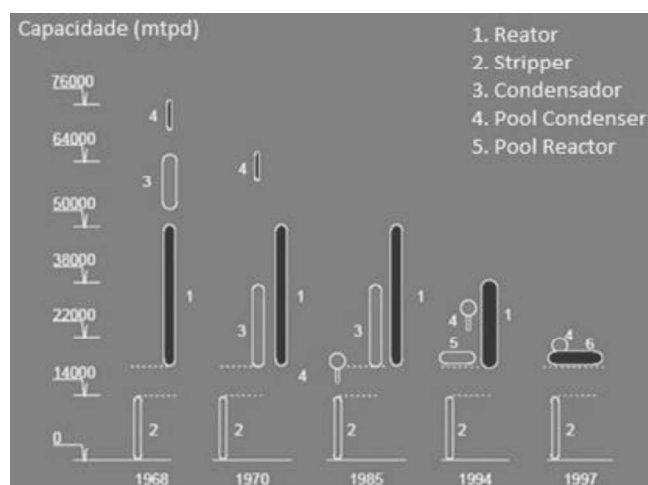


Figure 2.2 – Plant size reduction into Urea 200plus™ technology. Adapted from (STANKIEWICZ A. , 2003)

Similar studies concerning development in synthesis sections can also be seen in JX Urea Technology. This Chinese urea synthesis concept improved the conventional technology to work with just one high pressure reactor and to obtain similar costs production as in stripping process. THESES (Technology of High Efficiency Synthesis and Energy Saving), also a Chinese technology, has a combination of a vertical submerged condenser and a reactor with a low elevation layout. In both cases, the number of equipment also has been decreased ( BROUWER, 2010). This innovation can be seen in a facility in Sichuan with a capacity production of 500 tnpd. A schematic figure of the THESES synthesis section can be seen in Fig. 2.3.

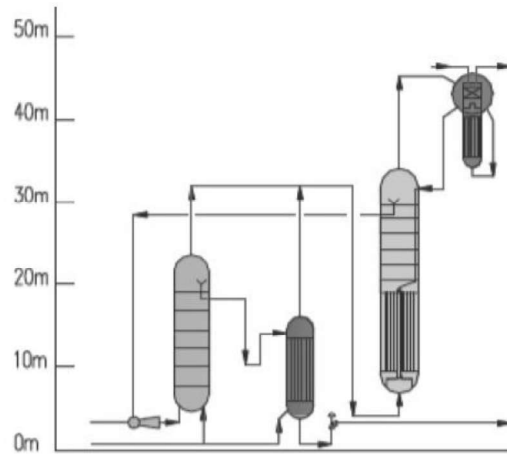


Figure 2.3 – THESE synthesis layout. Adaptated from (Eijkenboom et al, 2015)

However, in a general way, all of the above cited examples were performed in order to attend the same peculiarities in urea process plant design: thermodynamic limit on  $\text{CO}_2$  conversion combined with the strongly non-ideal behavior of  $\text{NH}_3\text{-CO}_2$  system in urea process conditions. In a practical way, this means they are restricted mainly to synthesis section.

There are 510 urea plants in operation around the world, 48% located in China, 18% in Asia and Oceania, 10% in the Americas and Caribbean, 8% in Europe and 16% in Africa and Middle East (EIJKENBOOM & BROUWER, 2015). In Brazil, there are 3 urea facilities in operation and 3 more in strategic planning (CHINDA, 2015).

The world's urea production capacity is around 195 million metric tons per year (EIJKENBOOM et al, 2015). For this different technologies are employed as it can be seen in Figure 2.4. It is noticed that a significant part, 42%, still operates through conventional process, which means without stripper technology. Most of these plants are Chinese and have, besides high energy consumption, low operating capacities. The second most employed technology is the technology commercialized by Stamicarbon through  $\text{CO}_2$  Stripping, followed by Saipem's  $\text{NH}_3$  Stripping and the Japanese Toyo technology.

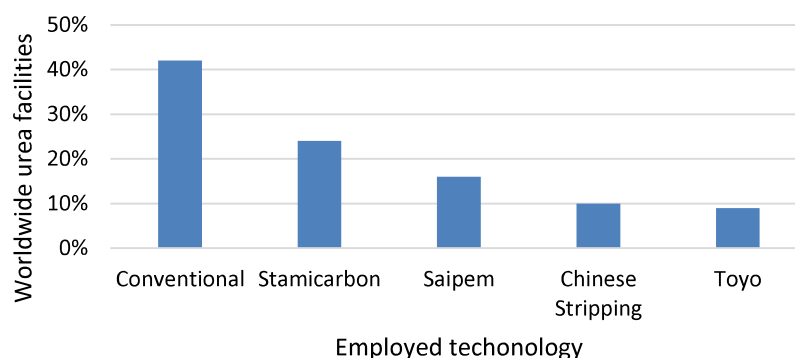


Figure 2.4 – Main employed technologies for worldwide urea production process. Data from (EIJKENBOOM et al, 2015).

Most part of urea facilities operating by conventional process are from the early 1960s / 1970s. They are large plants with low yields and high energy consumption. Over the years, these plants trend to be replaced by modern units. However, the Chinese JX Chengdu has developed JC Urea Technology, which can be used to revamp plants operating by the conventional technology and through innovations into the reactor.

Mega Urea Plants are another trend in urea technology market. Mega Plants are production units of 3000 tmpd or more. Stamicarbon has 17 Mega Plants, given that 15 are already in operation. Saipem has 15 Mega Plantas, given that 6 are in operation and, finally, Toyo has 3, given that only 1 in already operating. Most of these units are producing granulated.

The world's three largest urea licensing companies are Stamicarbon, Saipem and Toyo. The focus of this thesis is to study currently commercialized technologies, so conventional technologies will not be considered. Thus, in order to have a clear idea of the state of the art a patent search was conducted with the major process licensors: Stamicarbon B.V., SAIPEM, TOYO. CASALE and UHDE.

In order to have a patent profile of innovations related to urea production process, through SPACENET and INPI database a search was performed in the period from 01/2000 to 09/2019. The name of the depositor: STAMICARBON, SAIPEM, CASALE, TOYO, UHDE and the keyword “urea” in the title. The analysis also considered patent applications as well as patent registrations.

Thus, a total of 204 patent registrations and / or patent applications were obtained from Spacenet website. In ascending order of the number of patent application there are Swiss Casale, Dutch Stamicarbon, Japanese Toyo, Italian Saipem and German Uhde. The graph in Figure 2.5 shows a classification of these patent deposit according to: process innovation, emission reduction, process control, materials engineering and SCR technology.

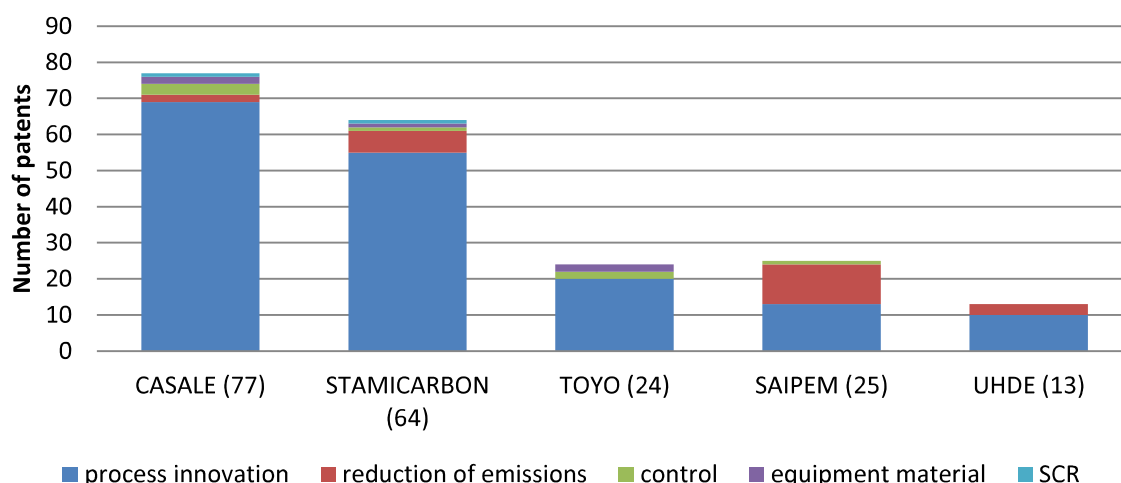


Figure 2.5 – Published patents correlation according to licensors.

According to the graph, it can be pointed out that 167 from 204 patents, which means more than 85%, concern about process innovation. Given that for process innovation it can be understood any modification in equipment construction, new equipment sequencing and new process equipment.

Thus, from these 167 patents and / or patent deposits related to process innovation, 61 have proposed minor changes throughout the process and will not be considered for the purposes of this study. Given that for minor changes can be understood as new proposals for process control, removal of dust in urea finishing, transportation of melted urea to prilling tower/granulation, among others. Production of urea and another different product, such as urea nitrate or melamine, will also not be considered. The result obtained with this data can be visualized in Figure 2.6.

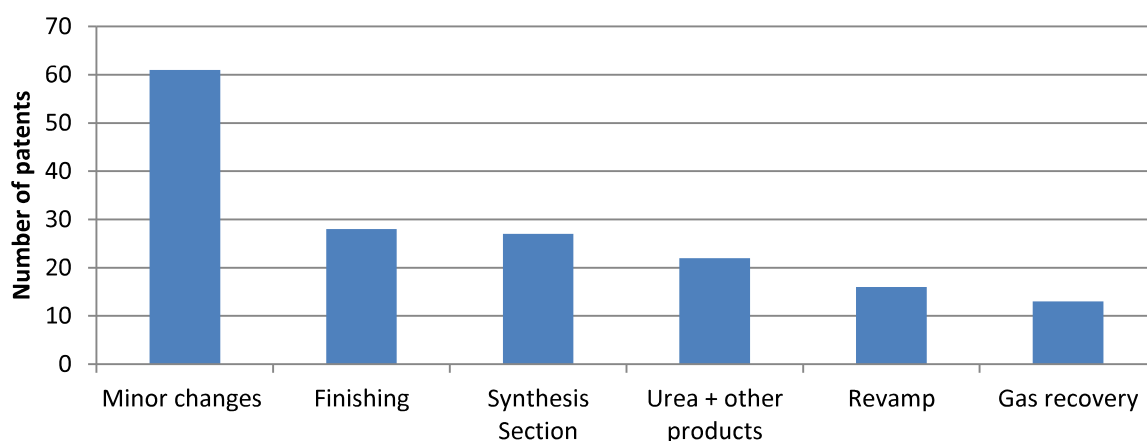


Figure 2.6 – Patents deposits concerning about process innovation.

Thus, 106 patents and / or deposits concern about finishing (28), Synthesis section (27), production of urea + other products (22), revamp (16), gas recovery (13).

From INPI website, a total of 69 patent registrations and / or patent applications were obtained using the same keywords and period of time as previously described. Casale is pointed out as the patent depositor, followed by, Stamicarbon, Toyo and Uhde. Stamicarbon, Casale and Uhde are investing in the prilling section and Toyo in producing urea plus another product, as melamine and urea nitrate.

Thus, it can be said that deposits and / or patents registrations made in Brazil are related to revamps of existing units through minor improvements along the process, mainly at the prilling unit. Stamicarbon and Casale are the largest depositors, which means the largest technology investors in Brazil. However, there is no focus on new urea units, since no patents covering more technologically advanced processes were found.

Considering deposits and / or patents worldwide, it can be said that there is a great investment in reducing size and number of equipment in synthesis section, increase in production and in keeping the  $\text{NH}_3$  or  $\text{CO}_2$  Stripping. There is also significant investment in prilling or granulation unit.

Based on the presented facts, it can be seen that there are opportunities for studying the entire urea unit production with a holist approach, which means considering not only the chemical perspective but also the economic and the sustainability ones.



## 2.4 Conclusion

- Most part of modeling and simulation works on urea process concerns only about the synthesis section.
- There are few studies considering biuret formation along the process.
- Worldwide patent search indicates innovation effort mainly in the synthesis and finishing sections.
- Local patent search indicates low investment on new urea production technologies in Brazil.
- There are no evidences reported on scientific literature of a holist approach on analyzing the urea production process.
- There are no evidences of a published study on process intensification applied to urea production process, although it is known licensors did it, giving the cited improvements in the synthesis section.
- Opportunities for process intensification should be investigated considering the entire unit and the challenges faced by industry.

### 3. METHODOLOGY

Methodology presented here is hierarchical and is composed of three levels. Each level can be used independently given that information from previous level is available. An illustrative schematic model can be seen in Fig. 3.1. Methodology for Level 2 is based on (Carvalho et al. 2008) and for Level 3 on (BABI et al., 2014).

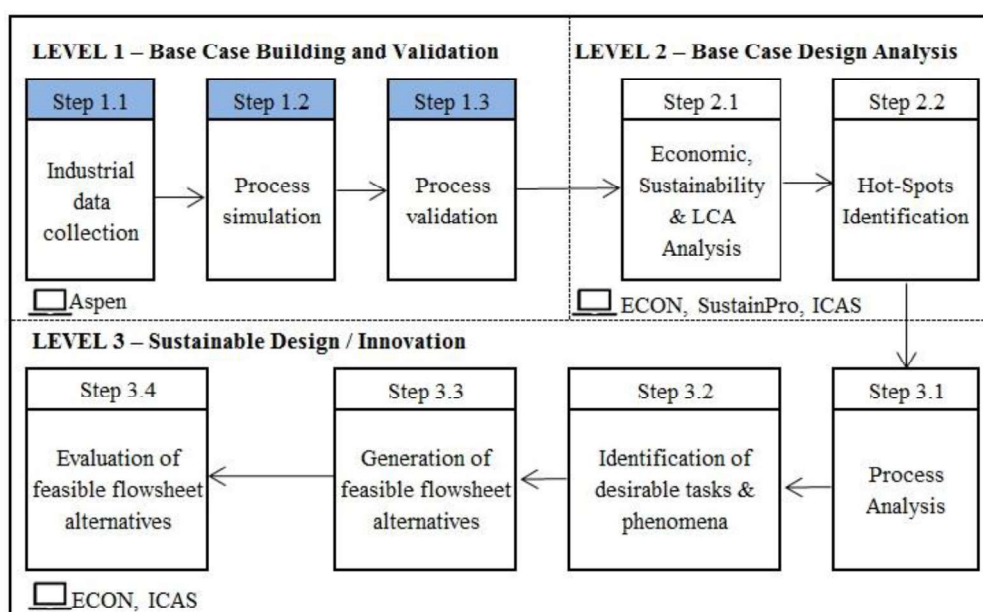


Figure 3.1 - Framework for base case building, analysis and intensification.

#### 3.1 Level 1 - Base Case Building and Validation

Level 1 consists in three steps, in which the objective is to obtain a process model which can guarantee assurance and reproducibility of outputs for the base-case. In principle, any data storage software and process simulator can be used. Software employed here are commercial Excel and Aspen Plus.

##### 3.1.1 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.

### **3.1.2 Step 1.2. Process Simulation**

The objective here is to perform a rigorous process simulation of the base case. Appropriate thermodynamic and unit operational models should be chosen.

Usually modern process simulator packages (Hysys, Aspen, SuperPro ...) are able to suggest the best thermodynamic approach according to the chemical substances the simulation will work with. However an exhaustive literature review is recommended, given that there are systems with difficult modeling, as urea system. Another important action is to specify the unit operations/equipment according to the equipment model library available in the chosen software, which requires a minimum knowledge of the process simulator.

This step results in detailed mass and energy balance data and the properties of all streams in the flowsheet.

### **3.1.3 Step 1.3. Process Validation**

The main objective of this step is to perform the validation of the simulation using the data collected in Step 1.1. 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 1.1, 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 operated 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 (CHINDA et al., 2015) 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 1.1, 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.

### **3.2 Level 2 - Base Case Analyses**

Level 2 consists in two steps, in which the objective is to analyze the base case and identify process bottlenecks / hotspots. In principle, any software for performing economic, sustainability and life cycle analyses can be used. Computer aided tools employed here are ECON, SustainPro and LCSOFT software, all of them available in ICAS-CAPEC.

#### **3.2.1 Step 2.1. Economic, Sustainability & Life Cycle Assessment Analysis**

Economic analysis here presented is used to obtain the distribution of the utility costs for each unit operation and it is performed using ECON. The ECON software was developed in visual basic and performs cost calculations based on the cost model given in "Plant Design and Economics for Chemical Engineers" (PETERS, TIMMERHAUS & WEST, 2004).

Sustainability analysis is used to identify hotspots otherwise not evident from the economic analysis, as for example raw material loss, and it is performed using SustainPro. The SustainPro software was developed in visual basic and performs sustainability analysis using as input mass and energy balance data and also several cost related data. SustainPro is based in an indicator-based methodology using a set of calculated open-paths (OPs) and closed- paths (CPs) indicators.

The closed-paths (CP) are the process recycles with respect to each compound in the process. In other words, they are the flow-paths which start and end in the same unit of the process. An open-path (OP) consists of an entrance and an exit of a specific compound in the process. The entrance of the compound in the system can be due to its entrance through a

feed stream or by its production in a reactor unit. The exit of the respective compound can be due to a “demand” (exit) stream or by its reaction in a reactor unit (CARVALHO, GANI & MATOS, 2008).

Sustainability indicators here considered are:

1. *Material value added (MVA)*: This indicator gives the value added between the entrance and the exit of a given compound, that is, the value generated or lost between the start and the end point of an open-path. Negative values of this indicator show that the compound has lost its value in this open-path and therefore point to a potential for improvement.

2. *Energy and waste cost (EWC)*: This indicator is applied to both open- and closed-paths. It takes into account the energy costs (EC) and the costs related with the compound treatment (WC). The value of EWC represents the maximum theoretical amount of energy that can be saved in each path within the process. High values of this indicator show high consumption of energy and waste costs and therefore these paths should be considered in order to reduce the indicator value.

3. *Total value added (TVA)*: This indicator describes the economic influence of a compound in a given path and is the difference between MVA and EWC. Negative values of this indicator show high potential for improvements in terms of decrease in the variable costs.

4. *Accumulation factor (AF)*: This indicator determines the accumulative behavior of the compounds in the closed-paths. This corresponds to the amount that is recycled relative to the input to the process and not the inventory. High values of this indicator show high potentials for improvements.

Life cycle assessment (LCA) analysis is used to obtain the environmental impact of the process in terms of carbon footprint and it is performed using LCSOFT. The LCSOFT software was developed in visual basic and LCA analysis.

### **3.2.2 Step 2.2. Hot-Spots Identification**

The objective at this step is to identify potential process hotspots of the base case through the simulation and the indicator based analyses, which means the sustainability metrics obtained through ECON, SustainPro, and LCSOFT. Thus, this step can be briefly described as a translation of the indicator values obtained at Step 2.1 into targets process hotspots using Table 3.1, followed by a translation of these hotspots into design targets using Table 3.2.

Table 3.1 - Translation of economic ( $\alpha$ ), sustainability ( $\beta$ ) and LCA ( $\gamma$ ) analysis into process hotspots. Adapted from (BABI, GANI & WOODLEY, 2014).

Indicator Value	Base-case property	Reason	Identified Process hot-spot
$\alpha_1$ = raw material recycle/cost $\beta_1$ = MVA	Un-reacted raw materials	Equilibrium reaction	-Activation problems - Limiting equilibrium/raw material loss - Contact problems of raw materials/limited mass transfer -Limited heat transfer
$\alpha_2$ = utility cost $\beta_2$ = EWC $\gamma_1$ = CO <sub>2</sub> equivalent	$\Delta H_{rxn}>0$ Reactor cooling	Exothermic reaction	-Highly exothermic reaction
$\alpha_2$ = utility cost $\beta_2$ = EWC $\gamma_1$ = CO <sub>2</sub> equivalent	$\Delta H_{rxn}<0$ Reactor heating	Endothermic reaction	-Highly endothermic reaction
$\alpha_2$ = utility cost $\alpha_3$ = capital cost	Reactor operating conditions	Temperature and pressure operating window for the reactor	-Explosive mixture -Product degradation by temperature
$\alpha_4$ = Product sale $\gamma_2$ = PEI	Formation of by-product(s)	NOP=number of desired products plus number of undesired products	-Formation of undesired side-products
$\alpha_2$ = utility cost $\beta_1$ = MVA $\beta_2$ = EWC $\gamma_1$ = CO <sub>2</sub> equivalent $\gamma_2$ = PEI	Un-reacted raw materials and products recovery	-Presence of azeotrope(s) -High energy usage heating and/or cooling	-Azeotrope -Difficult separation: low driving force -High energy consumption and/or demand

Table 3.2 - Identified design targets from the identified process hot-spots. Adapted from (BABl et al, 2014).

[illegible]

### 3.3 Level 3 - Sustainable Design / Innovation

Level 3 consists in four steps, in which the main objective is to achieve a more sustainable process design. Phenomena based process intensification method is applied. A brief explanation of the method is presented here and the reader can obtain further details in (LUTZE et al, 2013). The method operates at different levels of aggregation where the flowsheet is represented in terms of unit operation from which the tasks are identified and from each task a group of phenomena is associated. Then, in a reverse pathway, different group of phenomena can be joined to form tasks, as well as tasks can be joined to form operations and group of operations to form process flowsheet. This concept is illustrated in Fig 3.2.

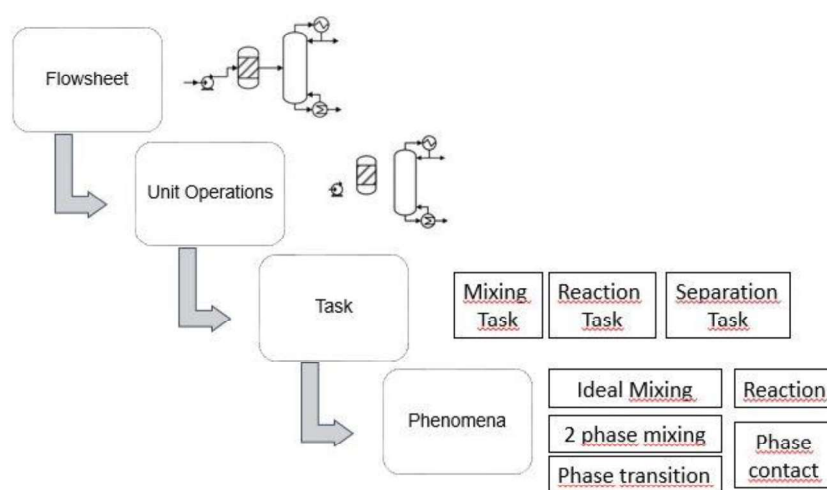


Figure 3.2 –Schematic concept of phenomena-based process intensification.

