CHAPTER 6

ANALYSIS OF OPERATIONAL PERFORMANCE OF CHEMICAL PRODUCTION FROM BIOGAS

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ABSTRACT: Biogas has great potential to build a sustainable chemical platform within the Brazilian economic context. It is estimated that the country has a total number of 755 operational biogas plants and 102 under construction. On the other hand, natural gas is still the main input for the synthesis of ammonia and methanol. Ammonia is being produced using the well-known Haber-Bosch process. Furthermore, 80% of its production is sent directly to the manufacture of nitrogen fertilizers, especially urea. The raw materials used in its process are ammonia and CO_2, these two compounds being the main products of the Haber-Bosch process. Biogas has its majority composition based on CH_4 and CO_2, which makes this product a great asset to replace natural gas as a raw material in some chemical industry supply chains and the possibility of converting CO_2 in higher added value products. Given this scenario, the present work presents the simulation and validation of two technical cases: (1) an integrated ammonia and urea plant and (2) a methanol plant. Both processes assumed biogas as the main raw material. The ammonia plant makes it possible to supply the total demand for urea synthesis, which reaches a production capacity close to 868 ton/day, indicating a plant in large industrial operating conditions. Moreover, the methanol plant has the potential to produce 500 ton/day. These results indicate the technical feasibility of the studied biorefinery concepts and offer a promising avenue for converting CO_2 into high-demand chemicals.

KEYWORDS: ammonia, fertilizer, methanol, modeling, process integration, simulation.

1. INTRODUCTION

The awareness of environmental issues and the finite aspect of non-renewable resources are becoming increasingly prominent on the global economic context. Thus, a coordinated worldwide movement's been started to promote the increased use of renewable energies and the replacement of petrochemical sources. Within this context, Brazil is a strong candidate to become one of the main actors in energy transition within the chemical industry. Based on the positive scenario for sustainability within the Brazilian economy, biogas is a promising alternative for building a chemical hub, either through its use as an energy source or as a raw material for verticalizing production chains (ABiogás, 2020). According to the definition used by the Brazilian National Petroleum, Gas and Biofuels Agency (ANP), biogas is generated from the biological digestion of organic matter and has characteristics like those of natural gas. Therefore, it is worth to highlight the possibility of implementing biogas as a potential replacement for natural gas in a wide range of applications (Poblete, 2019).

As stated in reports released by the International Center for Renewable Energies (CIBiogás), Brazil has seen a significant growth in the number of biogas plants over the last five years. The 2020 data showed the existence of 675 facilities, 148 of those being new plants, representing a 22% increase from the year of 2019. The new report released in 2021 indicates a total of 755 plants in operation and another 102 under construction (CIBiogás, 2022). Figure 1 shows the total growth in the number of plants in Brazil between 2017 and 2021.

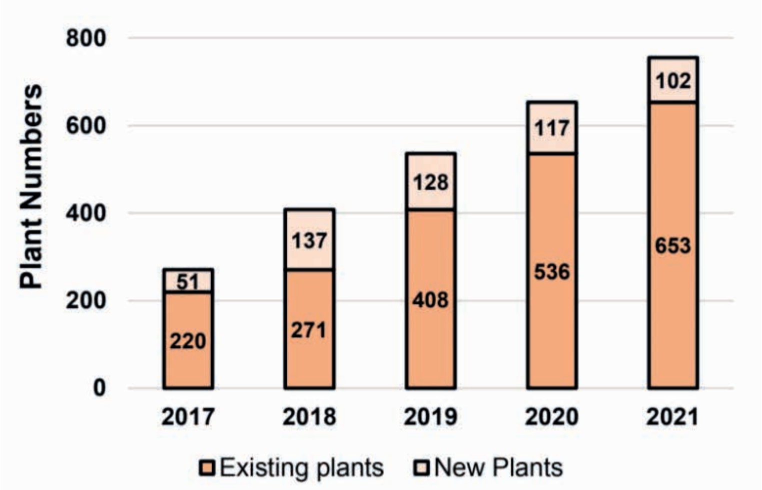

Figure 1 - Biogas plants growth in Brazil between 2017 and 2021 (adapted from CIBiogás, 2021).

