

A Brief Overview of Ammonia and Urea Production and Their Simulations Strategies

Artur Santos Bispo^{1*}, Fernando Luiz Pellegrini Pessoa¹, Ana Lucia Barbosa de Souza¹

¹SENAI CIMATEC University Center; Salvador, Bahia, Brazil

To engender a simulation of the integrated Ammonia - Urea process, a literature review was carried out about these industrial processes, focusing on extracting information from the literature, such as the types of processes and their description, thermo-physical-chemical properties, and thermodynamic and kinetic models related to the process. Furthermore, research was carried out on thermodynamic models for $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ systems, capable of describing an integrated Ammonia-Urea plant.

Keywords: Ammonia. Urea. Simulation. Literature Review.

Introduction

The high relevance of studies involving ammonia and urea can be verified when discussing the market importance and the various applications of these two products.

Therefore, it is almost essential to develop simulation strategies for their production, serving as a basis for more in-depth studies of intensification and optimization, to enhance the production and commercialization of products and their derivatives.

Thus, for more specific studies to be carried out, it is necessary to have a general knowledge about the synthesis and applications of both ammonia and urea.

Ammonia

The production of ammonia, in general, and summarized, is carried out from the reaction between N_2 and H_2 (Equation 1) (Haber-Bosch reaction) [1].



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Address for correspondence: Artur Santos Bispo. Av. Orlando Gomes, 1845 - Piatã, Salvador - BA- Brazil. Zipcode: 41650-010. E-mail: artur.bispo@outlook.com.br.

The enthalpy of formation of this reaction ($\Delta_f H^0$), at a temperature of 298.15 K, corresponds to -45.898 kJ/mol (exothermic reaction) [2]. As for its applications, ammonia serves as raw material for different types of products. Among the areas of activity of ammonia, we have [3]:

- Fertilizer production – Ammonium sulfate, ammonium phosphate, ammonium nitrate, and urea (the focus of this study).
- Explosives – Nitric Acid
- Polymers – Nylon, fibers, and other types of plastics.

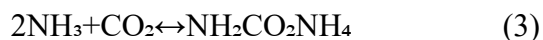
On an industrial scale, in short, ammonia is produced from water, air, and energy - generally, hydrocarbons, which, in turn, also provide hydrogen. In this scenario, the hydrocarbons are converted into methane (NH_4), which, subsequently, by hydrolysis, are converted into H_2 (which will be used in the synthesis, together with the N_2 feed), CO , and CO_2 (removed during the process) [1,2].

Urea

In general, urea is produced, on an industrial scale, through the reaction between ammonia (NH_3) and carbon dioxide (CO_2) which normally occurs under high pressure and temperature conditions (13 - 30 MPa and 170 - 300 °C), being represented by the following stoichiometric Equation 2 [4,5].



However, the generation of $\text{CO}(\text{NH}_2)_2$ does not occur directly, instead, the process is divided into two steps. At first, ammonium carbamate is formed at the expense of the direct reaction between NH_3 and CO_2 (Equation 3) [5].



Then, the process of dehydration of $\text{NH}_2\text{CO}_2\text{NH}_4$ can be observed, causing the formation of the product of interest (urea) and water (Equation 4) [5].



In addition to the previous reactions, another process that occurs in parallel and that is often not considered in the formation of biuret ($\text{NH}_2\text{CONHCONH}_2$) (Equation 5) [5].



As for urea's market applications, the compound is despicable in its performance as a fertilizer, being the most used nitrogen fertilizer in Brazil. All this highlight is mainly due to its high concentration of nitrogen (about 46% of its composition), which is an extremely important compound for the vitality and growth of plants [4].

Bearing in mind the importance of the market of both products, mainly for economic sectors that involve agribusiness (since ammonia is used to produce urea, which is a widely used fertilizer), this work aims to carry out a bibliographical review of the production processes of both and their simulation strategies and about thermodynamic models for $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ systems, capable of describing an integrated Ammonia-Urea plant.

Materials and Methods

We did a literature review on ammonia and urea production and simulation processing. Data were collected from open-source platforms like Google Scholar, SciELO, and CAPES, also portals/

websites such as UreaKnowHow and the Aspen Plus simulation files. The keywords used for the state-of-the-art search were: urea, ammonia, simulation, synthesis, Aspen Plus, industrial production, and thermodynamic models.

The research included data about the different technologies used to produce ammonia and urea and the differences between them, thermo-physical-chemical properties; product formation kinetics, and thermodynamic models appropriate for $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ systems.