The phenomena currently considered are classified into eight different classes:

1. M – ideal mixing, mass flow with one or several phases
2. PC – phase contact, the contact and resistances at phase boundaries of phases
3. PT – phase transition, mass transfer of compounds between two phases
4. 2phM – phase change, state change of a complete stream at no phase transition
5. PS – phase separation, the degree of separation of two phases
6. R – reaction, change in mass of a compound or compounds generates or consumed between inlet and outlet
7. H/C – energy transfer, energy transfer between sources and sinks of energy
8. D – stream dividing, division of a stream into two or more streams

Each phenomena can also be associated to the component / mixture phase considered, ie, PT(VL) – phase transition vapor/liquid; PS(LS) – phase separation liquid/solid, in which V, L and S represent vapor, liquid and solid phases, respectively.



### 3.3.1 Step 3.1. Process Analysis

The flowsheet is transformed from the unit operations scale to a task based flowsheet (TBF). Each unit operation is identified and replaced by a single or multiple tasks to obtain a task-based flowsheet; i.e., “reactor” is translated to “reaction task”; “distillation tower” is translated to “separation task”. Unit operations which affect a change in temperature and pressure are not included in the task-based flowsheet. All inlet and outlet streams connecting unit operations maintain their structural position in that task-based flowsheet as in the unit operation-based flowsheet.

Thus, the TBF is translated to a phenomena based flowsheet (PBF) using Table 1 available in Appendix A, adapted from (BABI et al, 2014). The phenomena set obtained is stored and constitute the initial search-space.

The identified hotspots are then associated to the corresponding tasks and phenomena of the unit operations in which they occur.

Further process analyses are required to obtain data enough for next steps. Thus, pure compound data from any appropriate properties database is retrieved and a mixture analysis is performed. For this, it is method from literature (JAKSLAND et al., 1995) is performed as: (1) analysis of pure compound properties using a binary ratio matrix, (2) azeotropic analysis including its pressure dependency and (3) miscibility analysis.

### 3.3.2 Step 3.2. Identification of desirable tasks & phenomena

The objective at this step is to identify desirable tasks and corresponding Phenomena Building Blocks (PBBs) for overcoming the process hot-spots. A desirable task is defined as a task that if performed has the potential to minimize/eliminate a process hot-spot.

For this, the PBBs based search-space is defined by identifying tasks and their associated PBBs needed to overcome the hotspots. With the identified hot-spots and using Table 1 in Appendix B, additional PBBs are selected and added to the initial PBBs search-space identified in previous step. Thus, the PBBs based search-space is reduced by selecting the desirable phenomena according to property analysis of each compound and mixture as well as reactions in the system.

### 3.3.3 Step 3.3 Generation of flowsheet alternatives

The objective of this step is to generate feasible flowsheet alternatives using an integrated task-phenomena based approach. For this, PBBs are combined according to a set of combination rules to fulfil the objectives of a task that performs an activity/action in the flowsheet.

Thus, using equations (01) and (02) [BABI et al., (2014)], the maximum number of phenomena (NSPBmax) that can be combined to form simultaneous phenomena building blocks (SPBs) is calculated.

SPBs are defined as the combination of one or more PBBs into pre-defined SPBs that can be further combined with each other to generate more SPBs.

$$n_{ph,Max} = Ph_{BB} - (Ph_E - 1) - (Ph_M - 1) - Ph_D \quad \text{Eq (01)}$$

$$NSPB_{Max} = \sum_{k=1}^{n_{ph,Max}} \left[ \frac{(Ph_{BB}-1)!}{(Ph_{BB}-k-1)!k!} \right] + 1 \quad \text{Eq (02)}$$

PhE is the total number of energy transfer phenomena, PhM is the total number of mixing phenomena, and PhD is the dividing phenomena.

Generate feasible SPBs from the combination of SPBs using PBB connectivity rules, according to Table 1 in Appendix C.

Based on a task-phenomena approach, intensified alternative flowsheets are built. The identified phenomena operating window is used, and phenomena are connected to form simultaneous phenomena building blocks (SPBs). SPBs are linked to form operations, which are transposed into unit operations, and are combined to form flowsheet alternatives. By combining phenomena, the same and new combined tasks can be performed, thereby leading to new and more sustainable alternatives that match the design targets.

### 3.3.4 Step 3.4. Comparison and selection of the best flowsheet alternatives

The objective at this step is to identify the best flowsheet alternative according to economic, sustainability and LCA analyses. Thus, the process alternatives generated at Step 3.3 are analyzed following the same patterns previously described at Step 2.1.

The economic, sustainability and LCA indicators are calculated for each of the generated flowsheet alternatives in order to compare them to the base case design for selecting the best flowsheet alternatives (more sustainable designs).

The flowsheet alternatives which satisfies the performance criteria and the design targets are selected as (more sustainable designs) and may or may not include hybrid equipment.

## 4. RESULTS AND DISCUSSION

### 4.1 Level 1 - Base Case Building and Validation

The process analyzed produces 2000 ton/day of urea through Stamicarbon CO<sub>2</sub> Stripping technology, as mentioned in item “2.1 Urea production process”. Figure 4.1 indicates temperature and pressure in which each section operates in normal conditions.

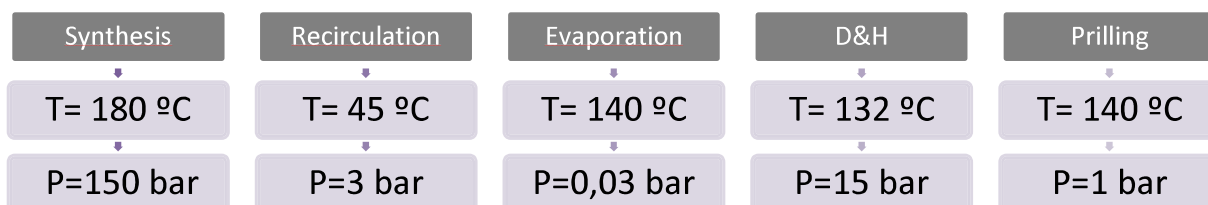


Figure 4.1 – Range of operational conditions for producing urea.

#### 4.1.1 Step 1.1. Industrial data collection

Industrial data collection was performed as described at Step 1.1. 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. 4.2 and 4.3. 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).

Process data for the period of 9 months is stored in Excel ®.

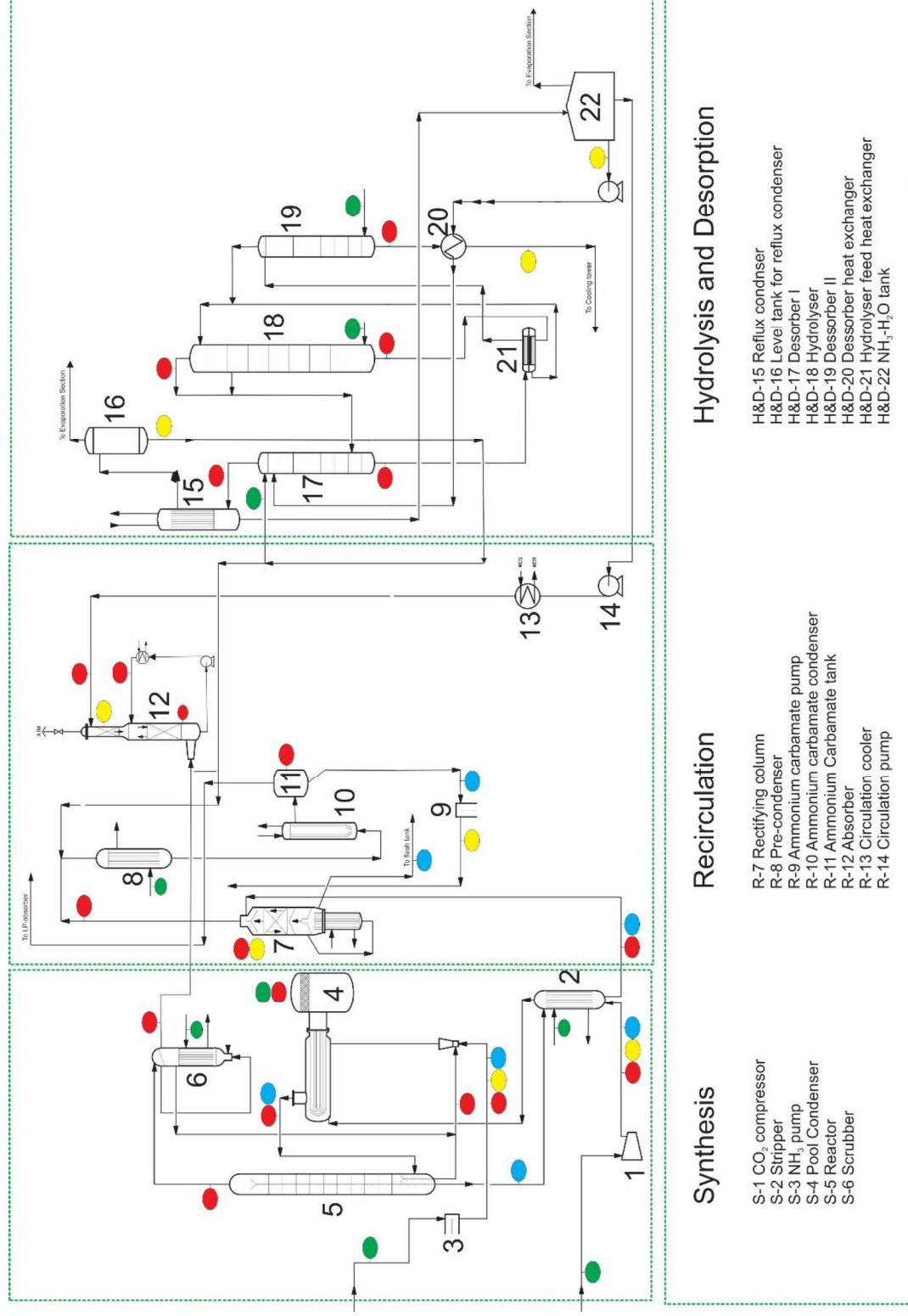


Figure 4.2 - Process flowsheet and data point collection for Synthesis, Recirculation and Hydrolysis & Desorption sections.

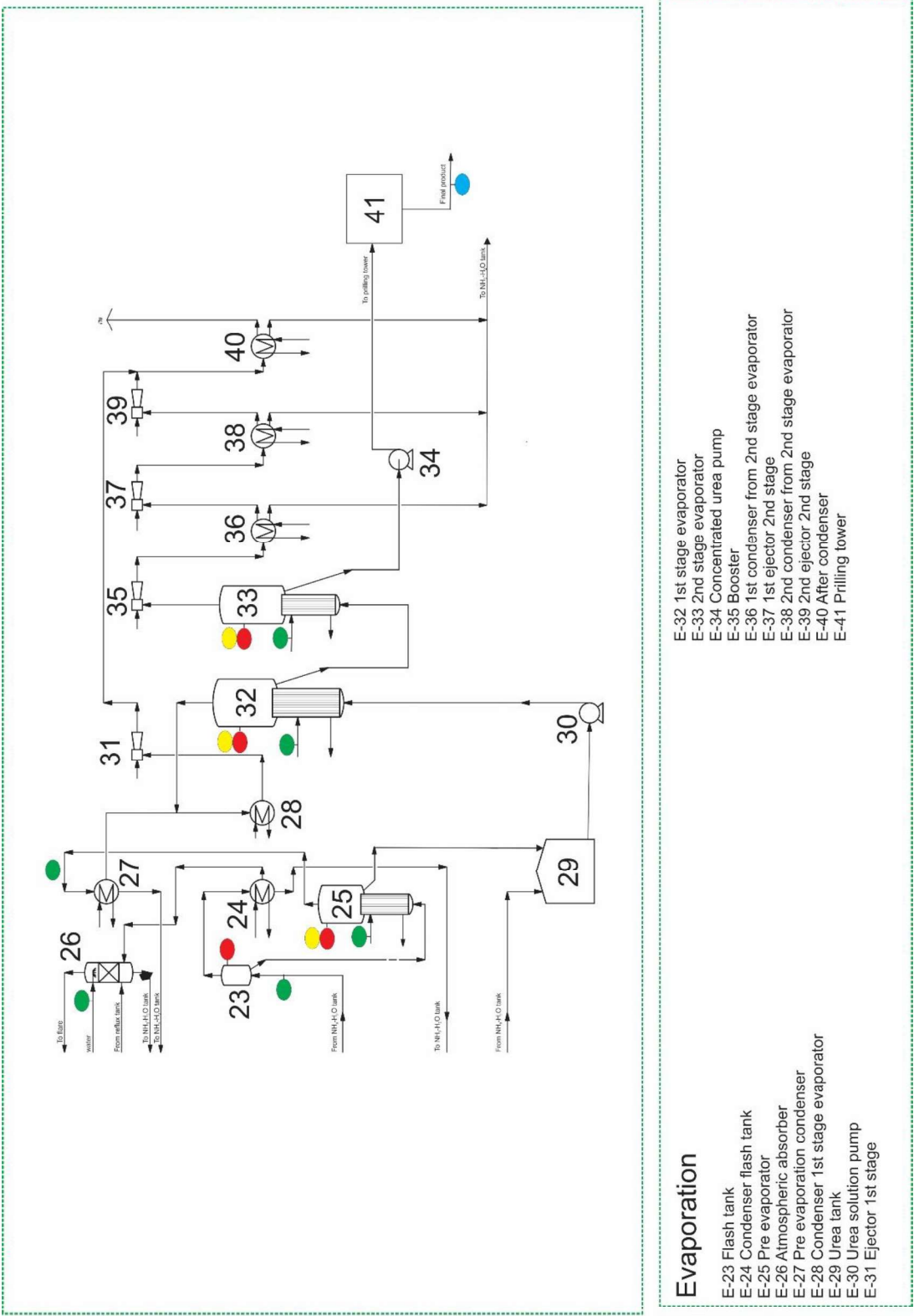


Figure 4.3 - Process flowsheet and data point collection for Evaporation section.

#### 4.1.2 Step 1.2. 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 CO<sub>2</sub> reacts to form ammonium carbamate, according to (Rasheed, 2011) and (Mark Brouwer, 2009).

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 SOAVE, (1972), SCHWARTZENTRUBER & RENON, (1989) and PENELOUX, RAUZY, & FREZE, (1982). Kinetic equations for reactions R.1, R.2 and R.3 are taken from (R. C. Chinda et al., 2015).

$$(R.1) \quad r_1 = 1628 \exp\left(\frac{-62801997}{RT}\right) C_{NH_3}^{0,4} C_{CO_2}^{-0,11} \quad \text{Eq. (09)}$$

$$(R.2) \quad r_2 = 12000 \exp\left(\frac{-62801997}{RT}\right) C_{CARB}^{0,39} \quad \text{Eq. (10)}$$

$$(R.3) \quad r_3 = 5,84 \exp\left(\frac{-80020000}{RT}\right) C_{UREIA}^4 \quad \text{Eq. (11)}$$

Pure component data and binary interaction parameters of NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O, urea, ammonium carbamate, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> 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 are urea.

Process simulation was performed as described in Step 1.2. 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 4.1.

Table 4.1 - Model library from AspenPlus.

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

This step results in detailed mass and energy balance data and the properties of all streams in the flowsheet.

#### 4.1.3 Step 1.3. Process Validation

At this step, the data collected from industrial urea plant for validating the simulation is analyzed. As described at Step 1.3, in order to guarantee consistency to the analysis, all the experimental points should be taken in the same operational condition. From those 270 operational data points (days), only 32 met this criterion.

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. Production capacity data with variation coefficient with values lower than 1.5% were selected. Table 4.2 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% for the 11 operational data points that met all the criteria.

Table 4.2 - Statistical Analyses with capacity plant data.

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

Validation of the simulation was performed calculating the difference between industrial and simulated data and dividing it per industrial data. Equations used for process validation step, can be seen in Table 1, Appendix D. A total of 37 different process parameters were



evaluated following this criterion, among them stream temperature, steam generation, mass fraction for CO<sub>2</sub>, NH<sub>3</sub>, urea, H<sub>2</sub>O and biuret, CO<sub>2</sub> 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 4.3.

Table 4.3 - Absolute average deviation for evaluated points.

Equipment	Parameter	This work	Literature	Ref.
<b>Pool Condenser</b>	LP steam flow	7.56%	-	-
	Urea MF	0.89%	-	-
<b>Reactor</b>	CO <sub>2</sub> MF	5.95%	8.84%	[6]
	NH <sub>3</sub> MF	4.33%	9.76%	[24]
	Urea MF	3.38%	2.65%	[5]
	H <sub>2</sub> O MF	4.38%	2.71%	[24]
	Biuret content	4.96%	-	-
	CO <sub>2</sub> conversion	2.41%	0.44%	[3]
	N/C ratio	4.83%	6.90%	[5]
	H <sub>2</sub> O /urea ratio	6.18%	-	-
<b>Scrubber</b>	T of the liquid outlet	4.77%	-	-
<b>Stripper</b>	CO <sub>2</sub> MF	5.00%	5.10%	[24]
	NH <sub>3</sub> MF	6.12%	4.14%	[24]
	urea MF	2.93%	0.20%	[4]
	H <sub>2</sub> O MF	4.32%	4.96%	[24]
	Biuret content	4.96%	-	-
	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%	-	-
<b>Rectifying column</b>	Urea MF	1.52%	-	-
	H <sub>2</sub> O MF	3.04%	-	-
	Biuret content	3.18%	-	-
<b>Urea tank</b>	Urea MF	4.17%	-	-
	H <sub>2</sub> O MF	4.83%	-	-
	Biuret content	3.82%	-	-

Table 4.3 - Absolute average deviation for evaluated points. (continuation)

Equipment	Parameter	This work	Literature	Ref.
Final product	H <sub>2</sub> O MF	6,91%	-	-
	Biuret content	5,73%	-	-
Reflux condensate tank	CO <sub>2</sub> MF	4.34%	-	-
	NH <sub>3</sub> MF	4.89%	-	-
	urea MF	2.58%	-	-
Ammonia water tank	CO <sub>2</sub> MF	4.31%	-	-
	NH <sub>3</sub> MF	4.55%	-	-
	Urea MF	3.49%	-	-
	H <sub>2</sub> O MF	0.34%	-	-

## 4.2 Level 2 - Base Case Design Analysis

### 4.2.1 Step 2.1. Economic, Sustainability and LCA Analysis

The economic analysis is performed using ECON software. Although ECON it is capable of estimating capital expenditure (CAPEX) and operative expenses (OPEX), in this analysis just OPEX is considered.

The main objective of this economic analysis is to help to identify hotspots, in order to overcome them and to generate more sustainable process alternatives. Thus, CAPEX main parameters, such as costs related to equipment purchase and installation, instrumentation and control, piping, electrical installations, buildings, yard improvements, service facilities and land would not affect the identification of hotspots.

In Table 4.4 it is possible to check the cost values associated to utilities, raw material and product, all of them provided by the urea facility.

Table 4.4 – Costs related to utilities, raw material and product.

Utilities	Cost	Raw material	Cost	Product	Cost
Heating (High pressure) (\$/GJ)	9.83	CO <sub>2</sub> (\$/kg)	0.03	Urea (\$/kg)	0.35
Heating (Medium pressure) (\$/GJ)	8.22	NH <sub>3</sub> (\$/kg)	0.5	-	-

Table 4.4 – Costs related to utilities, raw material and product. (continuation)

Utilities	Cost	Raw material	Cost	Product	Cost
Cooling (\$/GJ)	0.35	H <sub>2</sub> O (\$/kg)	0.0008	-	-
Electricity (\$/kWh)	0.06	-	-	-	-

The main parameters can be seen in Table 4.5. Costs associated to maintenance, operator training and abnormal operation are not considered.

Table 4.5- Parameters considered for economic analysis.

Operating time (hr/year)		8000
Urea product (kg/hr)		76782
Raw materials (kg/hr)	NH <sub>3</sub>	44653
	CO <sub>2</sub>	57732
Total utility cost (\$/year)		13,420,129
Total energy consumption (kJ/h)		1.50x10 <sup>8</sup>
Product/Raw material (kg/kg)		0.75
Energy/product (MJ/kg)		1.94
Cooling water (GJ/hr)		452
Water for cooling/product (m <sup>3</sup> /kg)		0.24
Hot water/steam (GJ/hr)		114
Total utility cost/ product (\$/kg)		0.022

Considering the entire urea production process, heating, cooling and electricity, respectively, are the main drivers for operating cost. This is already evidenced in (Jeenchay & Siemanond, 2018) work, in which total energy consumption for urea process was calculated to be  $1,945 \times 10^9$  kJ/h.

In terms of percentage of total utility cost, the main drivers are: Evaporator E-32 (32.98%), CO<sub>2</sub> compressor S1-A (23.44%), Rectifying Column R-7 (16.88%), CO<sub>2</sub> Compressor S1-B (10.20%), Pre Evaporator E-25 (6.14%) and Pool Condenser S-4 (3.34%), as it can be seen in Fig 4.4.

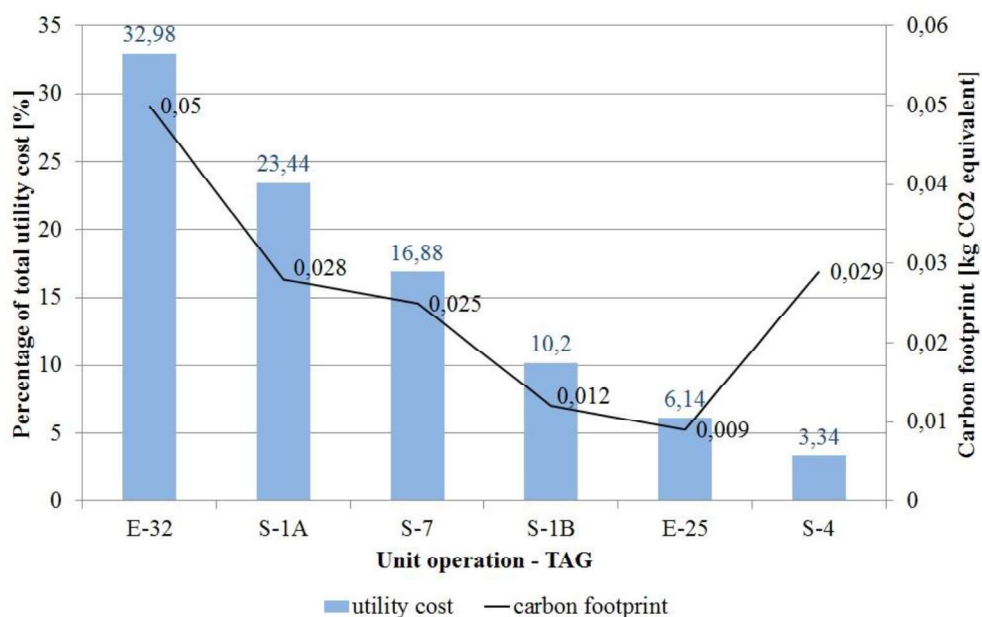


Figure 4.4 – Percentage of utility costs and carbon footprint with respect to each unit operation.