Since biogas has a high concentration of methane and CO_2 in its composition, direct emission into the atmosphere without prior control can cause major damage to the environment. The main gases that biogas is composed of are part of the group responsible for intensifying the greenhouse effect, in addition to the high potential for fire and explosion accidents, mainly because methane is a highly flammable gas (Ensinas *et al.*, 2003).

Although the use of biogas as a fuel contributes to the reduction of methane emissions, given that methane has 21 times more potential to cause the greenhouse effect than CO_2, other ways of utilizing biogas must be sought so that direct CO_2 emissions can also be reduced, especially with a greater increase in the restrictions imposed by environmental legislation worldwide.

The beginning of the 20th century saw the phenomenon of exponential population growth, fostered by technological advances and improvements in productivity. In this context, the Haber-Bosch process is widely recognized as one of the main discoveries in the chemical engineering field, responsible for the synthesis of ammonia through the reaction of nitrogen and hydrogen gases. The process is carried out at high temperature and pressure and is the basis of industrial projects that are still being implemented today. In the ammonia production, natural gas is the main feedstock for syngas production. Hence, biogas is a strong candidate to replace the fossil fuel chemical in favor of a more sustainable alternative. It is important to note that, globally, most of the ammonia produced is used to manufacture nitrogen fertilizers, especially urea (Carvalho, 2016; Paixão, 2018).

Considering the national economic profile, the agricultural sector's share of Brazil's gross domestic product (GDP) has been increasing in recent years. Thus, national demand for fertilizers is becoming increasingly important to supply production capacity and promote continuous growth. Ammonia is considered the main raw material to synthesize nitrogen fertilizers, while urea is the one most widely sold in the world. It is important to highlight that CO_2 produced as a byproduct can be directed feed into urea synthesis with pre-treatment steps. However, data released by the National Association for the Diffusion of Fertilizers (ANDA) indicates a contradictory scenario regarding national fertilizer production and the amount imported, as showed by Figure 2.

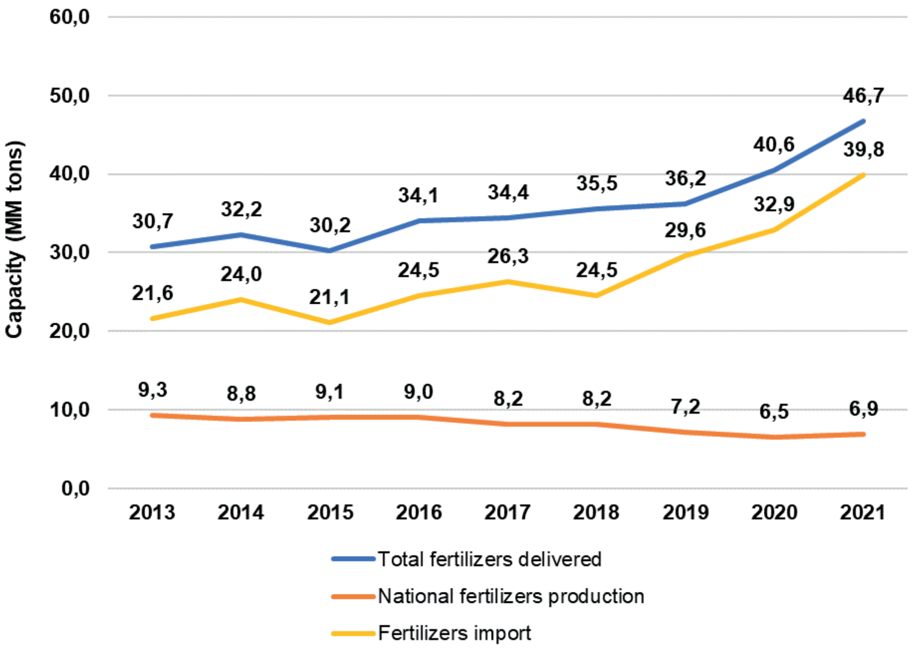

Figure 2 – Sector macro indicators of the fertilizer industry in Brazil according to ANDA.