Results and Discussion

This section will approach the review results. Initially, the research focused on obtaining data and information about ammonia production. For this, the main references used were Pattabathula (2016), Sunny (2016), Christensen (2001), Garcês (2021), and the files and reports of the Aspen Plus software.

Ammonia

Process Description

As mentioned in the previous sections, ammonia is produced from the Haber-Bosch reaction (Equation 1), which consists of reacting H_2 and N_2 to form NH_3 . However, on an industrial scale, some steps precede and follow this synthesis [1].

To understand these steps, it is necessary to define the type of technology used to produce ammonia. Among the various types of technologies found in the literature, - such as BASF (1910), Kellogg (1960), KBR (Kellogg modified by Braun) - the research focus was given to the Haldor Topsoe's plant (as it is the plant used as a base by Aspen Plus to simulate the ammonia production process) [6].

The process itself can be separated into 8 steps, namely: Natural gas desulfurization, Reforming, CO Conversion, CO_2 Removal, Methanation, Synthesis, Tailgas Scrubbing, and Refrigeration [2].

Natural Gas Desulfurization

The natural gas fed to the plant is supplied dry and contains a maximum of 40 ppm - by weight - of sulfur (a poison for the catalyst in the subsequent step) [2,7].

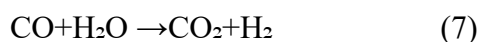
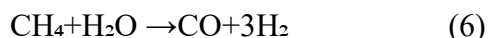
Thus, this step has the function - as the name suggests - to reduce the concentration of sulfur. This reduction is separated into two parts called PDS (Pre-Desulfurization) and FDS (Final Desulfurization). At first, the organic compounds containing sulfur are removed through a catalytic conversion process into H₂S, and then catalytic hydrogenation is carried out to remove the residual sulfur [2,7].

Reforming

This stage of the process, like the previous one, is also divided into two parts: primary and secondary reform [1,2].

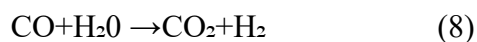
Here, the hydrocarbons in the feed - now sulfur-free - are converted into hydrogen and carbon oxides (CO and CO₂), so at the end of the process, the reformed gas contains about 0.3% - by volume - of CH₄ [2].

The two main reactions that occur at this stage are as follows (Equations 6 and 7):



CO Conversion / CO₂ Removal

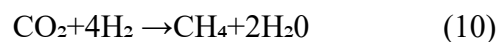
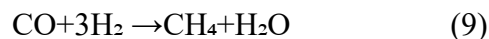
In these two steps, the objective is to remove all carbon oxides from the mixture to generate Syngas. At first, most of the CO present in the reformed gas is converted into CO₂ in two catalytic stages, the first is high and the second at low temperature, considering the following stoichiometry (Equation 8) [2,7]:



Then, almost all the CO₂ contained in the mixture is removed through absorption in a solution with a concentration of 0.31% methyl-diethanolamine (MDEA). At the end of this process, syngas is obtained - with about 0.1% vol. of CO₂ in the mixture [2].

Methanation

Even in small amounts, carbon oxides are poisonous to the catalyst of the ammonia synthesis step. Thus, these are converted to CH₄ with the aid of a nickel catalyst (Equations 9 and 10). In the end, the remaining carbon oxides do not exceed 10 ppm [2].