LCA analysis was performed using LCSofT and, as it can be seen in Fig. 4.4, confirms the economic analysis. The same equipment shown as main drivers in economic analysis - columns (S-7, E-25, E-32); compressors (S-1A/B); pool condenser (S-4); heat exchanger (E-28) - have the largest carbon footprint. This is because of their high utility consumption.

Sustainability analysis was performed using SustainPro. The steady state mass and energy data obtained in Step 1.3 are used as input here. For this case study it was obtained 495 closed-paths and 192 open-paths. Complete results for open- and closed-paths can be seen in Appendix E.

Sustainability analysis results for the most relevant paths in terms of MVA, TVA, EWC and AF for the open- and closed-paths, respectively, are shown in Table 4.6 and in Fig. 4.5.

Table 4.6- Paths in the base case with highest improvement potential.

Path	OP1	CP1	CP2
Compound	H <sub>2</sub> O	NH <sub>3</sub>	H <sub>2</sub> O
Flowrate (kg/h)	13,471.370	23,161.300	3,438.333
MVA (10 <sup>3</sup> \$/year)	-11	-	-
TVA (10 <sup>3</sup> \$/year)	-177.204	-	-
EWC (10 <sup>3</sup> \$/year)	166,427	36,148	47,220
AF (10 <sup>3</sup> \$/year)	-	0.295	0.030

In Table 4.5, water in OP1 has a very negative value in terms of MVA and TVA indicators and positive value for EWC. This means that a lot of money is wasted from the time the material (compound - water) enters to system to the time they exit the system. Thus, water is losing its value as it exits the process through this path.

CP2, which follows the path of water, has a high EWC and low AF. This means that water is being recycled resulting in high loads of energy and waste/use of utilities for raw material recovery. The same also applies to ammonia in CP1, which means that there is a high potential for improvement in these paths.

In order to facilitate the comparison with the flowsheet alternatives that will be obtained further, Table 4.7 gives a selected list of sustainability metrics for the base case design.

Table 4.7 - Sustainability metrics for the base case design.	
<b>Sustainability Metrics</b>	<b>Base case</b>
Total utility cost (10 <sup>6</sup> \$/year)	13.4
Total energy consumption (GJ/h)	149.35
Product/raw material (kg/kg)	0.75
Energy/ products (MJ/kg)	1.94
Hot Utility (GJ/hr)	114
Cold Utility (GJ/hr)	452
Total carbon footprint (kg CO <sub>2</sub> equivalent)	0.20
HTPI (1/LD <sub>50</sub> )	4005

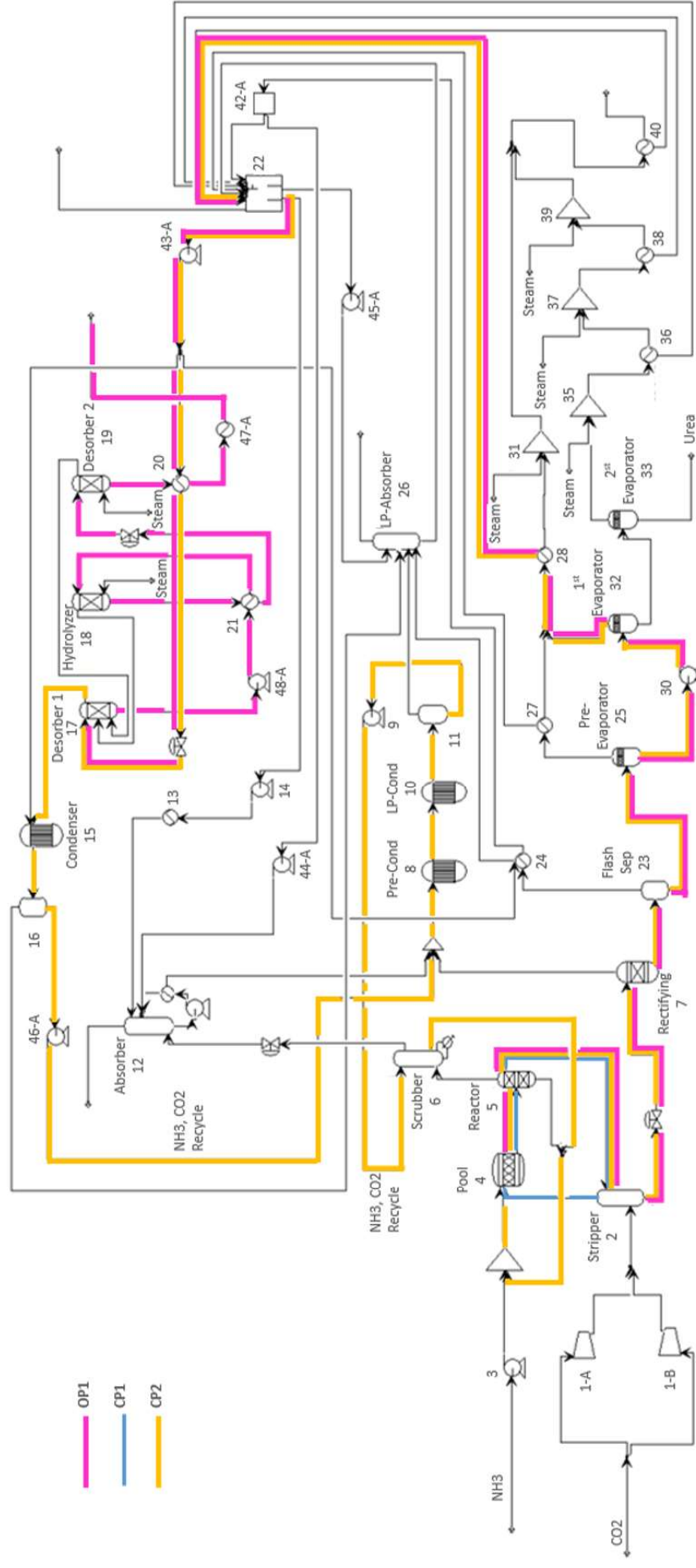


Figure 4.5 - Open- and closed-paths for industrial urea production.

#### 4.2.2 Step 2.2. Hot-Spots Identification

Once economic, sustainability and LCA analysis are performed, it is possible to identify the main bottlenecks in the current industrial process. The main identified potential points for improvement are synthesized in Table 4.8.

Table 4.8 - Main potential improvement points with respect to sustainability, economic and LCA analysis.

Unit	TAG	Sustainability	LCA	Economic
Pool Condenser	S-4	X		X
Reactor	S-5	X	X	
Scrubber	S-6	X		
Stripper	S-2	X		
Rectifying column	S-7	X	X	X
Pre-evaporator	E-25	X	X	X
1 <sup>st</sup> stage Evaporator	E-32	X	X	X
Condenser	E-28	X	X	
CO <sub>2</sub> Compressor	S-1A		X	X
CO <sub>2</sub> Compressor	S-1B		X	X

Results from analyses of Step 2.1 and Step 2.2 for equipment indicated with dashed line in Table 4.8 are translated into process hot-spots using Table 3.1. A list of equipment, according to their identification as a major bottleneck in the three (economic, sustainability and LCA) analyses, is given in Table 4.9.

Table 4.9 - Identified process hotspots for urea production process.

Indicator values	$\alpha_1$ = Raw material recycle/cost $\beta_1$ = MVA	$\alpha_2$ = Utility cost $\beta_1$ = MVA $\gamma_1$ = CO <sub>2</sub> equivalent $\gamma_2$ = PEI
Base case property	Un-reacted raw materials	Products recovery and/or cooling
Cause	Equilibrium reaction	High energy usage heating
Identified process hotspot	Limiting equilibrium/ raw material loss	High energy consumption and/or demand
Industrial Equipment / Section	Rectifying column / Recirculation	Pre-evaporator and first stage of evaporation / Evaporation

Note: Economic ( $\alpha$ ), sustainability ( $\beta$ ) and LCA ( $\gamma$ ) analysis, MVA – mass value added, EWC – Energy to waste cost, CO<sub>2</sub> equivalent – carbon footprint, PEI – potential, environmental impact.

These process hotspots were identified in recirculation (Rectifying Column; R-7) and evaporation (Pre-evaporator and first stage of evaporation; E-25 and E-32) sections and can be seen in Table 4.8. The major bottleneck of the process is the very high energy consumption.

In recirculation section, the non-converted ammonium carbamate is decomposed into  $\text{NH}_3$  and  $\text{CO}_2$ . The rectifying column is the main equipment in recirculation and it can be divided into three parts: (1) top separator, where the released gases are separated; (2) middle decomposer, filled with pall rings where the carbamate decomposition will take place and (3) sump, where the concentrated urea solution will pass through a heat exchanger and ammonium carbamate is decomposed again. Outlet gases are directed to heat exchangers to be condensed and sent to synthesis via scrubber. Outlet liquid, rich in urea and carbamate, is directed to flash tank and then to evaporation section.

The evaporation section consists of three evaporation stages. The first equipment is the pre-evaporator, in which liquid outlet from rectifying is received, followed by the 1st and 2nd stages of evaporation. The main purpose is to concentrate the liquid urea for Prilling unit. All equipment in evaporation operate under vacuum and have the gaseous outlets directed to condensers and, thereafter, to hydrolysis & desorption section.

The identified hotspots in these sections are translated into design targets using Table 3.2. Thus, the design targets identified for alternatives flowsheets are set as:

- a. Reduce energy consumption
- b. Reduce utility cost
- c. Improvements in LCA/sustainability indicators
- d. Unit operations reduction
- e. Production target

### **4.3 Level 3 - Sustainable Design / Innovation**

#### **4.3.1 Step 3.1. Process Analysis**

Once previous steps evidence hotspots at recirculation and evaporation sections, efforts from Step 3.1 to Step 3.4 will be directed only to these sections.

Fig 4.6 illustrate the operational unit flowsheet from Recirculation and evaporation sections.



These operational flowsheet is then translated into a task based flowsheet (TBF). Each unit operation is transcribed in terms of mixing, reaction and/or separation tasks. TBF obtained can be seen in Fig 4.7, where dashed lines identify recirculation and evaporation sections.

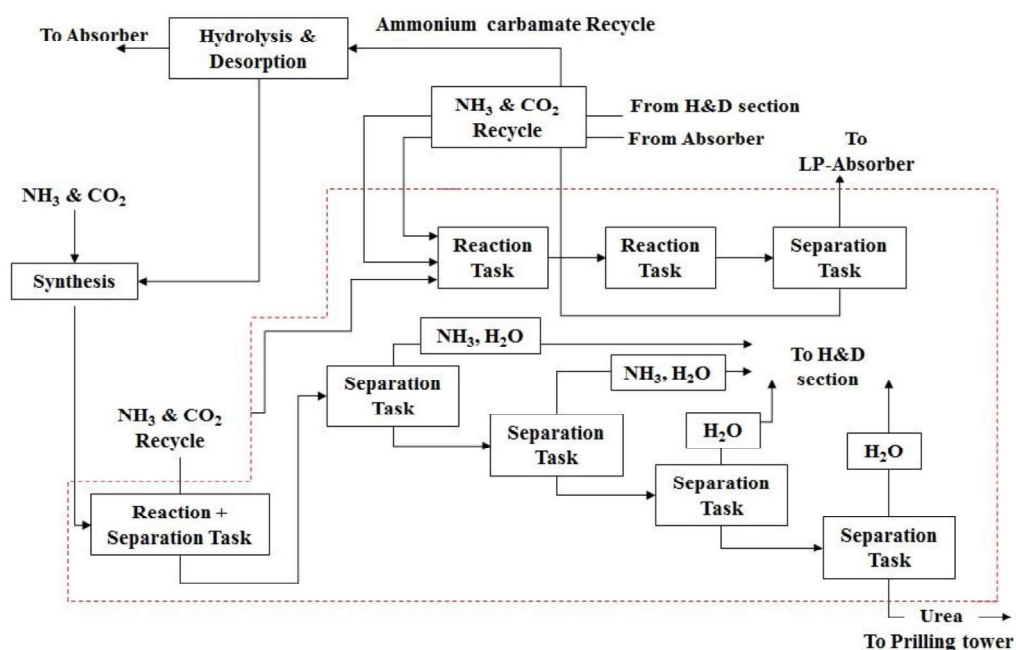


Figure 4.7- Task based flowsheet for recirculation and evaporation sections.

This TBF is then translated into a phenomena based flowsheet (PBF). The PBF obtained for recirculation and evaporation sections can be seen in Fig 4.8.

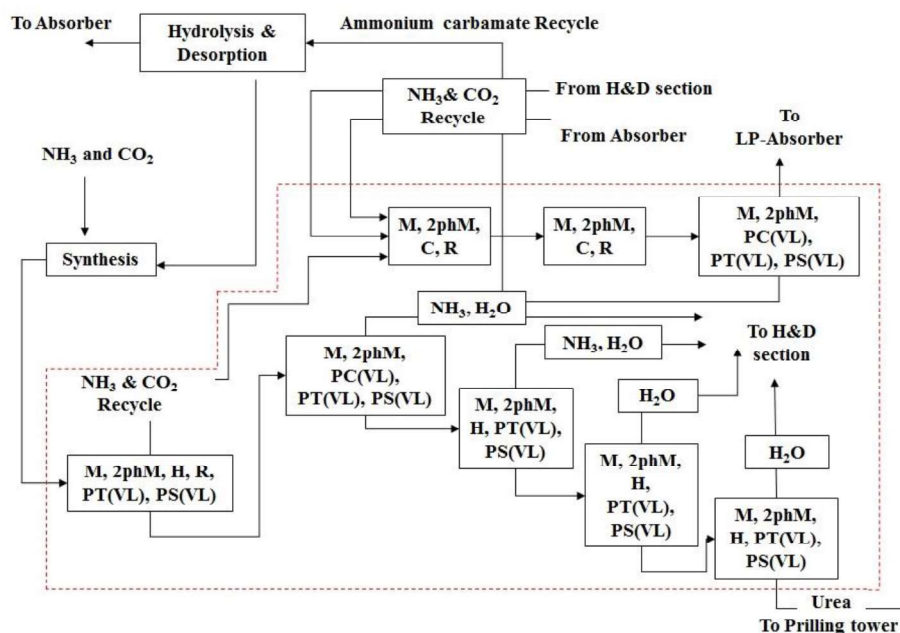


Figure 4.8 - Phenomena based flowsheet for urea production process, focusing on recirculation and evaporation sections

The identified phenomena building blocks (PBB) are:

- R (reaction)
- M (mixing)
- 2phM (two phase mixing)
- PC(VL) (phase contact vapor/liquid)
- PT(VL) (phase transition vapor/liquid)
- PS(VL) (phase separation vapor/liquid)
- H (heating)
- C (cooling)

This phenomena set obtained is stored and constitute the initial PBB search-space. To further analyze the system to identify hotspots, the needed pure compound properties are retrieved from ICAS and AspenPlus databases. Results are given in Table 4.10 for pure compound properties and Table 4.11 for binary ratio matrix.

Table 4.10 – Pure compound properties

Compound	MW (g/mol)	Tm (K)	Tb (K)	Solubility parameter (MPa <sup>0.5</sup> )	Radius of gyration (Å)	VdW m <sup>3</sup> /kmol	VM m <sup>3</sup> /kmol
NH <sub>3</sub>	17.03	195.41	239.72	29.23	0.85	0.0138	0.0250
CO <sub>2</sub>	44.01	216.58	185.16	14.56	1.04	0.0197	0.0373
CARB	78.07	333	636.84	NA	NA	0.0319	0.0587
UREA	60.06	405.85	465	36.24	2.6	0.0323	0.0488
H <sub>2</sub> O	18.01	273.15	373.15	47.81	0.62	0.0124	0.0181
N <sub>2</sub>	28.01	63.15	77.34	9.08	0.55	0.0158	0.0347
H <sub>2</sub>	2.02	13.95	20.39	6.65	0.37	0.0063	0.0286
O <sub>2</sub>	32.00	54.36	90.19	8.18	0.68	0.013	0.0280
BIURET	103.08	470.72	725.47	38.42	NA	0.0456	0.1566

Table 4.11 - Binary ratio matrix for a set of selected properties.

rij (binary pair)	Property binary ratio						
	MW	Tm	Tb	SolPar	RG	VdW	VM
NH <sub>3</sub> /CO <sub>2</sub>	2.58	1.11	1.29	2.01	1.22	1.43	1.49
NH <sub>3</sub> /CARB	4.58	1.70	2.66	NA	NA	2.31	2.35
NH <sub>3</sub> /UREA	3.53	2.08	1.94	1.24	3.05	2.34	1.95
NH <sub>3</sub> /H <sub>2</sub> O	1.06	1.40	1.56	1.64	1.39	1.12	1.38
NH <sub>3</sub> /N <sub>2</sub>	1.64	3.09	3.10	3.22	1.56	1.14	1.39
NH <sub>3</sub> /H <sub>2</sub>	8.45	14.01	11.76	4.40	2.30	2.18	1.14
NH <sub>3</sub> /O <sub>2</sub>	1.88	3.59	2.66	3.57	1.25	1.06	1.12
NH <sub>3</sub> /BIURET	6.05	2.41	3.03	1.31	NA	3.30	6.27
CO <sub>2</sub> /CARB	1.77	1.54	3.44	NA	NA	1.62	1.57
CO <sub>2</sub> /UREA	1.36	1.87	2.51	2.49	2.50	1.64	1.31
CO <sub>2</sub> /H <sub>2</sub> O	2.44	1.26	2.02	3.28	1.69	1.59	2.06
CO <sub>2</sub> /N <sub>2</sub>	1.57	3.43	2.39	1.60	1.90	1.25	1.08
CO <sub>2</sub> /H <sub>2</sub>	21.83	15.53	9.08	2.19	2.80	3.12	1.30
CO <sub>2</sub> /O <sub>2</sub>	1.38	3.98	2.05	1.78	1.53	1.52	1.33
CO <sub>2</sub> /BIURET	2.34	2.17	3.92	2.64	NA	2.31	4.20
CARB/UREA	1.30	1.22	1.37	NA	NA	1.01	1.20
CARB/H <sub>2</sub> O	4.33	1.22	1.71	NA	NA	2.58	3.25
CARB/N <sub>2</sub>	2.79	5.27	8.23	NA	NA	2.02	1.69
CARB/H <sub>2</sub>	38.73	23.87	31.23	NA	NA	5.05	2.05
CARB/O <sub>2</sub>	2.44	6.13	7.06	NA	NA	2.46	2.09
CARB/BIURET	1.32	1.41	1.14	NA	NA	1.43	2.67
UREA/H <sub>2</sub> O	3.33	1.49	1.25	1.32	4.23	2.61	2.70
UREA/N <sub>2</sub>	2.14	6.43	6.01	3.99	4.75	2.05	1.41
UREA/H <sub>2</sub>	29.79	29.09	22.81	5.45	7.01	5.12	1.71
UREA/O <sub>2</sub>	1.88	7.47	5.16	4.43	3.82	2.49	1.74
UREA/BIURET	1.72	1.16	1.56	1.06	NA	1.41	3.21
H <sub>2</sub> O/N <sub>2</sub>	1.56	4.33	4.82	5.26	1.12	1.28	1.92
H <sub>2</sub> O/H <sub>2</sub>	8.94	19.58	18.30	7.19	1.66	1.96	1.58
H <sub>2</sub> O/O <sub>2</sub>	1.78	5.02	4.14	5.84	1.11	1.05	1.55

H <sub>2</sub> O/BIURET	5.72	1.72	1.94	1.24	NA	3.68	8.67
N <sub>2</sub> /H <sub>2</sub>	13.90	4.53	3.79	1.37	1.47	2.50	1.21
N <sub>2</sub> /O <sub>2</sub>	1.14	1.16	1.17	1.11	1.24	1.22	1.24
N <sub>2</sub> /BIURET	3.68	7.45	9.38	4.23	NA	2.88	4.52
H <sub>2</sub> /O <sub>2</sub>	15.87	3.90	4.42	1.23	1.83	2.06	1.02
H <sub>2</sub> /BIURET	51.13	33.74	35.58	5.78	NA	7.21	5.48
O <sub>2</sub> /BIURET	3.22	8.66	8.04	4.70	NA	3.51	5.59

MW – molecular weight (g/mol), Tb – normal boiling point (K), RG – radius of gyration (Å), Tm – normal melting point (K), VM – molar volume (m<sup>3</sup>/kmol), SolPar – solubility parameter, VDW – Van der Waal volume (m<sup>3</sup>/kmol), VP – vapor pressure (atm), NA – not available.

### 4.3.2 Step 3.2. Identification of desirable tasks and phenomena

According to BABI et al., (2014), the process hotspots can be reduced and/or eliminated through the use of additional, desirable PBBs using thermodynamic insights. As it can be seen in Table 4.12, each process hotspot is linked to a binary ratio property and translated into a desirable PBB. The rule for selection is that if the binary ratios are greater than 1.2, the corresponding PBBs are selected. For binary ratios close to unity or less than 1.2, the separation promoted by the PBBs is not feasible. From Table 4.12, it can be seen Urea/H<sub>2</sub>O binary pair, the molar volume is 2.7 then the PBB PT(PVL) is selected.

Table 4.12 - List of selected desirable PBBs linked to the identified tasks V – vapour, L – liquid, LL – liquid–liquid, MSA – mass separating agent. Adapted from BABI et al., (2014).