According to the data presented, there has been an increase in the number of imported products, followed by a decrease in production capacity to continuously supply the agricultural sector. As a result, there is a clear trend towards a gap between domestic production and the total volume imported, which could worsen in the face of the expected growth in the agricultural sector over the next few years. If this conjuncture is maintained, Brazil could experience a vulnerable situation in terms of feedstocks availability and high external dependence.

Considering this scenario, ammonia and urea play a key role in the continuous supply of the fertilizer industry. However, the traditional fertilizer process is energy-intensive and depends on the extraction of finite resources. Considering the availability of raw materials for biogas production, agricultural business can play an important role in reducing the environmental impacts associated with fertilizer production while contributing to maintaining the sector's competitiveness in the long term.

The methanol economy concept described by Olah *et al.* (2009) presents methanol as an alternative for replacing fossil fuels as energy storage, fuel transportation, and chemical raw materials. The use of methanol can result in a strengthened and more secure energy capacity, reducing CO_2 emissions and air pollution and also adding value to the national domestic economy.

Methanol is an important primary chemical, working as precursor to a wide range of products used in various industrial sectors, such as petrochemicals, automobiles, plastics, paints, pharmaceuticals and others, and it can also be used as a fuel and as an organic solvent. Global demand for methanol has grown in recent years, reaching 106 million tons in 2022 (Methanol Institute, 2023). Methanol is also produced from synthesis gas, where natural gas is the main feedstock. Thus, biogas is a promising alternative for renewable synthesis rote of methanol production.

In addition to the environmental benefits, the use of alternative energy sources can have a positive impact on the economy. Brazil offers government funding lines and tax incentives for renewable energy projects, which can drive biogas production as a significant raw material within a fundamental value chain for the Brazilian economy. Given that natural gas is a finite and non-renewable resource, the aim of this work is to present, validate and analyze the operational performance of biorefinery plants using biogas as feedstock to produce ammonia, urea and methanol, identifying the main challenges regarding the implementation of this strategy, taking into account Brazilian economic aspects.

2. PROCESS DESCRIPTION & METHODOLOGY

This work studies alternative production routes using biogas as the main feedstock applied to three possible products: ammonia, urea, and methanol. An integrated use of these routes, as a biorefinery, is illustrated in Figure 3.

The three different routes have, as a common step, the reforming of the biogas to produce synthesis gas (syngas). The syngas must be treated and adjusted according to the desired product. As biogas can have different compositions depending on its source, it was assumed a composition of 60% CH_4 and 40% CO_2 for this work. These values were chosen because they belong to an average composition range for most sources. In the following topics, the steps of each process will be described individually.

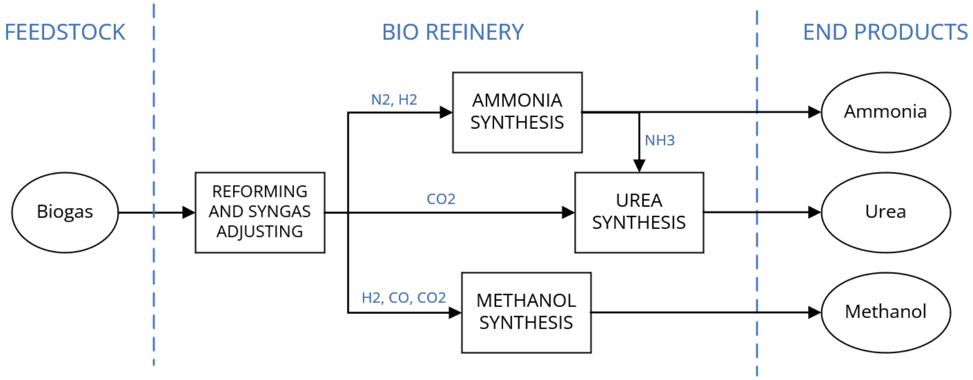

Figure 3 – Block diagram of possible production rotes.