Synthesis

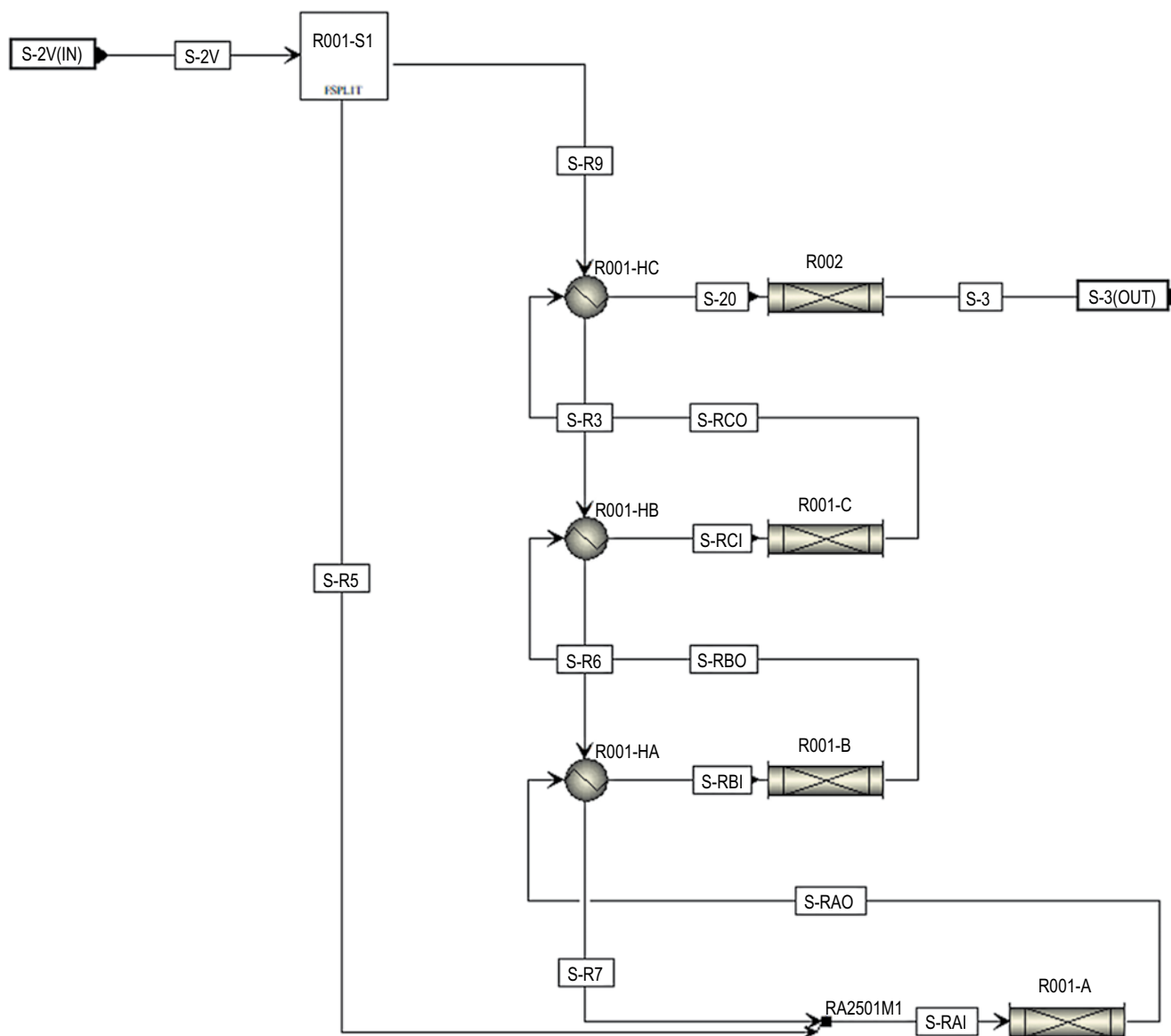
The syngas, in this step, goes through a centrifugal compressor that raises its pressure to approximately 300 bar and the hydrogen and nitrogen react and are catalytically converted into ammonia by the Haber-Bosch Equation (Equation 1) [2].

In the plant simulated in the aspen plus files, this step uses Haldor Topsoe's S-200 ammonia conversion strategy (Figure 1), which consists of a two-bed radial flow converter with indirect heat exchange between the two beds. In this way, efficient use of the converter volume, low-pressure drops, and high conversion occur - due to indirect cooling [2].

Tailgas Scrubbing/Refrigeration

In tailgas scrubbing, the ammonia present in the purge gas is recovered and fed into the refrigeration unit and the rest of the gas is used as fuel in the reform stage - more specifically in the primary reformer [2].

Finally, the ammonia fed into the refrigeration unit is liquefied and directed to its intended

Figure 1. Ammonia synthesis step – Aspen Plus (hereda 2021).

purpose, whether it is feeding the urea plant or for storage. Figure 2 shows an ammonia synthesis plant, which uses the Haldor Topsoe technology, by Profertil [2,7].