Process Hotspot	Main Task	Property Binary Ratio	Alternative Task	MSA	PBB desirable
Limiting equilibrium	Reaction	Vapor pressure Heat of vaporization Boiling point	Separation	No	PC(VL) PT(VL) PS(VL)
		Molar volume Solubility parameter Molar volume Radius of gyration Dipole moment			PT(PVL) PT(VV) PS(VV)
High energy consumption / demand	Separation	Vapor pressure Heat of vaporization Boiling point Solubility parameter	Separation	Yes	PC(VL) PT(VL) PS(VL)
		Vapor pressure Heat of vaporization Boiling point	Separation	No	PC(VL) PT(VL) PS(VL)
		Molar volume Solubility parameter Molar volume Radius of gyration Dipole moment			PT(PVL) PT(VV) PS(VV)

The identified phenomena added to the initial search space, constitute the search space. A total of 15 phenomena building blocks are identified:

1. Three M (ideal: Mid, tubular flow: Mtub, rectangular flow: Mrec),
2. 2phM
3. H
4. C
5. R
6. PT(VL)
7. PT(PVL)
8. PT(VV)
9. PC(VL)
10. PS(VL)
11. PS(VV)
12. D

#### 4.3.3 Step 3.3. Generation of flowsheet alternatives

Using equations (01) and (02), from (BABI et al., 2014), the maximum number of phenomena that can be combined to form simultaneous phenomena building blocks (SPBs) is calculated. PhE is the total number of energy transfer phenomena, 2, PhM is the total number of mixing phenomena, 3, and PhD is the dividing phenomena, 1.

$$n_{Ph,Max} = Ph - (Ph_E - 1) - (Ph_M - 1) - Ph_D = 11 \quad Eq(1)$$

$$NSPB_{Max} = \sum_{k=1}^{n_{Ph,Max}} \left[ \frac{(Ph_{BB} - 1)!}{(Ph_{BB} - k - 1)!} \right] + 1 = 16278 \quad Eq(2)$$

The total number of SPBs that can be generated, having a maximum of 11 PBBs is calculated to be 16278. However, not all combinations are feasible. Thus, using connectivity rules, 70 SPBs are found to be feasible. The list of feasible SPBs assuming three types of mixing (ideal (Mid), tubular flow (M<sub>tub</sub>), rectangular flow (M<sub>rec</sub>)) is presented in Table 4.13.

Table 4.13 - List of feasible SPBs.

SPB	Connected PBB	In	Out	Task they may perform
SPB.1	$M_{id}$	1..n(L, VL, V)	1(L, VL, V)	Mix.
SPB.2	$M_{id}=2phM$	1..n(L, VL, V)	1(L, VL, V)	Mix.
SPB.3	$M_{id}=R$	1..n(L, VL, V)	1(L, VL, V)	Mix.+ React.
SPB.4	$M_{id}=H$	1..n(L, VL, V)	1(L, VL, V)	Mix.+ Heat.
SPB.5	$M_{id}=C$	1..n(L, VL, V)	1(L, VL, V)	Mix.+ Cool.
SPB.6	$M_{id}=R=H$	1..n(L, VL, V)	1(L, VL, V)	React.+ Heat.
SPB.7	$M_{id}=R=C$	1..n(L, VL, V)	1(L, VL, V)	React.+ Cool.
SPB.8	$M_{id}=R=H=PC(VL)=PT(VL)$	1..n(L, VL, V)	1(L, VL, V)	React.+ Heat.
SPB.9	$M_{id}=R=C=PC(VL)=PT(VL)$	1..n(L, VL, V)	1(L, VL, V)	React.+ Cool.
SPB.10	$M_{id}=R=2phM=PC(VL)=PT(VL)$	1..n(L, VL)	2(V/L)	React.+ Sep.
SPB.11	$M_{id}=R=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L, VL)	2(V;L)	React.+ Sep.
SPB.12	$M_{id}=R=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L, VL)	2(V;L)	React.+ Sep.
SPB.13	$M_{id}=R=H=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L, VL)	2(V;L)	React.+ Sep.
SPB.14	$M_{id}=R=C=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L, VL)	2(V;L)	React.+ Sep.
SPB.15	$M_{id}=2phM=PC(VL)=PT(VL)$	1..n(L, VL)	2(V;L)	Mix.+ Ph. Cr
SPB.16	$M_{id}=2phM=C=PC(VL)=PT(VL)$	1..n(L, VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.17	$M_{id}=2phM=H=PC(VL)=PT(VL)$	1..n(L, VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.18	$M_{id}=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L, VL)	2(V;L)	Mix.+ Sep.
SPB.19	$M_{id}=C=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L, VL)	2(V;L)	Cool.+ Sep.
SPB.20	$M_{id}=H=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(VL)	2(V;L)	Heat.+ Sep.
SPB.21	$M_{id}=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(VL)	2(V;L)	Mix.+ Sep.
SPB.22	$M_{id}=2phM=PC(VL)=PT(VV)=PS(VV)$	1..n(L, VL, V)	2(V;V)	Mix.+ Sep.
SPB.23	$M_{id}=2phM=PT(VV)=PS(VV)$	1..n(V)	2(V;V)	Mix.+ Sep.
SPB.24	$M_{tub}$	1..n(L, VL, V)	1(L, VL, V)	Mix.
SPB.25	$M_{tub}=2phM$	1..n(L, VL, V)	1(L, VL, V)	Mix.
SPB.26	$M_{tub}=R$	1..n(L, VL, V)	1(L, VL, V)	Mix.+ React.
SPB.27	$M_{tub}=H$	1..n(L, VL, V)	1(L, VL, V)	Mix.+ Heat.

SPB.28	$M_{tub}=C$	1..n(L,VL,V)	1(L,VL,V)	Mix.+ Cool.
SPB.29	$M_{tub}=R=H$	1..n(L,VL,V)	1(L,VL,V)	React.+ Heat.
SPB.30	$M_{tub}=R=C$	1..n(L,VL,V)	1(L,VL,V)	React.+ Cool.
SPB.31	$M_{tub}=R=H=PC(VL)=PT(VL)$	1..n(L,VL,V)	1(L,VL,V)	React.+ Heat.
SPB.32	$M_{tub}=R=C=PC(VL)=PT(VL)$	1..n(L,VL,V)	1(L,VL,V)	React.+ Cool.
SPB.33	$M_{tub}=R=2phM=PC(VL)=PT(VL)$	1..n(L,VL)	2(V/L)	React.+ Sep.
SPB.34	$M_{tub}=R=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.35	$M_{tub}=R=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.36	$M_{tub}=R=H=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.37	$M_{tub}=R=C=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.38	$M_{tub}=2phM=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr
SPB.39	$M_{tub}=2phM=C=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.40	$M_{tub}=2phM=H=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.41	$M_{tub}=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Sep.
SPB.42	$M_{tub}=C=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	Cool.+ Sep.
SPB.43	$M_{tub}=H=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(VL)	2(V;L)	Heat.+ Sep.
SPB.44	$M_{tub}=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(VL)	2(V;L)	Mix.+ Sep.
SPB.45	$M_{tub}=2phM=PC(VL)=PT(VV)=PS(VV)$	1..n(L,VL,V)	2(V;V)	Mix.+ Sep.
SPB.46	$M_{tub}=2phM=PT(VV)=PS(VV)$	1..n(V)	2(V;V)	Mix.+ Sep.
SPB.47	$M_{rec}$	1..n(L,VL,V)	1(L,VL,V)	Mix.
SPB.48	$M_{rec}=2phM$	1..n(L,VL,V)	1(L,VL,V)	Mix.
SPB.49	$M_{rec}=R$	1..n(L,VL,V)	1(L,VL,V)	Mix.+ React.
SPB.50	$M_{rec}=H$	1..n(L,VL,V)	1(L,VL,V)	Mix.+ Heat.
SPB.51	$M_{rec}=C$	1..n(L,VL,V)	1(L,VL,V)	Mix.+ Cool.
SPB.52	$M_{rec}=R=H$	1..n(L,VL,V)	1(L,VL,V)	React.+ Heat.
SPB.53	$M_{rec}=R=C$	1..n(L,VL,V)	1(L,VL,V)	React.+ Cool.
SPB.54	$M_{rec}=R=H=PC(VL)=PT(VL)$	1..n(L,VL,V)	1(L,VL,V)	React.+ Heat.
SPB.55	$M_{rec}=R=C=PC(VL)=PT(VL)$	1..n(L,VL,V)	1(L,VL,V)	React.+ Cool.
SPB.56	$M_{rec}=R=2phM=PC(VL)=PT(VL)$	1..n(L,VL)	2(V/L)	React.+ Sep.

SPB.57	$M_{rec}=R=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.58	$M_{rec}=R=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.59	$M_{rec}=R=H=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.60	$M_{rec}=R=C=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(L,VL)	2(V;L)	React.+ Sep.
SPB.61	$M_{rec}=2phM=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr
SPB.62	$M_{rec}=2phM=C=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.63	$M_{rec}=2phM=H=PC(VL)=PT(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Ph. Cr.
SPB.64	$M_{rec}=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	Mix.+ Sep.
SPB.65	$M_{rec}=C=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(L,VL)	2(V;L)	Cool.+ Sep.
SPB.66	$M_{rec}=H=2phM=PC(VL)=PT(VL)=PS(VL)$	1..n(VL)	2(V;L)	Heat.+ Sep.
SPB.67	$M_{rec}=2phM=PC(VL)=PT(PVL)=PS(VL)$	1..n(VL)	2(V;L)	Mix.+ Sep.
SPB.68	$M_{rec}=2phM=PC(VL)=PT(VV)=PS(VV)$	1..n(L,VL,V)	2(V;V)	Mix.+ Sep.
SPB.69	$M_{rec}=2phM=PT(VV)=PS(VV)$	1..n(V)	2(V;V)	Mix.+ Sep.
SPB.70	D	1(L;VL,V)	1..n(L;V;VL)	Stream Div.

Note: mixing; ideal (Mid), tubular flow (Mtub), rectangular flow (Mrec), V = vapor, L = liquid, “/” means “or”, “;” means “and”, “In” provides number of inlet streams (1 to n) and phase, “Out” provides number of outlet streams (1 or 2) and phase.

The identified feasible SPBs are combined to form basic structures. These basic structures are formed in a way that it is possible to satisfy the identified reaction and/or separation tasks. These combinations of basic structures are then translated to unit-operations, as show in Table 4.14.



Table 4.14 - Generation of hybrid/intensified unit operations from combination of PBBs.

Alternative	SPB	Combined SPBs (basic structure)	Task Performed	Operation unit
A	SPB.6	$M(VL)=R(VL)=H$		Conventional Reactor
B	SPB.18 SPB.19 SPB.20	$M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)$ $M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)$ $M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)$		Conventional distillation column
C	SPB.11 SPB.19 SPB.20	<div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <math>M(VL)=R(VL)=H</math> </div> <div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <math>M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)</math>  <math>M(VL)=2phM=PC(VL)=PT(VL)=PS(VL)</math>  <math>M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)</math> </div> <p style="text-align: center;">↓</p> <div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> <math>M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL)</math>  <math>M(VL)=R=2phM=PC(VL)=PT(VL)=PS(VL)</math>  <math>M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL)</math> </div> <p style="text-align: center;">Basic structures are combined</p>		Reactive distillation column
D	SPB.2 SPB.4 SPB.21	$M(VL)=2phM$ $M(L)=2phM=PC(VL)=PT(VL)=PS(VL)$ $M(L)=H$		Pervaporation membrane unit
E	SPB.23	$M(V)=2phM=PT(VV)=PS(VV)$		Vapor permeation membrane unit

Options A, B and C are alternatives for rectifying column replacement. In the current process, pall rings, heater and a flash section in rectifying column are used to improve the separation between gases, vapors and liquid mixture with water, ammonium carbamate and urea. Thus, conventional reactor it is not capable of attending urea concentration in the liquid outlet to enter evaporation section. The same occurs with conventional distillation. Reactive distillation it is also a non-feasible option for this case, since there is no evidence of the

existence of a catalyst for ammonium carbamate decomposition into ammonia and carbon dioxide. Thus, these three options are also not feasible for replacing Rectifying column.

Along these lines, pervaporation membrane (alternative D) and vapor permeation membrane (alternative E), options for Evaporation section, can be considered for the next steps of the studied framework.

- ✓ Alternative D - pervaporation membrane  
[SPB. 21 M=2phM=PC(VL)=PT(PVL)=PS(VL)]

The integration of basic structures for separation tasks in pre-evaporator and 1st stage of evaporation is considered. This is possible as both separation tasks involve SPB with separation of water from urea in liquid phase. Thus, a basic structure having phenomena PT(VL), PT(PVL) and PS(VL) is selected. Additional PBBs like cooling, heating and mixing can also be added to the selected SPBs. Thus, in flowsheet alternative D the combined basic structure is translated to a pervaporation membrane to obtain reduced energy consumption.

At the pervaporation process a liquid feed stream is heated and routed to the membrane module. The permeate transported through the membrane is vaporized on the permeate side and heat is dissipated from the feed. The feed mixture needs to be re-heated in order to avoid a decrease in the driving force for mass transportation. It is common to have the re-heating unit outside the membrane module, in heat exchangers. Therefore, for large plants it can be necessary to provide a large number of small membrane modules with upstream heat exchangers. The vaporous permeate stream can be condensed in an external heat exchanger.

The intensified flowsheet alternative for pervaporation membrane is generated and can be seen in Fig 4.9.

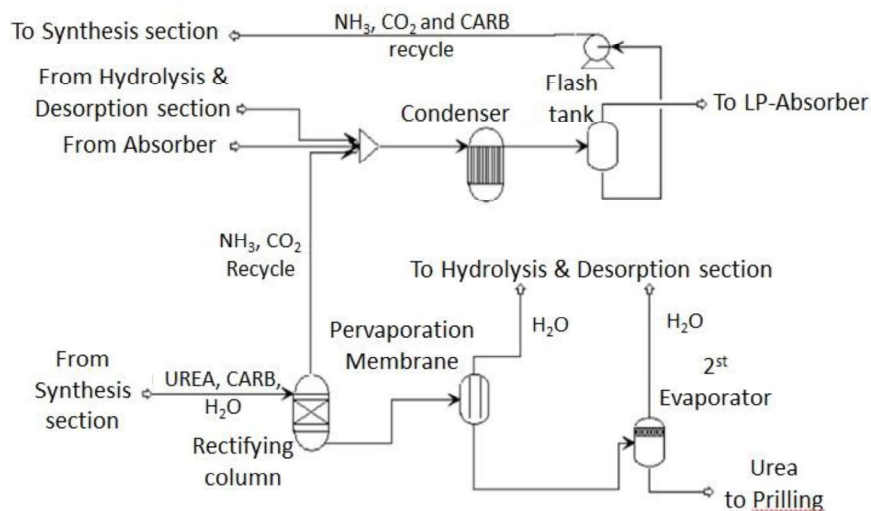


Figure 4.9- Flowsheet alternative D: Pervaporation membrane unit for the separation of H<sub>2</sub>O/Urea.

- ✓ alternative E – vapor-permeation membrane  
[SPB. 23  $M=2phM=PT(VV)=PS(VV)$ ]

In alternative E, vapor permeation membrane, for separation of ammonia and carbon dioxide from water in vapor phase at the gaseous rectifying column, a basic structure having phenomena  $PT(VV)$  and  $PS(VV)$  is selected. Thus, in flowsheet alternative E the combined basic structure is translated to vapor permeation membrane.

In the vapor permeation process, saturated vapor instead of the liquid feed solution is passed through the membrane module. The series of heat exchangers can be dispensed, once the necessary energy is provided by an evaporator. Usually, overall larger modules can be used. Vapor permeation is advantageous if feed mixture has non-volatile or undissolved constituents.

Both intensified alternatives indicate membranes as a better option for this part of the process. A brief literature survey shows there are some works reporting membranes capable of doing the task here required, as it can be seen in Table 4.15.

Table 4.15 – Works concerning about membranes capable of doing the required task.

Alternative	Literature reference
<b>Pervaporation membrane</b> <b>Urea concentration</b>	(Sanawar et al., 2019) - Pilot-Scale Assessment of Urea as a Chemical Cleaning Agent for Biofouling Control in Spiral-Wound Reverse Osmosis Membrane Elements
	DK00106443T - A method of isolating urea using membranes and their preparations (2000)
	JP 2000281638A - Separation of urea
<b>Vapor permeation membrane</b> <b>Separation of NH<sub>3</sub> and CO<sub>2</sub> from H<sub>2</sub>O</b>	US 2019 233 296 A1 Systems and methods for ammonia recovery, acid gas separation, or combination thereof - Concentrating said acid gas rich ammoniated solution using a semipermeable membrane
	(Yang et al., 2014) - A Pervaporation Study of Ammonia Solutions Using Molecular Sieve Silica Membranes
	(Daniel et al., 1990) - Selective Permeation of Ammonia and Carbon Dioxide by Novel Membranes

It is not in the scope of this thesis to specify the most suitable membrane to do the task required. However it is evidenced that this a feasible and innovative option capable of being applied in industrial production process.

In order to compare both alternatives and select the best one in terms of economic, LCA and sustainability factors these options must be simulated and evaluated in ECON, LCSoft, and SustainPro.

In order to consider the effects of these modifications in the entire urea process, membranes were simulated in Aspen Plus assuming the hypothesis of 90% of efficiency in both cases.

The intensified flowsheet alternative for vapor permeation membrane is generated and can be seen in Fig 4.10.

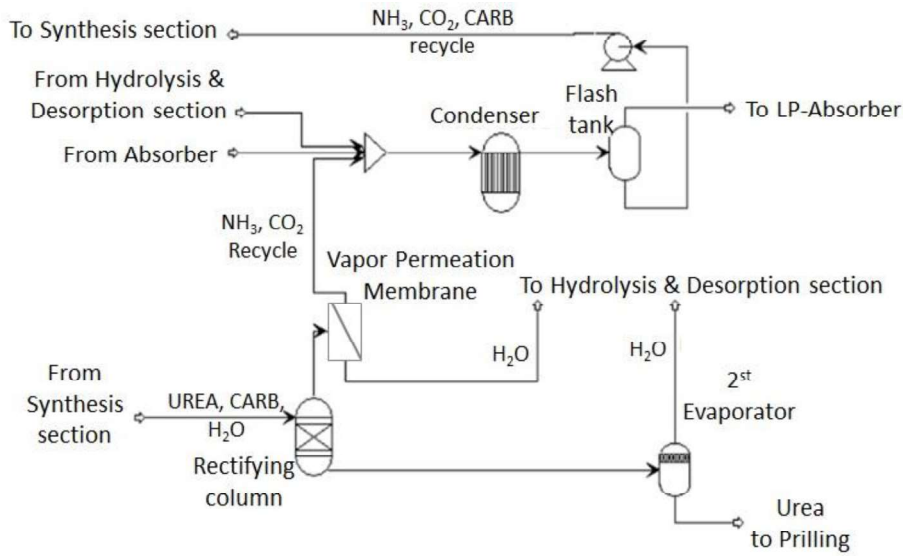


Figure 4.10 - Flowsheet alternative E: Vapor-permeation membrane unit for the separation of  $\text{NH}_3$ ,  $\text{CO}_2/\text{H}_2\text{O}$ .

#### 4.3.4 Step 3.4. Comparison and selection of the best flowsheet alternatives

At this step, performance of generated alternatives is compared in terms of sustainability metrics, economic and life cycle assessment factors. The most important performance criteria for the base case and the intensified alternatives are given in Table 4.16.

Table 4.16 - Performance metrics and LCA analysis for the base case and the two flowsheet alternatives generated.

Sustainability Metrics	Base case design	Alternative D	Alternative E
Total utility cost (10 <sup>6</sup> \$/year)	13.4	7.8	11.9
Total energy consumption (GJ/h)	149.35	70.68	131.12
Product/raw material (kg/kg)	0.75	0.76	0.76
Energy/ products (MJ/kg)	1.94	0.90	1.67
Hot Utility (GJ/hr)	114	36	96
Cold Utility (GJ/hr)	452	320	351
Total carbon footprint (kg CO <sub>2</sub> equivalent)	0.20	0.12	0.16
HTPI (1/LD <sub>50</sub> )	4005	3389	3297
GWP (CO <sub>2</sub> eq.)	0.30	0.04	0

From the results presented in Table 4.16 and the design targets set, it can be said that both process alternatives offer superior performance in terms of all indicators when compared to the base case process.

A comparative spider diagram can be seen in Fig 4.11. The best process alternative is Alternative D - pervaporation membrane. The energy consumption per one unit of urea is significantly reduced (53.5%) as well as utility cost (42.3%). The hot (steam/hot water) and cold utilities usage were reduced to 68.6% and 29.2%, respectively. In addition, the carbon footprint, HTPI and GWP were reduced to 41.6%, 1.5% and 1.4%, respectively.

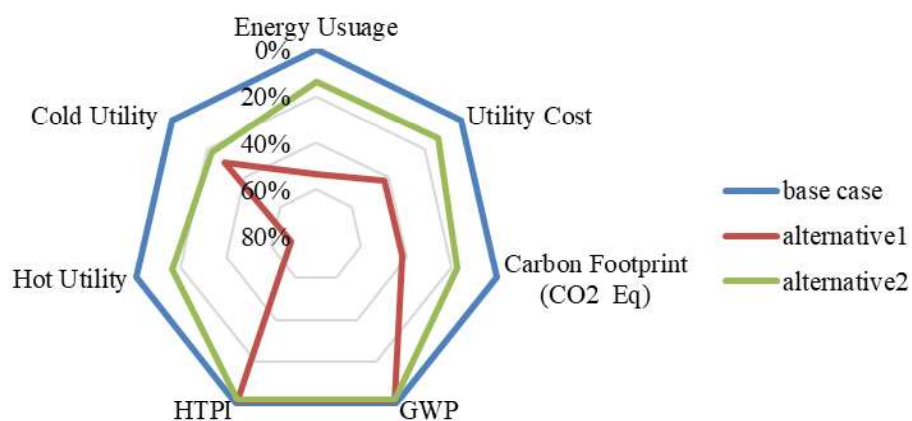


Figure 4.11 - Economic and LCA improvements relative to the base case design.

It can be said that using pervaporation membrane in order to concentrate urea in the first step of Evaporation section of a urea process is a significantly more sustainable alternative.

## 5. CONCLUSIONS AND FUTURE PERSPECTIVE

Literature review presented urea production process Stamicarbon licensed. The most recent studies on modeling and simulation about this process were discussed and the main issues on performing such simulation were presented. It can be said there are a great number of works dealing only about synthesis section. There is also a lack of physical-chemical data availability mainly of biuret in urea process conditions as well as a lack in industrial data availability in the open literature. Studies dealing with industrial data do not disclose many relevant process parameters and then are not completely reproducible to others industrial units. Just one work concerning further analysis from an industrial built simulation was found.

Studies of process intensification applied to urea production process were presented and the new/hybrid equipment generated by them were shown. Worldwide patent trend study indicated Stamicarbon, Saipem and Toyo as the main inventors. Most part of these patents are related to minor changes along the process as process control, dust removal in urea finishing, transportation of melted urea to prilling tower / granulation. The most relevant modification in the process is a result of process intensification studies: the Pool Condenser equipment in synthesis section of Urea2000 Plus technology. Brazilian patent trend points out Casale and Stamicarbon as the main inventors and the new proposals deal mainly on granulation and prilling, which means, urea finishing.