2.1. BIOGAS PURIFICATION

The anaerobic digestion of biomass, which generates biogas, produces substances such as sulfur and nitrogen gases at very low levels. These gases can impair the operational performance of plants, such as catalyst poisoning, if they are not preliminarily removed. Conventionally, desulphurization units such as iron oxide adsorption columns are used, and the removal of halogenated compounds and siloxanes is carried out in activated carbon-based filtration units (Muñoz *et al.*, 2015).

2.2. BIOGAS REFORMING

In the reforming stage, the reactant gases are converted into the product called syngas, a mixture composed primarily of H_2 and CO. This reforming process is carried out together with a reforming agent, which can be steam, CO_2, oxygen or a mixture of these agents (Medrano-García *et al.*, 2017). Considering methane as a carbon source, there are three main types of reforming: partial oxidation (1), steam reforming (2), dry reforming (3), whose reactions are described as follow, respectively:

$$CH_4 + \frac{1}{2}O_2 \leftrightharpoons CO + 2H_2 \tag{1}$$

$$CH_4 + H_2O \leftrightharpoons CO + 3H_2 \tag{2}$$

$$CH_4 + CO_2 \leftrightharpoons 2\,CO + 2H_2 \tag{3}$$

Furthermore, due to the presence of carbon oxides and water, attention must be paid to the presence of the water-gas shift reaction, described by Eq. (4):

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \tag{4}$$

Reforming processes are costly due to the high temperatures required for the chemical reactions to occur. There is also high fuel consumption, which considerably increases emissions during plant operation (Medrano-García *et al.*, 2017). The combination of endothermic reforms with exothermic reforms, such as auto thermal reforming, has gained prominence because the energy provided by the combustion of part of the methane with oxygen fed reduces the heat required by the reformer and, consequently, the fuel needed (De Rosa *et al.*, 2018).

For some processes, such as ammonia synthesis, it is necessary to use an equipment configuration containing two different reformers. Conventionally, the primary reformer, based on steam reforming, is a furnace-type equipment in which the reaction takes place in pipes filled with catalysts at high temperatures and pressures, while the secondary reformer is based on autothermal reforming, in which oxygen is added to the reactant stream and the oxidation reaction itself is responsible for supplying energy to the system.

2.3. SYNGAS UPGRADING

For most reforming scenarios, a post-treatment section is required to refine and adjust the H_2/CO ratio in the syngas according to the desired product. This upgrading stage consists of intermediate units such as pressure swing adsorption (PSA) columns, water-gas shift (WGS) reactors, or separation membranes (Entesari *et al*., 2020).

Water-gas shift (WGS) reactors works with the reaction previously described by Eq. (4), as a basis for adjusting the stoichiometric number. The reaction has little dependence on pressure, is reversible and exothermic. Due to the thermodynamic aspect, higher temperatures favor lower H_2/CO ratios (Bertau *et al*., 2014).

The WGS unit can consist of a high temperature shift (HTS) and lower temperature shift (LTS). In the HTS reactor, the operating temperature is between 350-500°C. Although WGS reaction is favored at lower temperatures, the catalyst used, composed of iron oxide promoted by chromium oxide, has low activity at lower temperature levels. This disadvantage is offset by the low cost of the catalyst and its high resistance to sintering (Bartholomew *et al*., 2005). LTS reactors operate in the 200-230 °C range and use catalysts based on zinc and copper oxides supported on alumina. These catalysts are highly selective for the shift reaction, while maintaining a low activity for the methanation reaction (Bartholomew *et al*., 2005).

In addition to the shift units, another step may be required to carry out syngas upgrading. Normally, systems are used to extract one of the components, H_2 or CO_2, using separation equipment, allowing the adjustment of the stoichiometric number. As biogas has high CO_2 content in its composition, the syngas produced during reforming tends to have an excess of this gas. Therefore, systems that remove CO_2 from the syngas should be used.