Urea

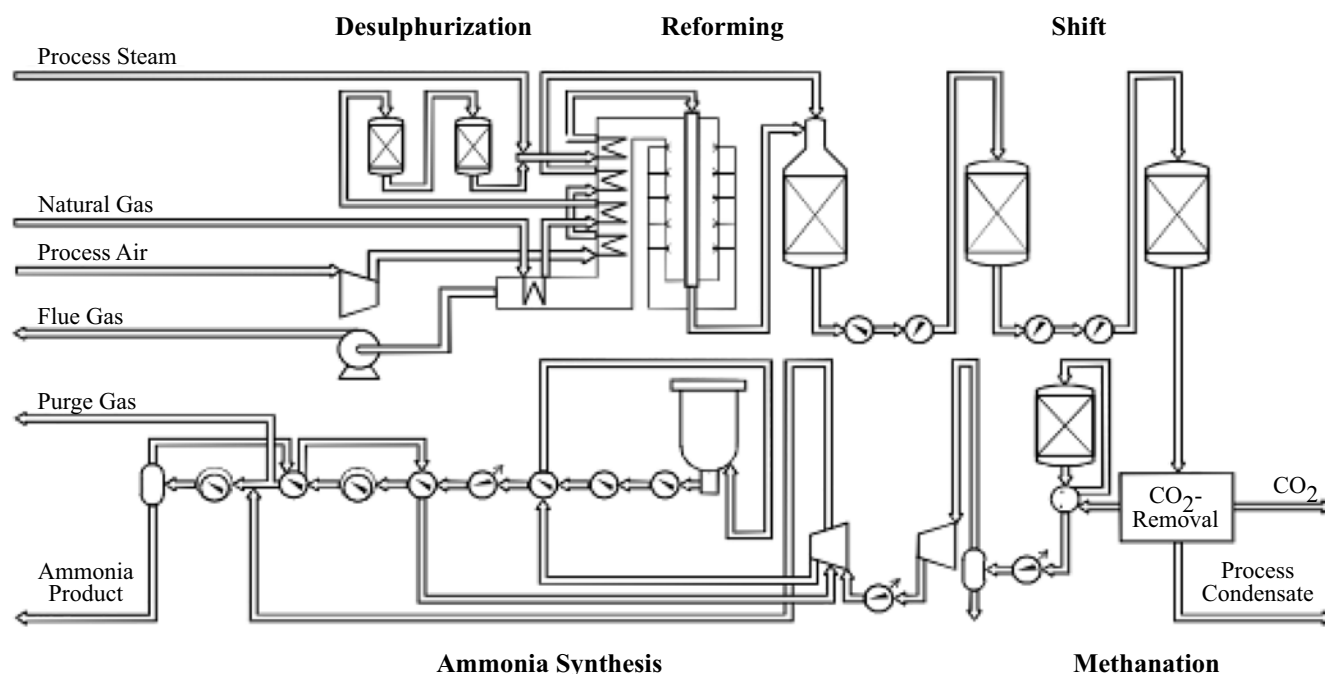
Process Description

Knowing the production of ammonia, the research was able to progress and deepen the urea production process. For this, the main

bibliographical references were used for Chinda (2015) and Bispo (2021).

As previously done, first the main urea synthesis technologies were searched and, according to the research, the two most used are those of the companies Stamicarbon and Toyo Engineering - other technologies were also found, such as that of the Snamprogetti company, however, will not be considered in this review [4].

The difference between these two technologies can be seen in the ammonia feed. In the Stamicarbon process, NH_3 is fed into the Carbamate Condenser/

Figure 2. Haldor Topsoe ammonia plant example - Profertil [2,7].

Pool Condenser, while in the ACES21 (Toyo) process, the feed occurs directly into the reactor. This distinction between plants may reverberate in the formation of biuret, since the direct insertion of ammonia into the reactor will increase its concentration in the equipment, disfavoring the reaction to form $\text{NH}_2\text{CONHCONH}_2$. The research focus was given to the Stamicarbon plant (as it is the plant used as a base by Aspen Plus to simulate the urea production process) (Figure 3) [4,8].

Figure 3 presents the synthesis section works using CO₂ stripping technology and is composed of four steps/equipment: Stripper, Pool Condenser/Carbamate Condenser, Reactor, and Scrubber [4,9,10].

Stripper

In the stripper, the decomposition of ammonium carbamate into NH_3 and CO_2 occurs due to the countercurrent contact between the pure CO₂ feed stream and the stream containing the reactor bottom product (composed of ammonium carbamate, urea, water, and biuret). Thus, a gaseous output stream is generated at the