Along these lines the presented methodology for building the industrial base case, identifying industrial hotspots and performing the process intensification was applied.

Industrial data was collected for the period of nine months, however after performing statistical analysis only 11 operational data points could be used to further validate the simulation. This fact evidence the difficult in collecting industrial data along an entire production unit for researches purposes. Laboratory agenda, if possible, should be rearranged in order to do so.

Simulation for all sections of urea production was developed and validated against more than 30 industrial parameters. Good consistency between simulation results and industrial data is presented, being in that a deviation of less than 6% is obtained for mass composition and less than 8% for other variables considered. Reproducibility for other industrial urea plants is therefore possible and permits using the simulation for reliable studies.

Economic analysis was performed and indicated heating, cooling and electricity as the main cost driver in urea industrial process. Synthesis, recirculation and evaporation sections

were the sections with high utilities consumption in equipment: evaporator (E-32), CO<sub>2</sub> compressor (S1A/B), rectifying column (R-7), pre-Evaporator (E-25) and pool condenser (S-4). LCA confirms the economic analysis pointing out the same equipment with the higher carbon footprint, due to their high energy consumption. Sustainability analysis indicates issues at the same sections pointed in economic and LCA analysis.

Identification of hotspots indicated rectifying column, pre evaporator and first evaporator as the equipment with the main bottlenecks in the process. From this, five design targets were set: reduction in energy consumption, reduction on utility cost, improvements in LCA/ sustainability indicators, reduction in the number of operational units and production capacity.

Design targets were reached through a task and phenomena process intensification method. Three alternatives for replacement of the rectifying column were obtained: conventional reactor, conventional distillation column and reactive distillation column. However none of these of feasible according to the chemical constraints of the process. Two alternatives more were obtained considering the rectifying gaseous outlet and the pre-evaporator and the first evaporator.

The first alternative consider the use of a pervaporation membrane to concentrate the urea solution before entering the second evaporator, replacing, on this way, pre-evaporator and evaporator. The second alternative consider the gaseous outlet of the rectifying column, passing it thorough a vapor permeation membrane. Both alternatives were simulated and evaluated in terms of economic and environmental factors.

Through process intensification studies, the pervaporation membrane unit for the concentrating urea solution before the main evaporator is suggested as an innovative and most sustainable process design for Evaporation section.

### **Proposed future work**

Future research considering the retrofitting of urea plants should consider studies to define the most suitable type of membrane to be employed. Once the right membrane is specified it is possible to improve the simulation of this new equipment in the process and perform sensitive analysis to available flow effects.

Once utilities consumption is pointed as one of the main hotspots, it is recommended to introduce the heuristic-algorithmic method Water Source Diagram, developed in Escola de



Química - UFRJ, in Step 3.1 – Process Analysis. WSD tool, aimed at minimizing the consumption of water in industrial processes, and can significantly contribute to the design of more sustainable process alternatives.

## 6. REFERENCES

- Babi, D. K., Gani, R., & Woodley, J. (2014). *Sustainable Process Synthesis-Intensification* (DTU). Retrieved from [http://orbit.dtu.dk/files/112087849/Deenesh\\_Kavi\\_Babi\\_PEC14\\_41.pdf](http://orbit.dtu.dk/files/112087849/Deenesh_Kavi_Babi_PEC14_41.pdf)
- Babi, D. K., Holtbruegge, J., Lutze, P., Górak, A., Woodley, J. M., & Gani, R. (2014). Sustainable process synthesis-intensification. *Computer Aided Chemical Engineering*, 34, 255–260. <https://doi.org/10.1016/B978-0-444-63433-7.50027-4>
- Babi, D., Kavi, Rafiqul, Gani, & Woodley, J. (2014). *Sustainable Process Synthesis-Intensification*. DTU Chemical Engineering.
- Brouwer, M. (2010). World Scale Urea Plants. Process Paper. *Urea Know How*, (October), 1–13.
- Brouwer, Mark. (2009). Thermodynamics of the Urea Process. *UreaKnowHow*.
- Carvalho, A., Gani, R., & Matos, H. (2008). Design of sustainable chemical processes: Systematic retrofit analysis generation and evaluation of alternatives. *Process Safety and Environmental Protection*, 86(5), 328–346. <https://doi.org/10.1016/j.psep.2007.11.003>
- Chinda, A. R. C., Yamamoto, C. I., Lima, D. F. B., & Pessoa, F. L. P. (2017). Modeling and simulating the synthesis section of an industrial urea plant analyzing the biuret formation. *UreaKnowHow*, (December 2015). Retrieved from <https://www.ureaknowhow.com/ukh2/library/1231-2017-07-chinda-modeling-and-simulating-the-synthesis-section.html>
- Chinda, R. (2015). *Simulação da Seção de Síntese de uma Unidade de Produção de Ureia - Processo Stamicarbon* (Universidade Federal do Rio de Janeiro). <https://doi.org/10.1017/CBO9781107415324.004>
- Chinda, R. C., Yamamoto, C. I., Lima, D. F. B., & Pessoa, F. L. P. (2015). Modeling and simulating the synthesis section of an industrial urea plant analyzing the biuret formation Modeling and simulating the synthesis section of an industrial urea plant-analyzing the biuret formation. *UreaKnowHow*.
- Curcio, S. (2007). Process intensification: Potential impact on the chemical industry. In V. Piemonte, M. De Falco, & A. Basile (Eds.), *Sustainable Development in Chemical Engineering – Innovative Technologies, First Edition*. (pp. 95–118).

<https://doi.org/10.1039/9781847550576-00032>

- Daniel, V., Laciak, L., Quinn, R., Pez, G. P., Appleby, J. B., & Puri, P. S. (1990). Selective permeation of ammonia and carbon dioxide by novel membranes. *Separation Science and Technology*, 25(13–15), 1295–1305. <https://doi.org/10.1080/01496399008050392>
- Dente, M., Pierucci, S., & Sogaro, A. (1988). Simulation program for urea plants. *Comput. Chem. Eng.*, 12(5), 389–400.
- Dente, M., Rovaglio, M., Bozzano, G., & Sogaro, A. (1992). Gas-Liquid Reactor in the Synthesis of urea. *Chemical Engineering Science*, 47(9–11), 2475–2480.
- Edrisi, A., Mansoori, Z., & Dabir, B. (2016). Urea synthesis using chemical looping process - Techno-economic evaluation of a novel plant configuration for a green production. *International Journal of Greenhouse Gas Control*, 44, 42–51. <https://doi.org/10.1016/j.ijggc.2015.10.020>
- Eijkenboom, J., & Brouwer, M. (2015). Worldwide trends in urea process technologies. *UreaKnowHow*.
- Hamidipour, M., Mostoufi, N., & Sotudeh-Gharebagh, R. (2005). Modeling the synthesis section of an industrial urea plant. *Chemical Engineering Journal*, 106(3), 249–260. <https://doi.org/10.1016/j.cej.2004.12.020>
- Harmsen, J. (2010). Process intensification in the petrochemicals industry: Drivers and hurdles for commercial implementation. *Chemical Engineering and Processing: Process Intensification*, 49(1), 70–73. <https://doi.org/10.1016/j.cep.2009.11.009>
- Isla, M. a., Irazoqui, H. a., & Genoud, C. M. (1993). Simulation of a urea synthesis reactor. 2. Reactor Model. *Industrial & Engineering Chemistry Research*, 32(11), 2662–2670. <https://doi.org/10.1021/ie00023a033>
- Jeenchay, J., & Siemanond, K. (2018). Ammonia/Urea Production Process Simulation/Optimization with Techno-Economic Analysis. In *Computer Aided Chemical Engineering* (Vol. 43, pp. 385–390). <https://doi.org/10.1016/B978-0-444-64235-6.50070-X>
- Lutze, P., Babi, D. K., Woodley, J. M., & Gani, R. (2013). Phenomena based methodology for process synthesis incorporating process intensification. *Industrial and Engineering Chemistry Research*, 52(22), 7127–7144. <https://doi.org/10.1021/ie302513y>
- Lutze, P., Gani, R., & Woodley, J. M. (2010). Process intensification: A perspective on

- process synthesis. *Chemical Engineering and Processing: Process Intensification*. <https://doi.org/10.1016/j.cep.2010.05.002>
- Moulijn, J., & Stankiewicz, A. (2004). RE-ENGINEERING THE CHEMICAL PROCESSING PLANT. In *World Wide Web Internet And Web Information Systems*.
- Peneloux, A., Rauzy, E., & Freze, R. (1982). A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilibria*, 8(1), 7–23. [https://doi.org/10.1016/0378-3812\(82\)80002-2](https://doi.org/10.1016/0378-3812(82)80002-2)
- Peters, M.S.; Timmerhaus, K.; West, R. (2004). *Plant design and economics for chemical engineers*. Singapore: McGraw-Hill.
- Rasheed, S. A. (2011). Revamping Urea Synthesis Reactor using Aspen Plus. *UreaKnowHow*, (September), 1–15.
- Sanawar, H., Bucs, S., Pot, M. A., Zlopasa, J., Farhat, N. M., Witkamp, G., ... Loosdrecht, M. C. M. Van. (2019). Pilot-Scale Assessment of Urea as a Chemical Cleaning Agent for Biofouling Control in Spiral-Wound Reverse Osmosis Membrane Elements. *Membranes*, 9(117).
- Satyro, M. A., Li, Y.-K., Agarwal, R. K., & Santollani, O. J. (2002). Modeling Urea Processes: A New Thermodynamic Model and Software Integration Paradigm. *Virtual Materials Group*.
- Schwartzentruber, J., & Renon, H. (1989). Extension of UNIFAC to high pressures and temperatures by the use of a cubic equation of state. *Industrial & Engineering Chemistry ...*, 28(1987), 1049–1055. <https://doi.org/10.1021/ie00091a026>
- Soave, G. (1972). Equilibrium constants from a modified Redkh-Kwong equation of state. In *Chemical Engineering Science* (Vol. 27). Pergamon Press.
- Stankiewicz, A. (2003). Reactive separations for process intensification: An industrial perspective. *Chemical Engineering and Processing*, 42(3), 137–144. [https://doi.org/10.1016/S0255-2701\(02\)00084-3](https://doi.org/10.1016/S0255-2701(02)00084-3)
- Yang, X., Fraser, T., Myat, D., Smart, S., Zhang, J., da Costa, J. C. D., ... Duke, M. (2014). A pervaporation study of ammonia solutions using molecular sieve silica membranes. *Membranes*, 4(1), 40–54. <https://doi.org/10.3390/membranes4010040>
- Zendehboudi, S., Zahedi, G., Bahadori, A., Lohi, A., Elkamel, A., & Chatzis, I. (2014a).

A dual approach for modelling and optimisation of industrial urea reactor: Smart technique and grey box model. *Canadian Journal of Chemical Engineering*, 92(3), 469–485. <https://doi.org/10.1002/cjce.21824>

Zendehboudi, S., Zahedi, G., Bahadori, A., Lohi, A., Elkamel, A., & Chatzis, I. (2014b). A dual approach for modelling and optimisation of industrial urea reactor: Smart technique and grey box model. *Canadian Journal of Chemical Engineering*, 92(3), 469–485. <https://doi.org/10.1002/cjce.21824>

Zhang, X., Zhang, S., Yao, P., & Yuan, Y. (2005a). Modeling and simulation of high-pressure urea synthesis loop. *Computers and Chemical Engineering*, 29(5), 983–992. <https://doi.org/10.1016/j.compchemeng.2004.10.004>

Zhang, X., Zhang, S., Yao, P., & Yuan, Y. (2005b). Modeling and simulation of high-pressure urea synthesis loop. *Computers and Chemical Engineering*, 29(5), 983–992. <https://doi.org/10.1016/j.compchemeng.2004.10.004>

## APPENDIX A

Table 1 – Tool for identification of phenomena building blocks. Adapted from (BABI et al., 2014)

Separation Operation	Feed phase	Task	Principle PBB	PBBs	Created or Added Phase	MSA-Y/N	Separating Agent(s)
Batch reactor	Solid, gas (vapor) and/or liquid	Reaction	R	R,C (exothermic),H (endothermic)	-	Y/N	Liquid solvent (MSA) and energy transfer (ESA)
Semi-batch reactor	Solid, gas (vapor) and/or liquid	Reaction	R	R,C (exothermic),H (endothermic)	-	Y/N	Liquid solvent (MSA) and energy transfer (ESA)
CSTR	Liquid	Reaction	R	R,C (exothermic),H (endothermic)	-	Y/N	Liquid solvent (MSA) and energy transfer (ESA)
Tubular Reactor (PFR)	Gas (Vapour)	Reaction	R	R,C (exothermic),H (endothermic)	-	N	Energy transfer (ESA)
Pack-bed reactor	Solid and/or gas (vapor)	Reaction	R	R,C (exothermic),H (endothermic)	-	N	Energy transfer (ESA)
Partial condensation or vaporization	Vapor and/or liquid	Separation	PT(VL)	PC(VL),PT(VL),PS(VL)	Liquid or vapor	N	Heat transfer (ESA)
Flash vaporization	Liquid	Separation	PT(VL)	PC(VL),PT(VL),PS(VL)	Vapor	N	Pressure reduction
Distillation	Vapor and/or liquid	Separation	PT(VL)	PC(VL),PT(VL),PS(VL),C,H	Vapor and liquid	N	Heat transfer (ESA) and sometimes work transfer
Extractive distillation	Vapor and/or liquid	Separation	PT(VL)	PC(VL),PT(VL),PS(VL),C,H	Vapor and liquid	Y	Liquid solvent (MSA) and heat transfer (ESA)
Reboiled absorption	Vapor and/or liquid	Separation	PT(VL)	PC(VL),PT(VL),PS(VL),H	Vapor and liquid	Y	Liquid absorbent (MSA) and heat transfer (ESA)
Absorption	Vapor	Separation	PT(VL)	PC(VL), PT(VL), PS(VL)	Liquid	Y	Liquid absorbent (MSA)

Stripping	Liquid	Separation	PT(VL)	PC(VL), PT(VL), PS(VL)	Vapor	Y	Stripping vapor (MSA)
Refluxed stripping (steam distillation)	Vapor and/or liquid	Separation	PT(VL)	PC(VL), PT(VL), PS(VL), C	Vapor and liquid	Y	Stripping Vapor (MSA) and heat transfer (ESA)
Reboiled stripping	Liquid	Separation	PT(VL)	PC(VL), PT(VL), PS(VL), H	Vapor	N	Heat transfer (ESA)
Azeotropic distillation	Vapor and/or Liquid	Separation	PC(LL)	PC(LL), PT(VL) PS(LL), C, H	Vapor and/or liquid	Y	Liquid entrainer (MSA) and heat transfer (ESA)
Liquid-liquid extraction	Liquid	Separation	PC(LL)	PC(LL), PS(LL)	Liquid	Y	Liquid Solvent (MSA)
Liquid-liquid extraction (two solvent)	Liquid	Separation	PC(LL)	PC(LL), PS(LL)	Liquid	Y	Two liquid solvents (MSA1 and MSA2)
Drying	Liquid/solid	Separation	PT(VL)	PT(VL), PS(VL), H	Vapor	Y	Gas (MSA) and/or heat transfer (ESA)
Evaporation	Liquid	Separation	PT(VL)	PT(VL), PS(VL), H	Vapor	N	Heat transfer (ESA)
Crystallization	Liquid	Separation	PT(LS)	PT(LS), PS(LS), C	Solid (and vapor)	N	Heat transfer (ESA)
Desublimation	Vapor	Separation	PT(VS)	PT(VS), PS(VS), C	Solid	N	Heat transfer (ESA)
Leaching (liquid-solid extraction)	Solid	Separation	PC(LS)	PC(LS), PS(LS)	Liquid	Y	Liquid Solvent (MSA)
Dividing Wall Column	Vapor and/or liquid	Separation	PT(VL)	PC(PL), PT(VL), PS(VL), C, H	Vapor and liquid	N	Heat transfer (ESA) and sometimes work transfer

Decanter	Liquid	Separation	PC(LL)	PC(LL), PS(LL)	Liquid	N	Heat transfer (ESA)
Supercritical extraction	Liquid	Separation	PC(LL)	PT(LL), PS(LL), C, H	Liquid	Y	Supercritical absorbent (MSA)
Membrane – pervaporation	Vapor	Separation	PT(PVL)	PC(VL), PT(PVL), PS(VL), C	Liquid	N	Heat transfer (ESA)
Membrane – vapor – permeation	Vapor	Separation	PT(VV)	PC(VL), PT(VV), PS(VV), C	Vapor	N	Heat transfer (ESA)
Reactor	Vapor and/or liquid	Reaction + Separation	R, PT(VL)	R, PC(VL), PT(VV), PS(VV), C	Vapor and Liquid	N	Heat transfer (ESA)
Reactive Distillation	Vapor and/or Liquid	Reaction+Separation	R,PT(VL)	R,PC(VL),PT(VL),PS(VL),C,H	Vapor and liquid	N	Heat transfer (ESA)
Reactive Dividing wall column	Vapor and/or Liquid	Reaction + Separation	R, PT(VL)	R, PC(VL), PT(VL), PS(VL), C, H	Vapor and Liquid	N	Heat transfer (ESA)



## APPENDIX B

Table 1 – Tool for identification of desirable tasks and phenomena building blocks. Adapted from (BABI et al., 2014)

Process-Hotspot	Main Task	Property/Binary Ratio	Alternative Task	Mass Separating agent?	Additional information	PBB
Activation problems	Reaction	Calculate $\Delta G_{rxn}$	Reaction	N	Use of catalyst	M, H
Limiting equilibrium	Reaction	Solubility parameter	Separation	Y	Equilibrium shift	PC(LL), PT(LL), PS(LL)
		Vapor pressure, heat of vaporization, boiling point	Separation	N	Equilibrium shift	PC(VL), PT(VL), PS(VL)
		Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	N	Equilibrium shift	PT(PVL), PT(VV), PS(VV)
Highly endothermic	Reaction	Calculate $\Delta H_{rxn}$	Reaction	N	Heating	H
Highly exothermic	Reaction	Calculate $\Delta H_{rxn}$	Reaction	N	Cooling	C
Formation of undesired side-products	Reaction		Reaction	N	Reaction for reacting away side products	R
Formation of undesired side-products	Reaction	Solubility parameter	Separation	Y	Separation of side-products	PC(LL), PT(LL), PS(LL)
		Vapor pressure, heat of vaporization, boiling point	Separation	N	Separation of side-products	PC(VL), PT(VL), PS(VL)
		Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	N	Separation of side-products	PT(PVL), PT(VV), PS(VV)
Contact problems of raw materials/limited mass transfer	Reaction		Mixing	N	Mixing alternatives	M, 2phM

Explosive mixture	Reaction	Mixture flash point	Reaction	Cooling	C
Explosive mixture	Reaction	Solubility parameter	Separation	Mixture flash point, removing one compound affects the flash point	PC(LL), PT(LL), PS(LL)
Explosive mixture	Reaction	Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	Mixture flash point, removing one compound affects the flash point	PT(PVL), PT(VV), PS(VV)
Degradation by temperature	Reaction		Reaction	Cooling	C
Degradation by temperature	Reaction	Solubility parameter	Separation	Removing products/desirable side-products that are degraded by high temperatures	PC(LL), PT(LL), PS(LL)
Degradation by temperature	Reaction	Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	Removing products/desirable side-products that are degraded by high temperatures	PT(PVL), PT(VV), PS(VV)
Limited heat transfer	Reaction		Mixing	Increase heat transfer	M
Explosive mixture	Separation	Flash point	Separation		
Azeotrope	Separation	Vapor pressure, solubility parameter	Separation	Formation of Azotrope(s)	PC(LL), PT(LL), PS(LL)
Azeotrope	Separation	Molar volume, solubility parameter, Van der Waal volume, radius of gyration, dipole moment	Separation	Formation of Azetropes(s)	PT(PVL), PT(VV), PS(VV)
Azeotrope	Separation	Solubility parameter	Separation	Formation of Azeotrope(s)	PC(LL), PT(LL), PS(LL)
Azeotrope	Separation	Vapor pressure, heat of vaporization, boiling point, solubility parameter	Separation	Formation of Azeotrope(s)	PC(VL), PT(VL), PS(VL)

Azeotrope	Separation	Vapor pressure, heat of vaporization, boiling point	Separation	N	Formation of Azeotrope(s)	PC(VL), PT(VL), PS(VL)
Azeotrope	Separation	Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	N	Formation of Azeotrope(s)	PT(PVL), PT(VV), PS(VV)
Degradation by temperature	Separation	Boiling point	Separation	N		C
Difficult separation due to low driving force	Separation	Vapor pressure, solubility parameter	Separation	Y	DF analysis	PC(LL), PT(LL), PS(LL)
Difficult separation due to low driving force	Separation	Solubility parameter	Separation	Y	DF analysis	PT(LL)
Difficult separation due to low driving force	Separation	Vapor pressure, heat of vaporization, boiling point, solubility parameter	Separation	Y	DF analysis	PC(VL), PT(VL), PS(VL)
Difficult separation due to low driving force	Separation	Vapor pressure, heat of vaporization, boiling point	Separation	N	DF analysis	PC(VL), PT(VV), PS(VV)
Difficult separation due to low driving force	Separation	Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	N	DF analysis	PT(PVL), PT(LL), PS(LL)
High energy consumption/demand	Separation	Vapor pressure, solubility parameter	Separation	Y	DF analysis	PC(LL), PT(LL), PS(LL)
High energy consumption/demand	Separation	Solubility parameter	Separation	Y	DF analysis	PC(LL), PT(LL), PS(LL)
High energy consumption/demand	Separation	Vapor pressure, heat of vaporization, boiling point, solubility parameter	Separation	Y	DF analysis	PC(VL), PT(VL), PS(VL)
High energy consumption/demand	Separation	Vapor pressure, heat of vaporization, boiling point	Separation	N	DF analysis	PC(VL), PT(VL), PS(VL)

High energy consumption/demand	Separation	Molar volume, solubility parameter, molar volume, radius of gyration, dipole moment	Separation	N	DF analysis	PT(PVL), PT(VV), PS(VV)
--------------------------------	------------	---	------------	---	-------------	-------------------------------

## APPENDIX C

Table 1 – SPB building block. Adapted from (BABI et al., 2014)

nSPB <sub>BB</sub> ;	SPB building block	Inlet	Rule
1	M=C	1...n(L,V,VL)	Perform cooling of a stream
2	M=H	1...n(L,V,VL)	Perform heating of a stream
3	M=2phM	1...n(L,V,VL)	Mixing of a stream with two phases
4	M=R	1...n(L,V,VL)	Perform a reaction without an external energy source
5	PC=PT	1...n(VL,LL)	Perform the contact of two phases
6	PT=PS	1...n(L,V,VL)	Perform the separation of two phases
7	PC=PT=PS	1...n(VL,LL)	Perform the separation of two phases