Currently, different technologies for capturing CO_2 are utilized in industrial plants, developed based on the separation using the physical-chemical properties of the components. The main technologies are absorption by organic solvents and PSA-type systems. In addition to these technologies, there is a growing development of membrane separation processes with high CO_2 selectivity (Muñoz *et al*., 2015).

For processes such as ammonia synthesis, a methanation stage is employed. The objective of this stage is to adjust the feed stream of the ammonia synthesis loop, avoiding the presence of contaminants and the loss of catalytic activity due to the presence of residual CO and CO_2 levels.

2.4. AMMONIA SYNTHESIS

The ammonia synthesis process is structured in two main sections as described in Figure 4. Before entering the synthesis loop, the syngas is compressed in a four-stage cycle to achieve 400 °C and 200 bar. The ammonia synthesis process takes place according to Eq. (5). This reaction is characterized by being highly exothermic and using iron catalysts. Figure 5 illustrates the simplified scheme for the Haber-Bosch circuit.

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g) \qquad (5)$$

Ammonia production process occurs through the Haber-Bosch synthesis according to Eq. (5). The fresh stream condition is specified at the end of 4-stage compression cycle. The main objective of all the previous stages is to keep the H_2/N_2 stoichiometric molar ratio close to 3 before the feed stream enters the first reactor. The operation of the synthesis loop is characterized by a high degree of complexity due to the challenges regarding kinetics of the reaction and the intrinsic thermodynamic equilibrium. As the reaction progresses, temperature raises, reaching close to the chemical equilibrium, which decreases the net reaction rate. To deal with this obstacle, the reactor needs to be cooled down between reactors beds when the temperature is too high. For this reason, industrial plants generally use a reactor with multiple beds and intermediate heat exchangers.

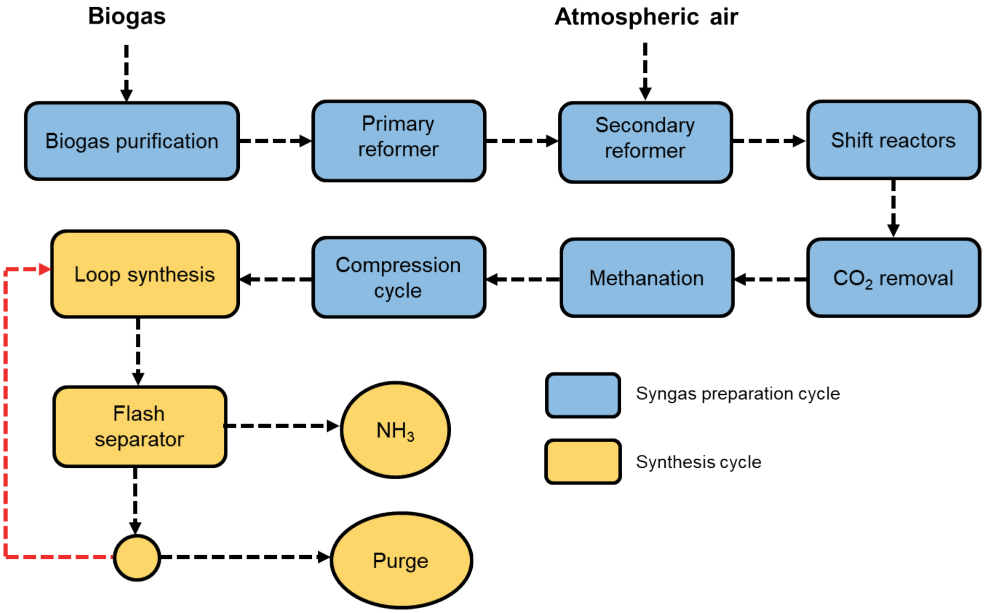

Figure 4 – Ammonia synthesis simplified process flowsheet.