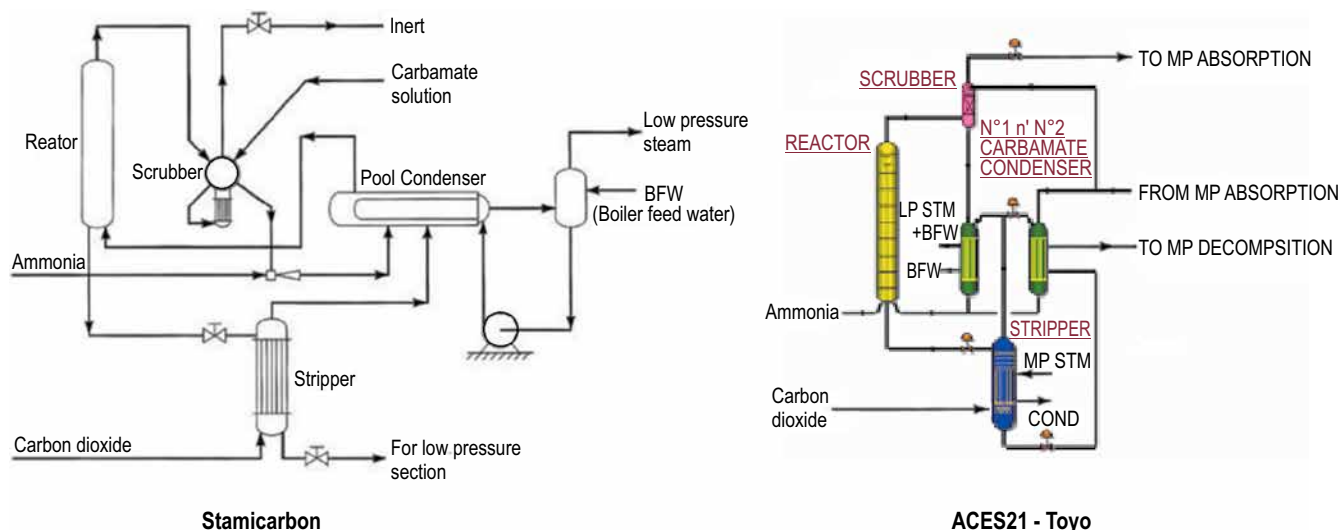
top of the equipment, containing ammonia and carbon dioxide, directed to the Pool Condenser, and an underflow containing urea, water, and biuret [4].

Pool Condenser

Feeding NH_3 , CO_2 , and ammonium carbamate, the Pool Condenser is responsible both for forming the liquid $\text{NH}_2\text{CO}_2\text{NH}_4$ that will dehydrate in the Reactor, forming urea and for synthesizing part of the urea resulting from the process. Then, two outputs are generated and directed to the Reactor, one in the liquid state (urea, ammonium carbamate, and water) and the other in the gaseous state (remaining NH_3 and CO_2) [4].

Reactor

Being fed with urea, carbamate, water, ammonia, and carbon dioxide, the reactor is responsible for providing the three main reactions of the process (Equations 3, 4, and 5). Thus, the equipment has two outlets, the bottom one – composed of ammonium carbamate, urea, H_2O ,

Figure 3. Urea synthesis – Stamicarbon x ACES21 (Toyo) [4].

and biuret – and the top one – with unreacted NH_3 and CO_2 [4].

Scrubber

Finally, the scrubber has the function of condensing the gaseous output of the Reactor and forming $\text{NH}_2\text{CO}_2\text{NH}_4$, to send it back to the process to be dehydrated and form the product of interest in the process, urea [4].

Comparison of Thermodynamics Models

After reviewing the functioning of ammonia and urea production plants, the research focused on finding thermodynamic models that better define the studied systems. For this, the main references used were Gudjonsdottir (2016), Chinda (2019), and the files and reports of the Aspen Plus software.

According to Chinda (2019), for example, for the urea synthesis unit explained in this study, the most appropriate thermodynamic model to represent the system, as it can predict non-ideal systems with high efficiency and accuracy, is the SR-POLAR model, used by authors such as Rasheed (2011) and Chinda herself [10].

As for the ammonia process, the aspen plus reports shows that the most appropriate

thermodynamic model to define the system is the RKS - BM. In addition, he also reports the use of the NRTL electrolyte method, together with the RKS - BM, to perform the calculations of the liquid and vapor properties in the CO_2 removal unit.

Another interesting approach is that of the author Gudjonsdottir, who performed a comparison between different models to assess their performance in an $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system. Some of the models analyzed were: E-NRTL, E-NRTL2, E-NRTL modified by Que and Chen (2011), extended UNIQUAC, among others [11]. Among the author's conclusions we have: The E-NRTL model modified by Que and Chen (2011) is accurate for CO_2 partial pressures at low temperatures ($10\text{-}40^\circ\text{C}$) and also presents better results for NH_3 partial pressure when compared to E-NRTL2; Its computational time is also better when compared to extended UNIQUAC, for example; The modified model of Que and Chen (2011) has an action limit, referring to the concentration - by weight - of NH_3 of 30% [11].

Conclusion

We concluded that it was possible to gather important data about the functioning of each stage

of the ammonia and urea production processes, the types of available technologies, simulation strategies, as well as important information about thermodynamic models used in both processes and for $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ systems in general.

The collected data can be used to start simulation attempts of an integrated Ammonia-urea plant, to facilitate future improvement procedures, intensifications, and optimizations.

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