# APPENDIX D

Table 1 - 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	$C_v = \frac{s}{\bar{x}}$
Deviation between simulated and industrial data	$deviation(\%) = \frac{industrialdata - simulationdata}{industrialdata} \times 100$
CO <sub>2</sub> 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	$biurelcontent = \frac{biuretmass}{biuretmass + ureamass} \frac{[kg]}{[kg]}$

## APPENDIX E

Indicators summary results

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 1	NH3	4609.739	Non Defined	9.6756	Non Defined
OP 2	NH3	2237.672	Non Defined	4.2981	Non Defined
OP 3	NH3	37091.230	Non Defined	24.4472	Non Defined
OP 4	NH3	2525.307	Non Defined	4.3912	Non Defined
OP 5	NH3	1225.841	Non Defined	1.9132	Non Defined
OP 6	NH3	20319.315	Non Defined	6.0765	Non Defined
OP 7	NH3	487.621	Non Defined	4.7583	Non Defined
OP 8	NH3	1784.933	Non Defined	17.0511	Non Defined
OP 9	NH3	0.484	-1	0.0138	-1.2090990
OP 10	NH3	41.688	-103	0.4521	-103.35540
OP 11	NH3	1909.495	Non Defined	18.63318518	Non Defined
OP 12	NH3	6989.690	Non Defined	66.77102387	Non Defined
OP 13	NH3	1.896	-5	0.054216223	-4.7347580
OP 14	NH3	163.246	-403	1.7702	-404.73344
OP 15	NH3	3.526	Non Defined	0.0057	Non Defined
OP 16	NH3	12.907	Non Defined	0.0182	Non Defined
OP 17	NH3	266.285	Non Defined	0.2400	Non Defined
OP 18	NH3	0.173	0	0.0000	-0.4270898
OP 19	NH3	0.339	Non Defined	0.0005	Non Defined

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 20	NH3	1.239	Non Defined	0.0017	Non Defined
OP 21	NH3	25.567	Non Defined	0.023039008	Non Defined
OP 22	NH3	9.348	-23.074	0	-23.075251
OP 23	NH3	18.291	Non Defined	0.030	Non Defined
OP 24	NH3	66.953	Non Defined	0.09	Non Defined
OP 25	NH3	1381.335	Non Defined	1.24	Non Defined
OP 26	CO2	0.119	0	0.00	-0.003721
OP 27	CO2	0.296	Non Defined	0.00	Non Defined
OP 28	CO2	1.082	Non Defined	0.00	Non Defined
OP 29	CO2	3751.755	Non Defined	2.287885115	Non Defined
OP 30	CO2	1991.853	Non Defined	1.081426426	Non Defined
OP 31	CO2	32910.577	Non Defined	8.84425	Non Defined
OP 32	CO2	0.220	Non Defined	0.00016	Non Defined
OP 33	CO2	337.097	Non Defined	0.23886	Non Defined
OP 34	CO2	1233.940	Non Defined	0.77851	Non Defined
OP 35	CO2	0.052	0	6.95294E-05	-0.0016191
OP 36	CO2	0.129	Non Defined	0.000196245	Non Defined
OP 37	CO2	0.471	Non Defined	0.000681785	Non Defined
OP 38	CO2	1632.513	Non Defined	0.995534725	Non Defined
OP 39	CO2	866.721	Non Defined	0.470564519	Non Defined
OP 40	CO2	14320.484	Non Defined	3.848428176	Non Defined
OP 41	CO2	0.096	Non Defined	6.78778E-05	Non Defined
OP 42	CO2	146.682	Non Defined	0.103936687	Non Defined
OP 43	CO2	536.928	Non Defined	0.34	Non Defined



Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 44	CO2	0.098	0	0.00	-0.0030559
OP 45	CO2	0.244	Non Defined	0.00	Non Defined
OP 46	CO2	0.895	Non Defined	0.00	Non Defined
OP 47	CO2	3101.759	Non Defined	1.24	Non Defined
OP 48	CO2	1646.762	Non Defined	1	Non Defined
OP 49	CO2	27208.782	Non Defined	2	Non Defined
OP 50	CO2	0.182	Non Defined	0	Non Defined
OP 51	CO2	278.695	Non Defined	0	Non Defined
OP 52	CO2	1020.159	Non Defined	0	Non Defined
OP 53	CO2	1.559	Non Defined	0.00	Non Defined
OP 54	CO2	2387.300	Non Defined	1.19	Non Defined
OP 55	CO2	8738.689	Non Defined	3.69	Non Defined
OP 56	CO2	0.211	Non Defined	0.00	Non Defined
OP 57	CO2	0.774	Non Defined	0.00	Non Defined
OP 58	CO2	0.011	0	0.00	-0.0003365
OP 59	CO2	0.069	Non Defined	0.00	Non Defined
OP 60	CO2	47.809	Non Defined	0.021874853	Non Defined
OP 61	CO2	256.684	Non Defined	0.117444174	Non Defined
OP 62	CO2	0.020	Non Defined	1.30807E-05	Non Defined
OP 63	CO2	0.075	Non Defined	4.20679E-05	Non Defined
OP 64	CO2	0.007	Non Defined	3.06566E-06	Non Defined
OP 65	CO2	4.625	Non Defined	0.00	Non Defined
OP 66	CO2	24.833	Non Defined	0.011361983	Non Defined
OP 67	CO2	1.328	Non Defined	0.00084951	Non Defined

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 68	CO2	4.861	Non Defined	0.002732049	Non Defined
OP 69	CO2	0.069	0	3.1768E-05	-0.0021147
OP 70	CO2	0.435	Non Defined	0.000199095	Non Defined
OP 71	CO2	300.381	Non Defined	0.137437429	Non Defined
OP 72	CO2	1612.722	Non Defined	0.737889547	Non Defined
OP 73	CARB	1044.332	0	7.190161935	-7.1901619
OP 74	CARB	12038.363	Non Defined	14.98953043	Non Defined
OP 75	CARB	35980.552	Non Defined	15.29285447	Non Defined
OP 76	CARB	20512.675	Non Defined	8.718525415	Non Defined
OP 77	CARB	225.961	0	1.566865008	-1.5668650
OP 78	CARB	2604.731	Non Defined	3.371631385	Non Defined
OP 79	CARB	7785.085	Non Defined	3.692542894	Non Defined
OP 80	CARB	4438.312	Non Defined	2.105135384	Non Defined
OP 81	CARB	307.217	0	2.22	-2.22127675
OP 82	CARB	3541.397	Non Defined	5.63	Non Defined
OP 83	CARB	10584.613	Non Defined	8.15	Non Defined
OP 84	CARB	6034.335	Non Defined	4.65	Non Defined
OP 85	CARB	83.928	0	0.60	-0.5989154
OP 86	CARB	967.465	Non Defined	1	Non Defined
OP 87	CARB	2891.583	Non Defined	2	Non Defined
OP 88	CARB	1648.504	Non Defined	1	Non Defined
OP 89	CARB	0.457	0	0	-0.0034346
OP 90	CARB	5.272	Non Defined	0.01	Non Defined
OP 91	CARB	15.756	Non Defined	0.02	Non Defined

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 92	CARB	8.982	Non Defined	0.01	Non Defined
OP 93	CARB	52.360	Non Defined	0.00	Non Defined
OP 94	CARB	541.262	Non Defined	0.00	Non Defined
OP 95	CARB	0.082	0	0.00	-0.0006469
OP 96	CARB	0.947	Non Defined	0.00	Non Defined
OP 97	CARB	2.830	Non Defined	0.004005799	Non Defined
OP 98	CARB	1.613	Non Defined	0.002283724	Non Defined
OP 99	CARB	50.444	0	0.382552093	-0.3825520
OP 100	CARB	581.490	Non Defined	1.130323895	Non Defined
OP 101	CARB	1737.971	Non Defined	1.953	Non Defined
OP 102	CARB	990.825	Non Defined	1.113	Non Defined
OP 103	CARB	0.008	Non Defined	0.000	Non Defined
OP 104	CARB	0.023	Non Defined	0.000	Non Defined
OP 105	CARB	0.013	Non Defined	0.000	Non Defined
OP 106	CARB	0.076	Non Defined	0.000	Non Defined
OP 107	CARB	0.784	Non Defined	0.000	Non Defined
OP 108	UREA	46056.018	-16120	275.471	-16395.077
OP 109	UREA	0.033	Non Defined	0.000	Non Defined
OP 110	UREA	286.365	Non Defined	1.840	Non Defined
OP 111	UREA	0.005	Non Defined	0.000	Non Defined
OP 112	UREA	0.358	0	0.002	-0.1277337
OP 113	UREA	0.148	Non Defined	0.001	Non Defined
OP 114	UREA	1285.037	Non Defined	8.212	Non Defined
OP 115	UREA	0.023	Non Defined	0.000	Non Defined

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 116	UREA	47.784	Non Defined	0.051	Non Defined
OP 117	UREA	171.870	Non Defined	0.060	Non Defined
OP 118	UREA	30738.889	-10759	181.423	-10940.033
OP 119	UREA	0.022	Non Defined	0.000	Non Defined
OP 120	UREA	191.127	Non Defined	1.213	Non Defined
OP 121	UREA	0.239	0	0.002	-0.0852336
OP 122	UREA	0.099	Non Defined	0.001	Non Defined
OP 123	UREA	857.664	Non Defined	5.413	Non Defined
OP 124	UREA	0.016	Non Defined	0.000	Non Defined
OP 125	UREA	31.892	Non Defined	0.031	Non Defined
OP 126	UREA	114.710	Non Defined	0.031	Non Defined
OP 127	H2O	1.322	0	0.016	-0.0167192
OP 128	H2O	-3.191	Non Defined	-0.043	Non Defined
OP 129	H2O	83.769	0	1.061	-1.1278490
OP 130	H2O	1.637	Non Defined	0.021	Non Defined
OP 131	H2O	37.485	0	0.028	-0.0576626
OP 132	H2O	-9.833	Non Defined	-0.014	Non Defined
OP 133	H2O	258.118	0	0.197	-0.4031014
OP 134	H2O	5.045	Non Defined	0.004	Non Defined
OP 135	H2O	-377.327	Non Defined	-0.585	Non Defined
OP 136	H2O	9904.521	-8	8.771	-16.694574
OP 137	H2O	193.604	Non Defined	0.169	Non Defined
OP 138	H2O	-220.754	Non Defined	-0.315	Non Defined
OP 139	H2O	5794.617	-5	4.423	-9.0584092

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 140	H2O	113.267	Non Defined	0.085	Non Defined
OP 141	H2O	39.859	0	0.029	-0.0613146
OP 142	H2O	-10.456	Non Defined	-0.015	Non Defined
OP 143	H2O	274.465	0	0.209	-0.4286312
OP 144	H2O	5.365	Non Defined	0.004	Non Defined
OP 145	H2O	8759.391	-7	0.105	-7.112807
OP 146	H2O	2116.416	-2	0.025	-1.7185741
OP 147	H2O	41.370	Non Defined	0.000	Non Defined
OP 148	H2O	212.676	0	2.453	-2.6228454
OP 149	H2O	-513.211	Non Defined	-6.681	Non Defined
OP 150	H2O	13471.370	-11	166.427	-177.2037
OP 151	H2O	263.325	Non Defined	3.250	Non Defined
OP 152	H2O	141.698	0	1.611	-1.7248404
OP 153	H2O	-341.935	Non Defined	-4.397	Non Defined
OP 154	H2O	8975.501	-7	109.448	-116.62870
OP 155	H2O	175.444	Non Defined	2.137	Non Defined
OP 156	N2	705.203	0	0.223	-0.2227747
OP 157	N2	0.022	0	0.000	-1.667E-05
OP 158	N2	2.371	0	0.001	-0.0014773
OP 159	N2	306.857	0	0.097	-0.0969366
OP 160	N2	0.010	0	0.000	-7.257E-06
OP 161	N2	1.032	0	0.001	-0.000642
OP 162	H2	11.988	0	0.048	-0.048295
OP 163	H2	0.067	0	0.001	-0.0005528

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 164	H2	5.216	0	0.021	-0.0210149
OP 165	H2	0.029	0	0.000	-0.000240
OP 166	O2	180.081	0	0.052	-0.0521343
OP 167	O2	0.199	0	0.000	-0.0001361
OP 168	O2	2.380	0	0.001	-0.0013422
OP 169	O2	0.056	0	0.000	-3.184E-05
OP 170	O2	78.359	0	0.023	-0.0226853
OP 171	O2	0.087	0	0.000	-5.922E-05
OP 172	O2	1.036	0	0.001	-0.0005840
OP 173	O2	0.025	0	0.000	-1.385E-05
OP 174	BIURET	189.153	0	1.036	-1.0361123
OP 175	BIURET	0.013	0	0.000	-8.253E-05
OP 176	BIURET	0.163	0	0.001	-0.000961
OP 177	BIURET	0.789	0	0.005	-0.0046195
OP 178	BIURET	0.016	0	0.000	-3.211E-05
OP 179	BIURET	244.632	0	1.293	-1.2925912
OP 180	BIURET	0.017	0	0.000	-0.0001034
OP 181	BIURET	0.211	0	0.001	-0.0012027
OP 182	BIURET	1.020	0	0.006	-0.0057767
OP 183	BIURET	0.021	0	0.000	-3.753E-05
OP 184	BIURET	78.625	0	0.425	-0.4249558
OP 185	BIURET	0.006	0	0.000	-3.390E-05
OP 186	BIURET	0.068	0	0.000	-0.0003947
OP 187	BIURET	0.328	0	0.002	-0.0018963

Open Path	Component	Flowrate (kg/h)	MVA (103\$/yr)	EWC (103\$/yr)	TVA(103\$/yr)
OP 188	BIURET	0.007	0	0.000	-1.286E-05
OP 189	BIURET	68.014	0	0.359	-0.3593741
OP 190	BIURET	0.059	0	0.000	-0.0003344
OP 191	BIURET	0.284	0	0.002	-0.0016060
OP 192	BIURET	0.006	0	0.000	-1.043E-05

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C1	NH3	23161.300	36.148	C249	N2	0.000	0.000
C2	CO2	2190.113	0.732	C250	H2	0.000	0.000
C3	CARB	30.350	0.013	C251	O2	0.000	0.000
C4	UREA	161.118	0.056	C252	BIURET	0.000	0.000
C5	H2O	3480.460	2.848	C253	NH3	0.001	0.000
C6	N2	0.000	0.000	C254	CO2	0.000	0.000
C7	H2	0.000	0.000	C255	CARB	0.002	0.000
C8	O2	0.000	0.000	C256	UREA	0.000	0.000
C9	BIURET	0.501	0.000	C257	H2O	0.072	0.001
C10	NH3	691.493	8.245	C258	N2	0.000	0.000
C11	CO2	1.977	0.002	C259	H2	0.000	0.000
C12	CARB	0.000	0.000	C260	O2	0.000	0.000
C13	UREA	0.000	0.000	C261	BIURET	0.000	0.000
C14	H2O	1574.541	5.735	C262	NH3	0.017	0.001
C15	N2	0.000	0.000	C263	CO2	0.000	0.000
C16	H2	0.000	0.000	C264	CARB	0.002	0.000
C17	O2	0.000	0.000	C265	UREA	2.112	0.016
C18	BIURET	0.000	0.000	C266	H2O	9.118	0.131
C19	NH3	20.022	0.042	C267	N2	0.000	0.000
C20	CO2	1.977	0.002	C268	H2	0.000	0.000
C21	CARB	0.000	0.000	C269	O2	0.000	0.000
C22	UREA	0.000	0.000	C270	BIURET	0.000	0.000
C23	H2O	2.225	0.003	C271	NH3	2.266	0.078
C24	N2	0.000	0.000	C272	CO2	0.000	0.000
C25	H2	0.000	0.000	C273	CARB	1.687	0.014
C26	O2	0.000	0.000	C274	UREA	10.217	0.075
C27	BIURET	0.000	0.000	C275	H2O	158.502	2.287
C28	NH3	288.092	0.001	C276	N2	0.000	0.000
C29	CO2	0.113	0.000	C277	H2	0.000	0.000
C30	CARB	526.428	0.001	C278	O2	0.000	0.000
C31	UREA	2320.132	0.003	C279	BIURET	0.000	0.000
C32	H2O	41734.153	0.106	C280	NH3	26.061	0.871
C33	N2	0.000	0.000	C281	CO2	0.000	0.000
C34	H2	0.000	0.000	C282	CARB	0.000	0.000
C35	O2	0.000	0.000	C283	UREA	0.000	0.000
C36	BIURET	0.000	0.000	C284	H2O	3438.333	47.220



Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C37	NH3	2.266	0.002	C285	N2	0.000	0.000
C38	CO2	0.000	0.000	C286	H2	0.000	0.000
C39	CARB	0.395	0.000	C287	O2	0.000	0.000
C40	UREA	1.006	0.000	C288	BIURET	0.000	0.000
C41	H2O	50.854	0.038	C289	NH3	0.001	0.000
C42	N2	0.000	0.000	C290	CO2	0.000	0.000
C43	H2	0.000	0.000	C291	CARB	0.002	0.000
C44	O2	0.000	0.000	C292	UREA	0.000	0.000
C45	BIURET	0.000	0.000	C293	H2O	0.072	0.001
C46	NH3	2.988	0.007	C294	N2	0.000	0.000
C47	CO2	0.002	0.000	C295	H2	0.000	0.000
C48	CARB	0.000	0.000	C296	O2	0.000	0.000
C49	UREA	0.000	0.000	C297	BIURET	0.000	0.000
C50	H2O	0.202	0.000	C298	NH3	7.934	0.264
C51	N2	0.000	0.000	C299	CO2	0.000	0.000
C52	H2	0.000	0.000	C300	CARB	1.687	0.013
C53	O2	0.000	0.000	C301	UREA	57.363	0.403
C54	BIURET	0.000	0.000	C302	H2O	704.365	9.638
C55	NH3	2.266	0.002	C303	N2	0.000	0.000
C56	CO2	0.001	0.000	C304	H2	0.000	0.000
C57	CARB	2.947	0.001	C305	O2	0.000	0.000
C58	UREA	10.221	0.004	C306	BIURET	0.000	0.000
C59	H2O	158.502	0.119	C307	NH3	0.017	0.000
C60	N2	0.000	0.000	C308	CO2	0.000	0.000
C61	H2	0.000	0.000	C309	CARB	0.000	0.000
C62	O2	0.000	0.000	C310	UREA	0.026	0.000
C63	BIURET	0.000	0.000	C311	H2O	9.118	0.082
C64	NH3	688.525	0.392	C312	N2	0.000	0.000
C65	CO2	4.475	0.000	C313	H2	0.000	0.000
C66	CARB	0.000	0.000	C314	O2	0.000	0.000
C67	UREA	0.001	0.000	C315	BIURET	0.000	0.000
C68	H2O	1755.540	0.011	C316	NH3	0.017	0.000
C69	N2	0.000	0.000	C317	CO2	0.000	0.000

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C70	H2	0.000	0.000	C318	CARB	0.000	0.000
C71	O2	0.000	0.000	C319	UREA	0.000	0.000
C72	BIURET	0.000	0.000	C320	H2O	9.118	0.075
C73	NH3	771.116	0.439	C321	N2	0.000	0.000
C74	CO2	0.000	0.000	C322	H2	0.000	0.000
C75	CARB	0.000	0.000	C323	O2	0.000	0.000
C76	UREA	0.000	0.000	C324	BIURET	0.000	0.000
C77	H2O	8255.726	0.052	C325	NH3	0.001	0.000
C78	N2	0.000	0.000	C326	CO2	0.000	0.000
C79	H2	0.000	0.000	C327	CARB	0.000	0.000
C80	O2	0.000	0.000	C328	UREA	0.000	0.000
C81	BIURET	0.000	0.000	C329	H2O	0.072	0.001
C82	NH3	87.488	0.079	C330	N2	0.000	0.000
C83	CO2	0.064	0.000	C331	H2	0.000	0.000
C84	CARB	0.000	0.000	C332	O2	0.000	0.000
C85	UREA	0.000	0.000	C333	BIURET	0.000	0.000
C86	H2O	16.487	0.011	C334	NH3	0.017	0.000
C87	N2	0.000	0.000	C335	CO2	0.000	0.000
C88	H2	0.000	0.000	C336	CARB	0.000	0.000
C89	O2	0.000	0.000	C337	UREA	0.026	0.000
C90	BIURET	0.000	0.000	C338	H2O	9.118	0.075
C91	NH3	2.988	0.005	C339	N2	0.000	0.000
C92	CO2	0.064	0.000	C340	H2	0.000	0.000
C93	CARB	0.000	0.000	C341	O2	0.000	0.000
C94	UREA	0.000	0.000	C342	BIURET	0.000	0.000
C95	H2O	0.202	0.000	C343	NH3	1.064	0.018
C96	N2	0.000	0.000	C344	CO2	0.000	0.000
C97	H2	0.000	0.000	C345	CARB	0.000	0.000
C98	O2	0.000	0.000	C346	UREA	0.026	0.000
C99	BIURET	0.000	0.000	C347	H2O	9.518	0.078
C100	NH3	0.001	0.000	C348	N2	0.000	0.000
C101	CO2	0.000	0.000	C349	H2	0.000	0.000
C102	CARB	0.000	0.000	C350	O2	0.000	0.000
C103	UREA	0.000	0.000	C351	BIURET	0.000	0.000
C104	H2O	0.072	0.000	C352	NH3	1.064	0.017
C105	N2	0.000	0.000	C353	CO2	0.000	0.000
C106	H2	0.000	0.000	C354	CARB	0.000	0.000