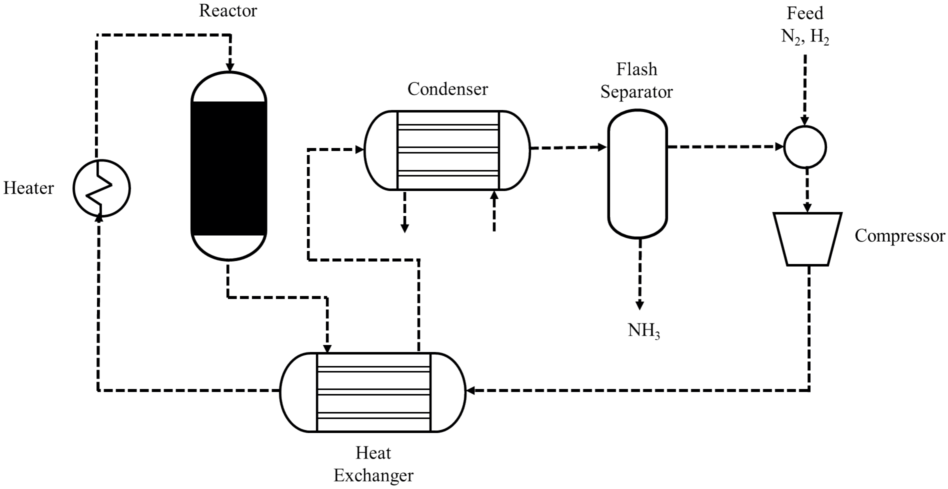

Figure 5 – Simplified schematic of the Haber-Bosch circuit (adapted from Reese et al., 2016).

The equipment was simulated as a plug flow reactor (PFR), with three catalytic beds and two intermediate heat exchangers. The unconverted reactants are recirculated into the synthesis loop and there is a purge stream to prevent an increase in the concentration of inert gases (Carvalho, 2016; Paixão, 2018). The pseudo-homogeneous kinetic model utilized in this work was proposed by Dyson and Simon (1968) by modifying and extending the expression initially developed by Temkin and Pyzhev (1939), with the driving force defined by the chemical activity of the components involved in the mixture. The equilibrium constant K_a was calculated according to the expression of Gillespie and Beatie (1930):

$$r_{NH_3} = 2\,k_{rev}\left[K_a^2\,\alpha_{N_2}\left(\frac{\alpha_{H_2}^3}{\alpha_{NH_3}^2}\right)^{\alpha} - \left(\frac{\alpha_{NH_3}^2}{\alpha_{H_2}^3}\right)^{1-\alpha}\right] \tag{6}$$

$$k_{rev} = 4.916 \times 10^{11}\, e^{\frac{-170298}{(R\,T)}} \tag{7}$$

$$\begin{aligned} log_{10}K_a &= -2.6911\ log_{10}(T) - 5.5193 \times 10^{-5}\,T + 1.8489 \times 10^{-7}T^2 \\ &\quad + \frac{2001.6}{T} + 2.6899 \end{aligned} \tag{8}$$

in which r_{NH3} corresponds to the kinetic reaction rate, in kmolNH_3 m^{-3} s^{-1} expressed by Eq. (6), k_{rev} is the reverse rate constant (kmol m^{-3} s^{-1}) expressed by Eq. (7), K_a is the equilibrium constant from Eq. (8), α_i corresponds to the chemical activity of each component in the gaseous mixture (dimensionless), T is the temperature, in K, R is the universal gas constant (8.31446 J K^{-1} mol^{-1}) and α corresponds to a parameter from the kinetic model, with value equals to 0.5.

2.5. UREA SYNTHESIS – STAMICARBON PROCESS

The Stamicarbon (STAC) process is divided in five main sections: synthesis, evaporation, desorption and hydrolysis, recirculation, and pearling/granulation. The synthesis section is the most important, as it is at this stage that ammonium carbamate is formed, followed by urea. The other stages of the process are aimed at recirculating unconverted reagents and purifying the desired product. The synthesis section consists of four pieces of equipment: carbamate condenser (pool condenser), reactor, scrubber, and stripper column. The process with a carbamate condenser is relatively recent, with its commercialization and implementation in industrial projects dating back to 1994 by Stamicarbon (Chinda, 2015).

The thermodynamic model used was the Soave-Redlich-Kwong (SRK) equation of state with the Schwartzenruber and Renon (SR-Polar) mixing rule, according to Rasheed (2011) and Chinda (2015). The SR-Polar model can be applied to non-polar and highly polar components, and non-ideal mixtures. In addition, it is recommended for systems that operate at high temperatures and pressures, such as the urea synthesis process, methanol and supercritical extraction (Koohestanian *et al.*, 2018; Zahid *et al.*, 2014).

The urea synthesis section was simulated using Stamicarbon's CO_2 stripping process, based on the following assumptions:

- The plant model was developed in steady state;
- Only two reactions were considered: carbamate and urea formation. The formation of biuret and possible parallel reactions were not considered for this work;
- Existing presence of inert gases such as N_2, O_2 and H_2, which were received directly from the NH_3 stream produced in the ammonia plant;
- In liquid streams, free CO_2 was present to a minimal extent in the form of the intermediate ammonium carbamate;
- Urea synthesis only took place in the liquid phase;
- The carbamate condenser was a direct part of urea synthesis, being responsible for both carbamate and urea formation;
- The initial project used in Aspen Plus was the Aspen Tech model plant (2008b), which underwent the necessary adaptations to improve the process equipment simulation strategy.

The urea synthesis reaction takes place in two main stages, the first being the formation of the intermediate ammonium carbamate (NH_2COONH_4) from the reaction given by Eq. (9) between ammonia and carbon dioxide. The second reaction, given by Eq. (10), promotes the dehydration of ammonium carbamate into urea and water.

$$2NH_{3\,(g)} + CO_{2\,(g)} \leftrightharpoons NH_2COONH_{4\,(l)} \tag{9}$$

$$NH_2COONH_{4\,(l)} \leftrightharpoons CO(NH_2)_{2\,(l)} + H_2O_{\,(l)} \tag{10}$$

The kinetic models for the carbamate and urea syntheses were described in the work of Rasheed (2011), Eq. (11) and (12):

Carbamate synthesis
$$r_1 = 1628 \, \exp\left(\frac{-62802}{R\,T}\right) C_{NH_3}^{1.4} C_{CO_2}^{-0.4} \tag{11}$$

Urea synthesis
$$r_1 = 12000 \, \exp\left(\frac{-62802}{R\,T}\right) C_{CARB}^{0.92} \tag{12}$$

in which r_1 corresponds to the carbamate synthesis reaction rate (kmol m^{-3} s^{-1}), C_{NH3} is the ammonia concentration (kmol m^{-3}), C_{CO2} is the carbon dioxide concentration (kmol m^{-3}), r_2 is the urea synthesis reaction rate (kmol m^{-3} s^{-1}), C_{CARB} is the ammonium carbamate concentration (kmol m^{-3}), T is the temperature (K) and R is the universal gas constant (8.31446 J mol^{-1} K^{-1}).

The urea synthesis flowsheet is detailed in Figure 6 to represent the equipment and streams of an industrial process. The diagram has continuous and dashed lines to indicate the liquid and gaseous streams, respectively. The goal is to highlight the two-phase operation that takes place during urea synthesis.

The CO_2 stream (coming directly from the ammonia synthesis process) is introduced into the stripper in an upward direction and counter-current configuration to the liquid stream leaving at reactor top outlet (4). The heat supplied from the high-pressure steam and the counterflow of the CO_2 stream cause the decomposition of the residual carbamate into NH_3 and CO_2 from the reverse reaction indicated by Eq. (9). The top stream (2), containing the unconverted reactants and steam, is sent directly to the carbamate condenser. The bottom liquid stream, containing a solution rich in urea, water and undecomposed carbamate, is directed to the product concentration section.