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C107	O2	0.000	0.000	C355	UREA	0.000	0.000
C108	BIURET	0.000	0.000	C356	H2O	9.518	0.071
C109	NH3	0.001	0.000	C357	N2	0.000	0.000
C110	CO2	0.000	0.000	C358	H2	0.000	0.000
C111	CARB	0.000	0.000	C359	O2	0.000	0.000
C112	UREA	0.000	0.000	C360	BIURET	0.000	0.000
C113	H2O	0.202	0.000	C361	NH3	0.001	0.000
C114	N2	0.000	0.000	C362	CO2	0.000	0.000
C115	H2	0.000	0.000	C363	CARB	0.000	0.000
C116	O2	0.000	0.000	C364	UREA	0.000	0.000
C117	BIURET	0.000	0.000	C365	H2O	0.072	0.001
C118	NH3	2.988	0.005	C366	N2	0.000	0.000
C119	CO2	0.007	0.000	C367	H2	0.000	0.000
C120	CARB	0.000	0.000	C368	O2	0.000	0.000
C121	UREA	0.000	0.000	C369	BIURET	0.000	0.000
C122	H2O	0.202	0.000	C370	NH3	1.064	0.017
C123	N2	0.000	0.000	C371	CO2	0.000	0.000
C124	H2	0.000	0.000	C372	CARB	0.000	0.000
C125	O2	0.000	0.000	C373	UREA	0.026	0.000
C126	BIURET	0.000	0.000	C374	H2O	9.518	0.071
C127	NH3	0.000	0.000	C375	N2	0.000	0.000
C128	CO2	0.000	0.000	C376	H2	0.000	0.000
C129	CARB	0.000	0.000	C377	O2	0.000	0.000
C130	UREA	0.201	0.002	C378	BIURET	0.000	0.000
C131	H2O	18.904	0.302	C379	NH3	2.266	0.036
C132	N2	0.000	0.000	C380	CO2	0.000	0.000
C133	H2	0.000	0.000	C381	CARB	0.001	0.000
C134	O2	0.000	0.000	C382	UREA	6.897	0.023
C135	BIURET	0.000	0.000	C383	H2O	158.502	1.167
C136	NH3	0.000	0.000	C384	N2	0.000	0.000
C137	CO2	0.000	0.000	C385	H2	0.000	0.000
C138	CARB	0.000	0.000	C386	O2	0.000	0.000
C139	UREA	0.000	0.000	C387	BIURET	0.000	0.000
C140	H2O	18.904	0.289	C388	NH3	387.769	5.854
C141	N2	0.000	0.000	C389	CO2	0.000	0.000
C142	H2	0.000	0.000	C390	CARB	0.000	0.000
C143	O2	0.000	0.000	C391	UREA	0.000	0.000

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C144	BIURET	0.000	0.000	C392	H2O	5020.386	33.460
C145	NH3	0.000	0.000	C393	N2	0.000	0.000
C146	CO2	0.000	0.000	C394	H2	0.000	0.000
C147	CARB	0.000	0.000	C395	O2	0.000	0.000
C148	UREA	0.000	0.000	C396	BIURET	0.000	0.000
C149	H2O	0.072	0.001	C397	NH3	0.001	0.000
C150	N2	0.000	0.000	C398	CO2	0.000	0.000
C151	H2	0.000	0.000	C399	CARB	0.001	0.000
C152	O2	0.000	0.000	C400	UREA	0.000	0.000
C153	BIURET	0.000	0.000	C401	H2O	0.072	0.000
C154	NH3	0.000	0.000	C402	N2	0.000	0.000
C155	CO2	0.000	0.000	C403	H2	0.000	0.000
C156	CARB	0.000	0.000	C404	O2	0.000	0.000
C157	UREA	0.201	0.002	C405	BIURET	0.000	0.000
C158	H2O	18.904	0.288	C406	NH3	7.934	0.119
C159	N2	0.000	0.000	C407	CO2	0.000	0.000
C160	H2	0.000	0.000	C408	CARB	0.001	0.000
C161	O2	0.000	0.000	C409	UREA	6.897	0.020
C162	BIURET	0.000	0.000	C410	H2O	704.365	4.659
C163	NH3	0.003	0.000	C411	N2	0.000	0.000
C164	CO2	0.000	0.000	C412	H2	0.000	0.000
C165	CARB	0.023	0.000	C413	O2	0.000	0.000
C166	UREA	10.217	0.080	C414	BIURET	0.000	0.000
C167	H2O	264.572	4.030	C415	NH3	22.013	0.304
C168	N2	0.000	0.000	C416	CO2	0.000	0.000
C169	H2	0.000	0.000	C417	CARB	0.000	0.000
C170	O2	0.000	0.000	C418	UREA	0.000	0.000
C171	BIURET	0.000	0.000	C419	H2O	50.854	0.258
C172	NH3	0.003	0.000	C420	N2	0.000	0.000
C173	CO2	0.000	0.000	C421	H2	0.000	0.000
C174	CARB	0.000	0.000	C422	O2	0.000	0.000
C175	UREA	0.000	0.000	C423	BIURET	0.000	0.000
C176	H2O	264.572	3.846	C424	NH3	0.001	0.000
C177	N2	0.000	0.000	C425	CO2	0.000	0.000
C178	H2	0.000	0.000	C426	CARB	0.001	0.000
C179	O2	0.000	0.000	C427	UREA	0.000	0.000
C180	BIURET	0.000	0.000	C428	H2O	0.072	0.000

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C181	NH3	0.001	0.000	C429	N2	0.000	0.000
C182	CO2	0.000	0.000	C430	H2	0.000	0.000
C183	CARB	0.002	0.000	C431	O2	0.000	0.000
C184	UREA	0.000	0.000	C432	BIURET	0.000	0.000
C185	H2O	0.072	0.001	C433	NH3	7.934	0.109
C186	N2	0.000	0.000	C434	CO2	0.000	0.000
C187	H2	0.000	0.000	C435	CARB	0.001	0.000
C188	O2	0.000	0.000	C436	UREA	1.006	0.002
C189	BIURET	0.000	0.000	C437	H2O	50.854	0.256
C190	NH3	0.003	0.000	C438	N2	0.000	0.000
C191	CO2	0.000	0.000	C439	H2	0.000	0.000
C192	CARB	0.023	0.000	C440	O2	0.000	0.000
C193	UREA	23.609	0.175	C441	BIURET	0.000	0.000
C194	H2O	264.572	3.833	C442	NH3	668.207	9.166
C195	N2	0.000	0.000	C443	CO2	0.000	0.000
C196	H2	0.000	0.000	C444	CARB	0.001	0.000
C197	O2	0.000	0.000	C445	UREA	2.909	0.006
C198	BIURET	0.000	0.000	C446	H2O	1256.654	6.313
C199	NH3	0.048	0.002	C447	N2	0.000	0.000
C200	CO2	0.000	0.000	C448	H2	0.000	0.000
C201	CARB	0.310	0.003	C449	O2	0.000	0.000
C202	UREA	10.217	0.076	C450	BIURET	0.020	0.000
C203	H2O	158.502	2.297	C451	NH3	289.356	3.999
C204	N2	0.000	0.000	C452	CO2	0.000	0.000
C205	H2	0.000	0.000	C453	CARB	0.000	0.000
C206	O2	0.000	0.000	C454	UREA	0.000	0.000
C207	BIURET	0.000	0.000	C455	H2O	407.790	2.071
C208	NH3	0.048	0.002	C456	N2	0.000	0.000
C209	CO2	0.000	0.000	C457	H2	0.000	0.000
C210	CARB	0.000	0.000	C458	O2	0.000	0.000
C211	UREA	0.000	0.000	C459	BIURET	0.000	0.000
C212	H2O	502.771	6.937	C460	NH3	0.001	0.000
C213	N2	0.000	0.000	C461	CO2	0.000	0.000
C214	H2	0.000	0.000	C462	CARB	0.001	0.000
C215	O2	0.000	0.000	C463	UREA	0.000	0.000
C216	BIURET	0.000	0.000	C464	H2O	0.072	0.000

Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)	Cycle Path	Component	Flowrate (kg/h)	EWC (103\$/yr)
C217	NH3	0.001	0.000	C465	N2	0.000	0.000
C218	CO2	0.000	0.000	C466	H2	0.000	0.000
C219	CARB	0.002	0.000	C467	O2	0.000	0.000
C220	UREA	0.000	0.000	C468	BIURET	0.000	0.000
C221	H2O	0.072	0.001	C469	NH3	7.934	0.109
C222	N2	0.000	0.000	C470	CO2	0.000	0.000
C223	H2	0.000	0.000	C471	CARB	0.001	0.000
C224	O2	0.000	0.000	C472	UREA	2.909	0.006
C225	BIURET	0.000	0.000	C473	H2O	407.790	2.050
C226	NH3	0.048	0.002	C474	N2	0.000	0.000
C227	CO2	0.000	0.000	C475	H2	0.000	0.000
C228	CARB	0.310	0.002	C476	O2	0.000	0.000
C229	UREA	57.363	0.404	C477	BIURET	0.000	0.000
C230	H2O	502.771	6.912	C478	NH3	5097.638	8.864
C231	N2	0.000	0.000	C479	CO2	1125.135	0.452
C232	H2	0.000	0.000	C480	CARB	0.000	0.000
C233	O2	0.000	0.000	C481	UREA	0.000	0.000
C234	BIURET	0.000	0.000	C482	H2O	775.832	0.708
C235	NH3	0.017	0.001	C483	N2	28.968	0.004
C236	CO2	0.000	0.000	C484	H2	0.716	0.001
C237	CARB	0.002	0.000	C485	O2	27.737	0.004
C238	UREA	2.112	0.016	C486	BIURET	0.000	0.000
C239	H2O	9.118	0.138	C487	NH3	692.122	1.080
C240	N2	0.000	0.000	C488	CO2	24.645	0.008
C241	H2	0.000	0.000	C489	CARB	4382.125	1.863
C242	O2	0.000	0.000	C490	UREA	542.297	0.189
C243	BIURET	0.000	0.000	C491	H2O	523.884	0.429
C244	NH3	0.017	0.001	C492	N2	0.000	0.000
C245	CO2	0.000	0.000	C493	H2	0.000	0.000
C246	CARB	0.000	0.000	C494	O2	0.000	0.000
C247	UREA	0.000	0.000	C495	BIURET	0.000	0.000
C248	H2O	9.118	0.132				

**APPENDIX F**

Renata Chinda, Rotjana Ponsatorn, Amata Anantpinijwatna, Fernando P. Pessoa, John M. Woodley, Seyed Soheil Mansouri,

Process model validation and analysis for intensification of an industrial scale process,

Editor(s): Anton A. Kiss, Edwin Zondervan, Richard Lakerveld, Leyla Özkan,

Computer Aided Chemical Engineering,

Elsevier,

Volume 46,

2019,

Pages 955-960,

ISSN 1570-7946,

ISBN 9780128186343,

<https://doi.org/10.1016/B978-0-12-818634-3.50160-0>.

(<http://www.sciencedirect.com/science/article/pii/B9780128186343501600>)

## Process model validation and analysis for intensification of an industrial scale process

Renata Chinda<sup>a,§</sup>, Rotjana Ponsatorn<sup>b,§</sup>, Amata Anantpinijwatna<sup>b</sup>, Fernando P. Pessoa<sup>c</sup>, John M. Woodley<sup>d</sup> and Seyed Soheil Mansouri<sup>d,\*</sup>

<sup>a</sup>*Department of Chemical Engineering, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos, 149, CT, Sala E-207, 21941-909, Rio de Janeiro - RJ, Brazil*

<sup>b</sup>*Department of Chemical Engineering, Faculty of Engineering, King Mongku's Institute of Technology Ladkrabang, Chalongkrung Rd., Ladkrabang, Bangkok, TH-10520*

<sup>c</sup>*SENAI CIMATEC, Av. Orlando Gomes, 1845, Salvador - Ba, Brazil*

<sup>d</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, Søtofts Plads, DK-2800 Kgs. Lyngby, Denmark*

<sup>§</sup> *Authors contributed equally to this work.*

<sup>\*</sup>*seso@kt.dtu.dk*

### Abstract

Adopting reliable process models is one of the main requisites for wide spread use of process models in industry for design, control, operation and troubleshooting purposes. Validating a model against operational conditions is a plausible way to guarantee assurance and reproducibility of model outputs. Economic and sustainability analysis together with process intensification (PI) can provide feasible solutions for industrial hot-spot identification and removal. In this work, an industrial scale urea plant was modelled and simulated in a commercial process simulator. More than thirty different industrial process parameters were statistically analysed and used to perform the model validation. Economic and sustainability analyses were performed and the main hot-spots were identified. Process intensification at phenomena-level was employed to obtain more sustainable intensified process flowsheets. The results show that economic and environmental factors can be improved to reliable extent since the process model is closely replicating the reality in the base case and it fits well with industrial data.

**Keywords:** industrial data validation, process intensification, sustainable solutions.

### 1. Introduction

Modelling and simulation plays an important role in the development of chemical engineering systems. For laboratory, pilot or even industrial scale, computer aided solutions are one of the most cost effective tools available and, sometimes, the only option for engineering judgments. In order to guarantee the accuracy of these judgments it is necessary that the computational models correspond very well to the industrial data. Then, they can also be a good tool for real improvements through analysis like economic, sustainability, Life Cycle Assessment (LCA) and even reaching Process Intensification in order to achieve a more sustainable process.

This paper is on demonstrating the importance of validating simulations against real industrial data to make development of more advanced modelling approaches and even intensified solutions for existing chemical process possible.



## 2. Process description and modelling

The base case studied in this paper is the production of urea through  $\text{CO}_2$  stripping. This process is divided into five blocks: Synthesis, Evaporation, Desabsorption and Hydrolysis, Recirculation and Prilling, as it can be seen in Fig.1.

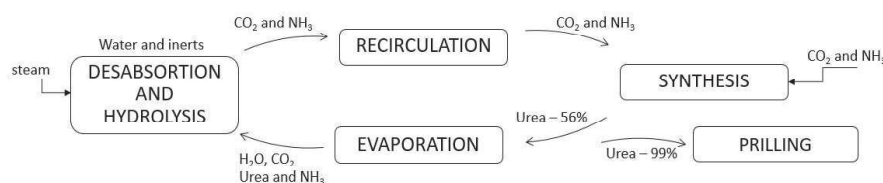


Figure 1: Simplified block diagram for the urea production process.

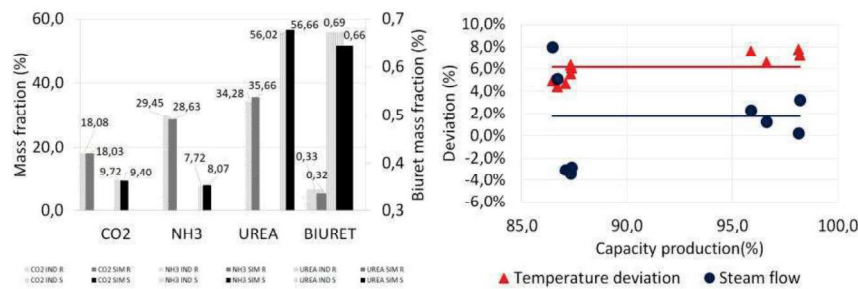
The principal section of this process is the Synthesis where reactions between  $\text{NH}_3$  and  $\text{CO}_2$  to produce ammonium carbamate and urea take place. The product of this section goes to Evaporation section to concentrate the urea and then it is sent to the Prilling. The remaining unconverted reactants are processed and recovered in the Hydrolysis and Desorption sections and, before they are sent again to Synthesis section, pressure and temperature need to be adjusted in the Recirculation step. The main equipment in each section are: Synthesis – pool condenser, reactor, stripper and scrubber; Evaporation – Pre-evaporator, 1<sup>st</sup> and 2<sup>nd</sup> evaporator; Desabsorption and Hydrolysis – adsorber, desorber I and II; Recirculation – rectifying column and condenser; Prilling – prilling tower. The reactions occurring at this process and considered in this paper are the well known ammonia and carbon dioxide producing ammonium and this one dehydrating in urea and, finally, the biuret formation, which presents a lack in literature of the area and it occurs from the condensation of two urea molecules resulting in biuret and ammonia. This process was modelled assuming steady state conditions, SR-POLAR for thermodynamic representation, production of biuret in the Pool Condenser, Reactor, Stripper and in all the Evaporators. Kinetics models were taken from Chinda et al. (2017).

## 3. Process validation

The experimental data used for validating the simulation was provided by an industrial urea plant in Brazil. A statistical analysis based on dispersion was performed with the plant capacity in order to exclude data that may have been taken in transient process conditions. For this, it was considered that coefficient of variation to be less than 1.5% would reflect stability in operation of the industrial plant. Statistical concepts such as arithmetic mean and standard deviation sample to calculate the variation coefficient were employed. Using this criteria it was found that the set of points at steady state available for validating the simulation was in range capacity from 86.45% to 98.21%. Validation of the simulation was performed by calculating the difference between industrial and simulated data and dividing it per industrial data.

A total of 37 different process parameters were evaluated following this criteria, among them stream temperature, steam generation, mass fraction composition for  $\text{CO}_2$ ,  $\text{NH}_3$ , urea,  $\text{H}_2\text{O}$  and biuret,  $\text{CO}_2$  conversion in the reactor and stripper efficiency. For all evaluated mass fractions, the deviation between the value predicted by the simulation

and the real value obtained from industrial data were less than 5%, while for steam generation and streams temperature the deviation was less than 8%. Fig. 2(a) shows the comparison between mass fraction for each component in the outlet of the reactor and the stripper. While in Fig 2(b) it is possible to see no deviation tendency for the 10 points evaluated in the steam generated in the Pool Condenser and in the outlet temperature of the Stripper liquid phase corresponding to the production capacity of the urea plant.



**Figure 2 (a):** Comparison between mass fraction composition in the outlet of the reactor and the liquid outlet of stripper. **(b)** Deviation analysis of the simulation data for the steam generation in the Pool Condenser and outlet temperature of the Stripper.

#### 4. Process performance analysis & Hot-spots identification

Economic analysis was performed using ICAS-ECON. Sustainability analysis was carried out using the framework by Carvalho et al. (2008), Mansouri et al. (2013), and Tallis (2002); and for LCA analysis UK Government GHG conversion factors and IPCC emission factors were used.

##### 4.1 Economic, life cycle assessment and sustainability analysis

The economic and life cycle assessment as a part of the performed analysis provide evidence that the main drivers for operating costs in urea production process are, heating (56.06 %), cooling (9.43 %) and electricity (34.51%). The analysis also showed that the rectifying column, the pre-evaporator, the 1<sup>st</sup> evaporator and the CO<sub>2</sub> compressor have the large utility cost, around 89.52% collectively. Furthermore, CO<sub>2</sub> compressor also has the largest carbon footprint because of its high-energy consumption, around 40.95 Wh.

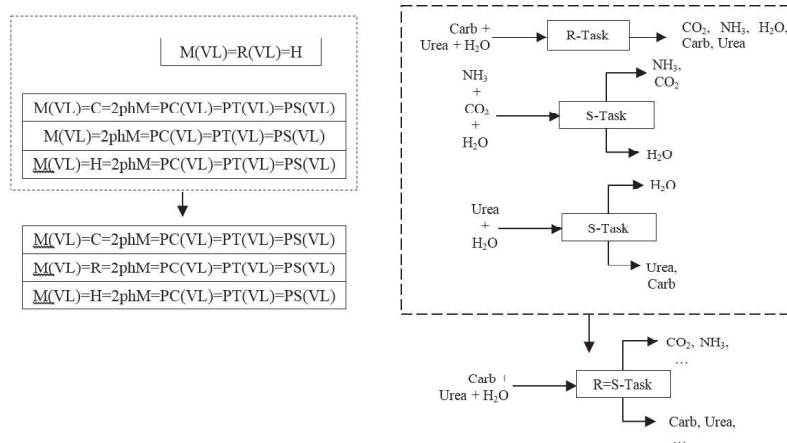
The sustainability analysis performed in this study is a set of calculated closed- and open- paths. The method calculates and ranks as a set of mass and energy indicators, from the data obtained from steady-state simulation validated with industrial data. The main sustainability indicators are given in Table 1; and their corresponding paths are given in Fig. 2.

**Table 2:** Urea Process hot-spots.

Hot-Spots	Design targets	Improvement solution
Limiting equilibrium	Un-reacted raw materials	-Reduction in number of unit operations
High energy consumption and/or demand	products recovery	- Improvement in sustainability and LCA factors

## 5. Process Intensification

Process Intensification was performed using a multi-stage framework according to (Babi et al, 2015) and (Garg et al, 2018). The base case was translated in a task-based flowsheet in order to identify Phenomena Building Blocks (PBB's), and generate Simultaneous Phenomena Building Blocks (SPB's). The total number of SPB's calculated were 16278, for 11 PBB's. Since, not all of them are feasible, following connectivity rules, it was found possible only 70 SPB's. The identified feasible SPB's are combined to form basic structures and then they were translated into unit-operations, as reactive distillation as it can be seen in Fig. 4.



**Figure 4:** Basic structures combined into intensified unit operations: reactive distillation.

Finally, two intensified flowsheet alternatives are generated, as shown in Fig. 5 for Evaporation and Recirculation sections. Alternative 1 is the combined basic structure translated into Pervaporation membrane, while in Alternative 2 it is translated to Vapour permeation membrane.

The two process alternatives offer superior performance in terms of all indicators to the base case process, given that the best process alternative is the pervaporation membrane option (alternative 1). The energy consumption per one unit of urea is significantly reduced (53.48%) as well as utility cost (42.27%). The hot utilities (steam/hot water) and cold utilities (cooling water) usage were reduced to 68.63% and 29.15%, respectively. In addition, the carbon footprint, HTPI and GWP were reduced to 41.63%, 1.51% and 1.39%, respectively.

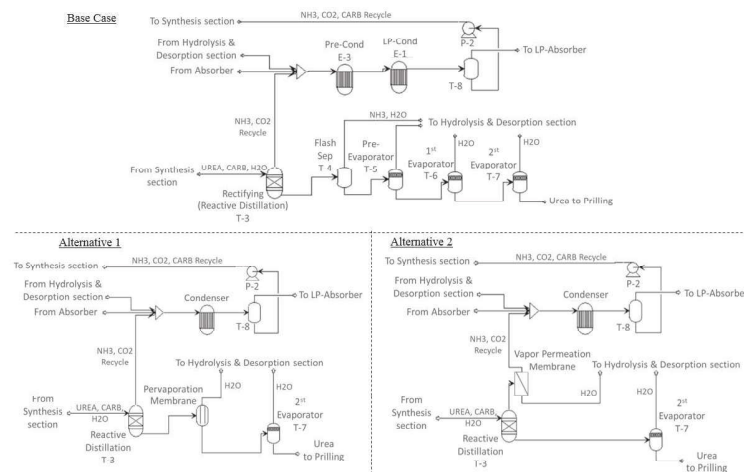


Figure 5: Base case and intensified flowsheet analysis.

## 5. Conclusions

Modelling and simulation of a urea plant was performed and validated with industrial data. Hot-spots were identified through economic and sustainability analyses. For Evaporation and Recirculation sections two feasible intensified alternatives were proposed using membranes. The pervaporation membrane unit for the separation of  $H_2O$ /Urea shows itself as the most sustainable one. The validation step with industrial data was an essential factor to perform a reliable and realistic study in order to suggest improvements to the process.

## Acknowledgments

R.C. would like to acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Finance Code 001) and R.P. would like to acknowledge KMITL (King Mongkut's Institute of Technology Ladkrabang) for the research grants.

## References

- Babi, D.; Holtbruegge J.; Lutze P.; Gorak, A.; Woodley, J.; Gani, R.. Sustainable Process Synthesis-Intensification. *Comput. Chem. Eng.* 2015, 81, 218–244.
- Carvalho, A.; Gani, R.; Matos, H. Design of sustainable chemical processes: Systematic retrofit analysis generation and evaluation of alternatives. *Process Saf. Environ. Prot.* 2008, 86, 328–346.
- Chinda, R., Yamamoto, C., Lima, D., & Pessoa, F. (2017/July). Modeling and Simulating the Synthesis Section of an Industrial Urea Plant: Analyzing the Biuret Formation. *UreaKnowHow.com*.
- Garg, N.; Kontogeorgis G.; Woodley, J.; Gani, R. A Multi-stage and multi-level Computer Aided Framework for Sustainable Process Intensification. *Proceedings of the 28th European Symposium on Computer Aided Process Engineering*. Graz, Austria.
- Mansouri, S.S.; Ismail, M.I.; Babi, D.K.; Simasatitkul, L.; Huusom, J.K.; Gani, R. Systematic sustainable process design and analysis of biodiesel processes. *Processes* 2013, 1 (2), 167–202
- Tallis, B., Sustainable Development Progress Metrics, IChemE Sustainable Development Working Group, IChemE, Rugby, UK, 2002.

**APPENDIX G**

Chinda, R., Yamamoto, C., Lima, D. and Pessoa, F. (2019). Industrial Urea Process – Simulation and Validation. *International Journal of Advanced Engineering Research and Science*, 6(8), pp.324-330.

# Industrial Urea Process – Simulation and Validation

Renata Chinda<sup>1</sup>, Carlos Yamamoto<sup>2</sup>, Daniel Lima<sup>3</sup> and Fernando Pessoa<sup>4</sup>

<sup>1</sup>Engenharia de Processos Químicos e Bioquímicos, Universidade Federal do Rio de Janeiro, Brazil.

Email: chinda@eq.ufrj.br

<sup>2</sup>LACAUT, Universidade Federal do Paraná, Brasil

Email: ciyama@ufpr.br

<sup>3</sup>Araucária Nitrogenados S.A.

Email: falleiros@petrobras.com.br

<sup>4</sup>SENAI 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<sub>x</sub> 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 CO<sub>2</sub> 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 NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>O, urea, ammonium carbamate, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> 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.

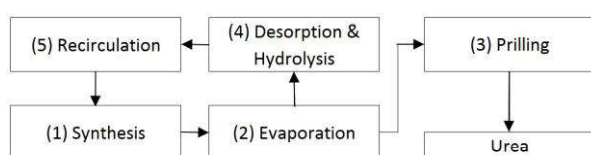


Fig.1 - Simplified block diagram for industrial urea production.

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  $\text{NH}_3$  and  $\text{CO}_2$ , besides condensing  $\text{NH}_3$  and  $\text{CO}_2$  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  $\text{NH}_3$ ,  $\text{CO}_2$  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.



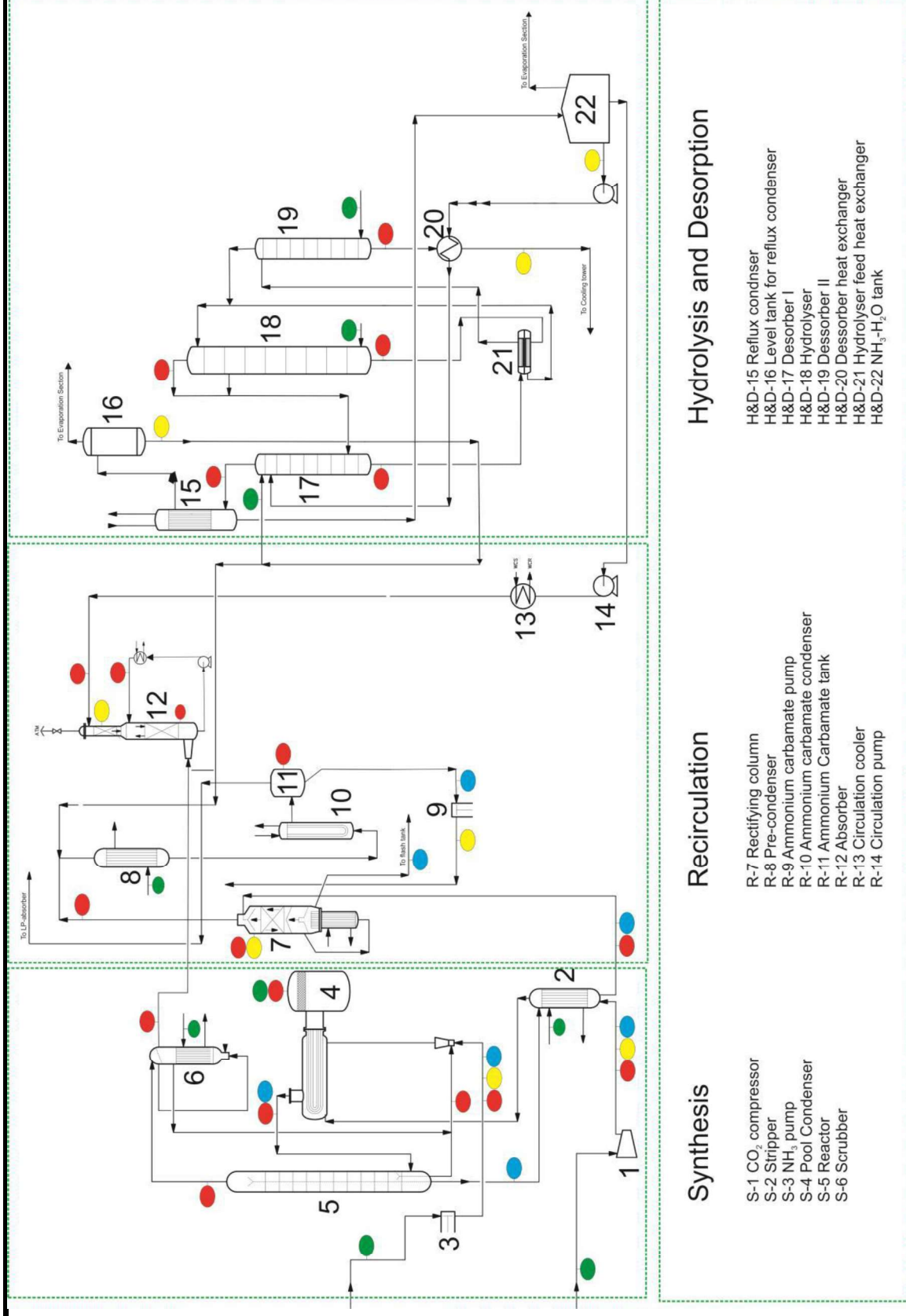


Fig.2 - Process flowsheet and data point collection for Synthesis, Recirculation and Hydrolysis & Desorption sections.

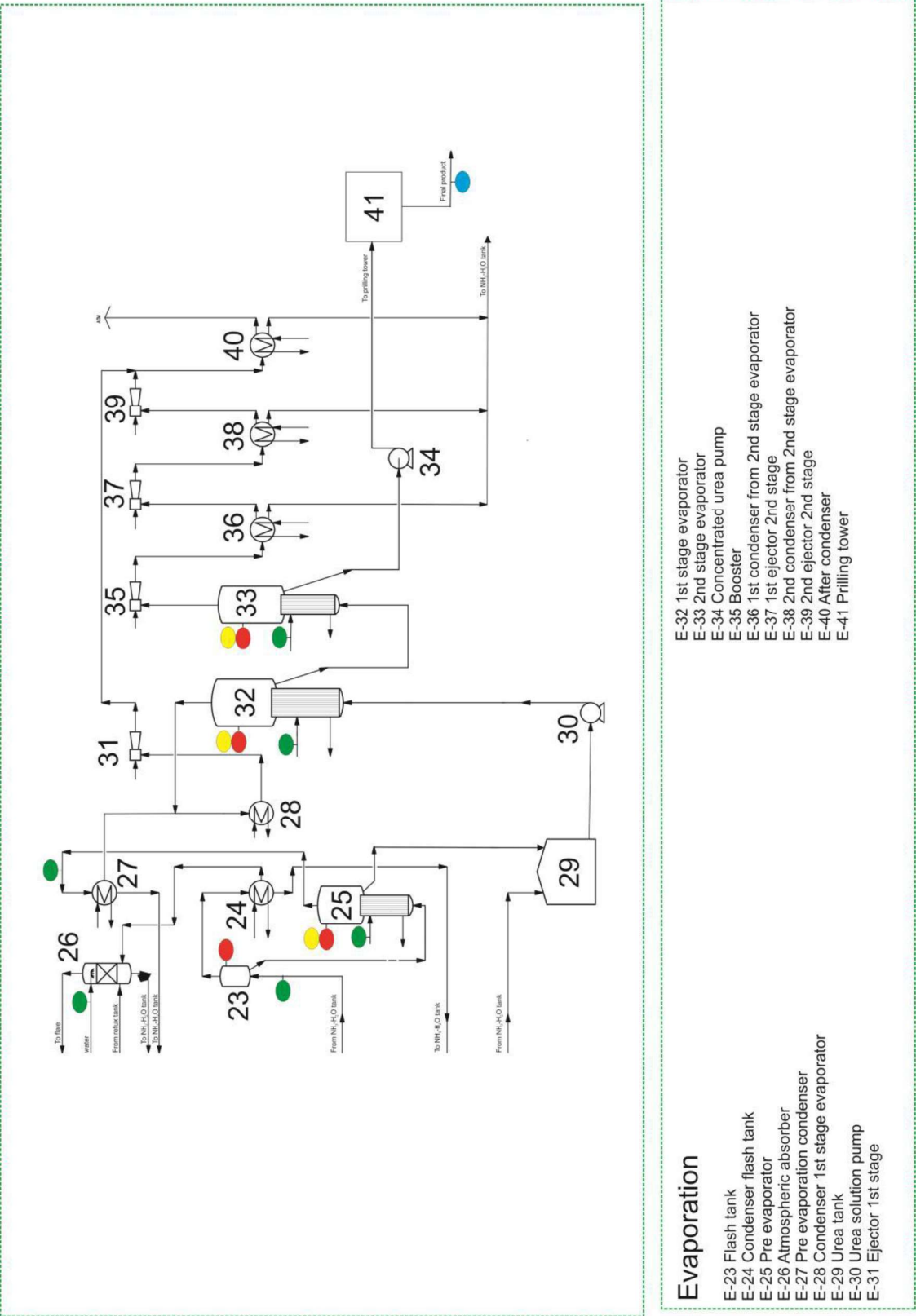


Fig.3 - Process flowsheet and data point collection for Evaporation section.

Table 2 - Statistical Analyses with capacity planta data.

Poin t	AM (%)	SS D	VC (%)	Poin t	AM (%)	SS D	VC (%)
A	86.4 5	0.39	0.45	G	95.6 6	0.14	0.1 5
B	86.7 0	0.39	0.45	H	95.8 7	0.29	0.3 0
C	87.0 6	1.05	1.21	I	96.6 2	0.63	0.6 5
D	87.3 3	0.07	0.08	J	98.1 3	0.11	0.1 1
E	87.3 7	0.52	0.60	K	98.2 1	0.49	0.4 2
F	87.4 1	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.

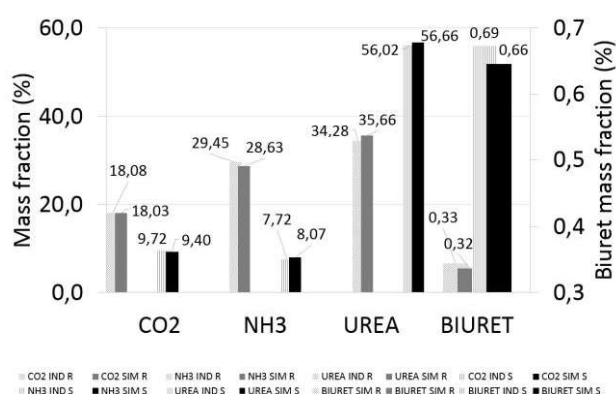


Fig.4 - Comparison between mass fraction composition in the outlet of the reactor and the liquid outlet of stripper.

A total of 37 different process parameters were evaluated, among them stream temperature, steam generation, mass fraction for CO<sub>2</sub>, NH<sub>3</sub>, urea, H<sub>2</sub>O and biuret, CO<sub>2</sub> 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 <sub>2</sub> MF	5.95%	8.84%	[6]
	NH <sub>3</sub> MF	4.33%	9.76%	[24]
	Urea MF	3.38%	2.65%	[5]
	H <sub>2</sub> O MF	4.38%	2.71%	[24]
	Biuret content	4.96%	-	-
	CO <sub>2</sub> conversion	2.41%	0.44%	[3]
	N/C ratio	4.83%	6.90%	[5]
	H <sub>2</sub> O /urea ratio	6.18%	-	-
Scrubber	T of the liquid outlet	4.77%	-	-
	CO <sub>2</sub> MF	5.00%	5.10%	[24]
	NH <sub>3</sub> MF	6.12%	4.14%	[24]
	urea MF	2.93%	0.20%	[4]
	H <sub>2</sub> O MF	4.32%	4.96%	[24]
	Biuret content	4.96%	-	-
	Efficiency	2.53%	-	-
	N/C	2.42%	-	-
Stripper	H/urea	6.50%	-	-
	Steam flow	4.27%	-	-
	T of liq outlet	6.16%	-	-
	Urea production	3.56%	-	-
	Urea MF	1.52%	-	-
	H <sub>2</sub> O MF	3.04%	-	-
	Biuret content	3.18%	-	-
	Urea MF	4.17%	-	-
Rectfying column	H <sub>2</sub> O MF	4.83%	-	-
	Biuret content	3.82%	-	-
Urea tank	H <sub>2</sub> O MF	6.91%	-	-
	Biuret content	5.73%	-	-
Final product	H <sub>2</sub> O MF	4.34%	-	-
	Biuret content	4.89%	-	-
Reflux condensate tank	urea MF	2.58%	-	-
	CO <sub>2</sub> MF	4.31%	-	-
Ammonia water tank	NH <sub>3</sub> MF	4.55%	-	-
	Urea MF	3.49%	-	-
	H <sub>2</sub> 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

#### ACKNOWLEDGEMENTS

R.C. would like to acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Finance Code 001) for the research grant.

#### REFERENCES

- [1] M. Brouwer, "World Scale Urea Plants. Process Paper," *Urea Know How*, no. October, pp. 1–13, 2010.
- [2] M. Dente, S. Pierucci, and A. Sogaro, "Simulation program for urea plants," *Comput. Chem. Eng.*, vol. 12, no. 5, pp. 389–400, 1988.
- [3] M. Dente, M. Rovaglio, G. Bozzano, and A. Sogaro, "Gas-Liquid Reactor in the Synthesis of urea," *Chem. Enginrcrx Sci.*, vol. 47, no. 9–11, pp. 2475–2480, 1992.
- [4] M. a. Isla, H. a. Irazoqui, and C. M. Genoud, "Simulation of a urea synthesis reactor. 2. Reactor Model," *Ind. Eng. Chem. Res.*, vol. 32, no. 11, pp. 2662–2670, 1993.
- [5] M. A. Satyro, Y.-K. Li, R. K. Agarwal, and O. J. Santollani, "Modeling Urea Processes: A New Thermodynamic Model and Software Integration Paradigm," *Virtual Mater. Gr.*, 2002.
- [6] M. Hamidipour, N. Mostoufi, and R. Sotudeh-Gharebagh, "Modeling the synthesis section of an industrial urea plant," *Chem. Eng. J.*, vol. 106, no. 3, pp. 249–260, 2005.
- [7] X. Zhang, S. Zhang, P. Yao, and Y. Yuan, "Modeling and simulation of high-pressure urea synthesis loop," *Comput. Chem. Eng.*, vol. 29, no. 5, pp. 983–992, Apr. 2005.
- [8] S. A. Rasheed, "Revamping Urea Synthesis Reactor using Aspen Plus," *UreaKnowHow*, no. September, pp. 1–15, 2011.
- [9] S. Zendejboudi, G. Zahedi, A. Bahadori, A. Lohi, A. Elkamel, and I. Chatzis, "A dual approach for modelling and optimisation of industrial urea reactor: Smart technique and grey box model," *Can. J. Chem. Eng.*, vol. 92, no. 3, pp. 469–485, Mar. 2014.
- [10] R. C. Chinda, C. I. Yamamoto, D. F. B. Lima, and F. L. P. Pessoa, "Modeling and simulating the synthesis section of an industrial urea plant analyzing the biuret formation Modeling and simulating the synthesis section of an industrial urea plant-analyzing the biuret formation," *UreaKnowHow*, 2015.

- [11] A. Edrisi, Z. Mansoori, and B. Dabir, "Urea synthesis using chemical looping process - Techno-economic evaluation of a novel plant configuration for a green production," *Int. J. Greenh. Gas Control*, vol. 44, pp. 42–51, Jan. 2016.
- [12] J. Jeenchay and K. Siemanond, "Ammonia/Urea Production Process Simulation/Optimization with Techno-Economic Analysis," in *Computer Aided Chemical Engineering*, vol. 43, Elsevier B.V., 2018, pp. 385–390.
- [13] M. Brouwer, "Thermodynamics of the Urea Process," *UreaKnowHow*, 2009.
- [14] G. Soave, "Equilibrium constants from a modified Redlich-Kwong equation of state," Pergamon Press, 1972.
- [15] J. Schwartzentruber and H. Renon, "Extension of UNIFAC to high pressures and temperatures by the use of a cubic equation of state," *Ind. Eng. Chem. ...*, vol. 28, no. 1987, pp. 1049–1055, 1989.
- [16] A. Peneloux, E. Rauzy, and R. Freze, "A consistent correction for Redlich-Kwong-Soave volumes," *Fluid Phase Equilib.*, vol. 8, no. 1, pp. 7–23, 1982.

#### APPENDIX A

Table A - Equations used in validation step.

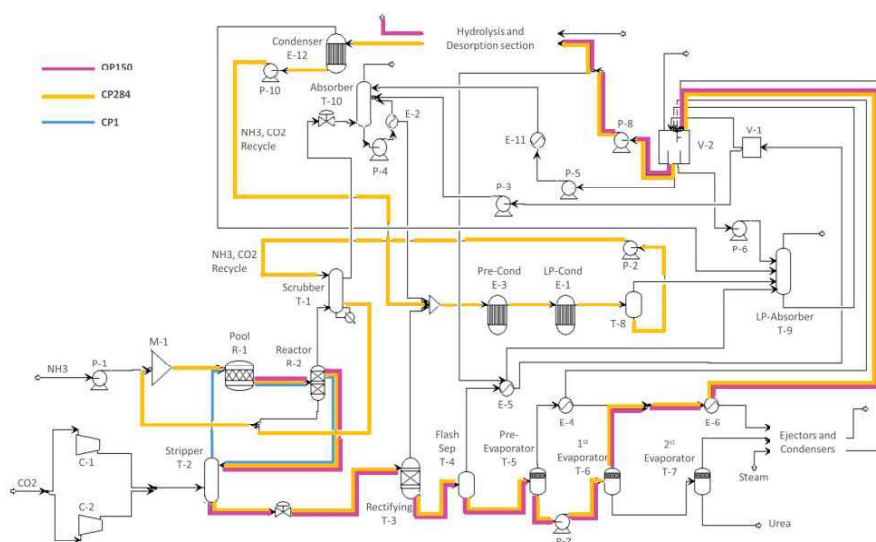
Simple Arithmetic Average	$\bar{x} = \sum_{i=1}^n x_i$
Sample Standard Deviation	$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$
Coefficient Of Variation	$Cv = \frac{s}{\bar{x}}$
Deviation between simulated and industrial data	$deviation(\%) = \frac{industrialdata - simulationdata}{industrialdata} \times 100$
CO <sub>2</sub> 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	$biuretcontent = \frac{biuretmass}{biuretmass + ureamass} \left[ \frac{kg}{kg} \right]$

**Table 1:** Base case more expressive economic and sustainability indicators.

Path	Compound	MVA (10 <sup>3</sup> \$ /year)	TA (10 <sup>3</sup> \$ /year)	EWC (10 <sup>3</sup> \$ /year)	AF (10 <sup>3</sup> \$ /year)	MJ energy/kg product	kg product/kg raw material	Total kg CO <sub>2</sub> Equivalent
OP150	H <sub>2</sub> O	-11	-177.204	166.427	-			
CP284	H <sub>2</sub> O	-	-	47.220	0.030	2.18	0.75	0.20
CP1	NH <sub>3</sub>	-	-	36.148	0.295			

Note: MVA – mass value added, TVA – total value added, EWC – energy to waste cost, CO<sub>2</sub> equivalent, carbon footprint, OP – open path, CP – closed path.

It can be seen in the Table 1, that water in the OP150 water is losing its value as it exits the process through this path. On the other hand, on the CP284 it is possible to see a high flow of water being recycled resulting in high loads of energy and waste/use of utilities for raw material recovery. The same also applies to ammonia in CP1 and water in the CP284. Fig. 3 shows a task-based flowsheet with the main closed- and open-paths.



**Figure 3:** Base-case design for Synthesis, Evaporation and Recirculation sections for the production of urea, including process bottlenecks, closed- and open- paths.

#### 4.2 Process hot-spots identification

The hot-spots identified based on the results of the economic, LCA and sustainability analysis are present in Table 2 and indicates the necessity of reducing the utility consumption. Utility is highly demanded in Evaporation and Recirculation sections. Thus, the Process Intensification was focused just in these sections.

**APPENDIX H**

UREA KNOW HOW – october 2019

# Industrial Urea Process Simulation and Validation

## Authors

Ms. Renata Chinda, Engenharia de Processos Químicos e Bioquímicos, Universidade Federal do Rio de Janeiro, Brazil.

Email: chinda@eq.ufrj.br

Mr. Carlos Yamamoto, LACAUT, Universidade Federal do Paraná, Brasil.

Email: ciy\_ama@ufpr.br

Mr. Daniel Lima, Araucária Nitrogenados S.A.

Email: falleiros@petrobras.com.br

Mr. Fernando Pessoa, SENAI CIM ATEC, 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 modelling 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.