The carbamate condenser receives the top stream from the stripper (2) and the stream from the ejector (1). This equipment is responsible for the partial formation of total urea produced in the synthesis section before it enters the main reactor. The ejector stream corresponds to the combination of the fresh NH_3 stream received directly from the ammonia synthesis plant and the bottom stream from the scrubber (8), a solution rich in carbamate and water. The product stream (3) is sent to the first CSTR in the series. The condenser pool was simulated as a stoichiometric reactor, where the conversion of ammonium carbamate and urea is specified based on the performance of the main reactor, considering the urea mass fraction in the liquid stream leaving the main reactor.

The aim of the series of CSTRs is to mimic the internal plates of the main urea reactor, which is responsible for most of the urea produced in the synthesis section. At the outlet of the last CSTR, there is a separator to split the liquid and gas streams. The stream (4), consisting of urea, water, carbamate and a small quantity of unreacted gases, is sent directly to the stripper. The gaseous stream (5), made up of unreacted and inert gases, is directed to the scrubber. The main urea reactor was modeled as a sequence of 10 CSTRs with the same volume of 20 m^3 (Chinda, 2015; Rasheed, 2011).

The scrubber is fed by two streams: the gaseous stream (5) coming from the reactor top outlet and a liquid stream (7) containing the recirculated carbamate solution that returns from urea product concentration. The equipment's shell supplies medium-pressure condensate to remove the heat released by carbamate synthesis. There are two output streams from this equipment: stream (6) is mainly made up of inerts fed into the system and unconverted reagents, while stream (8) is rich in carbamate and sent to mix with the fresh NH_3 stream.

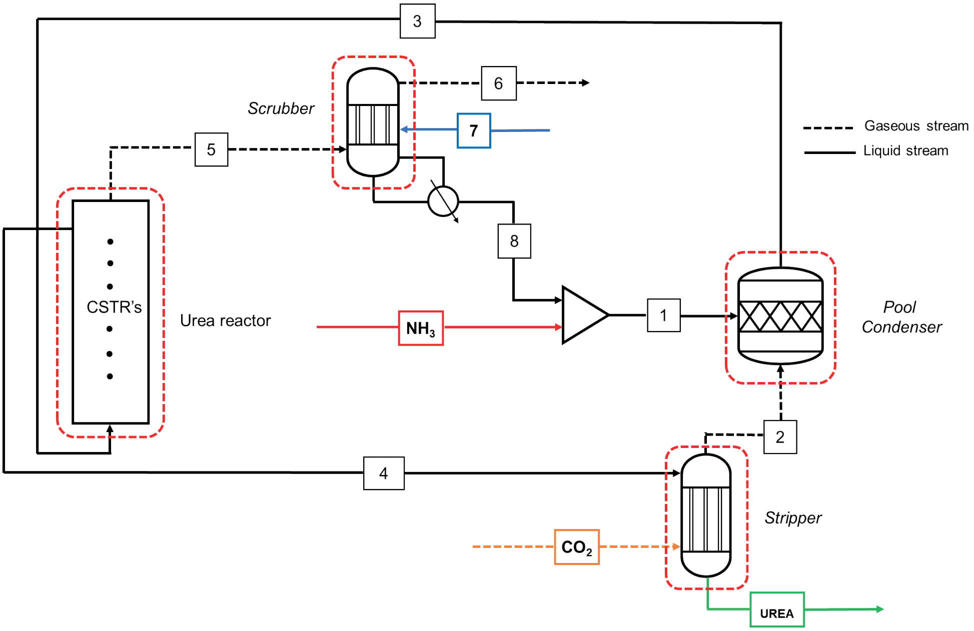

Figure 6 – Urea synthesis process simulation flowsheet (adapted from Chinda, 2015).

2.6. METHANOL SYNTHESIS

The process of converting syngas to methanol, commonly referred to as the methanol synthesis loop, is illustrated in Figure 7. Methanol is produced by processes operating in pressure ranges of 50-100 atm and temperatures between 200-300 °C (Bozzano *et al.*, 2016). To achieve these pressure conditions, the synthesis gas leaving the upgrading unit needs to pass through a battery of compressors before entering the synthesis loop.

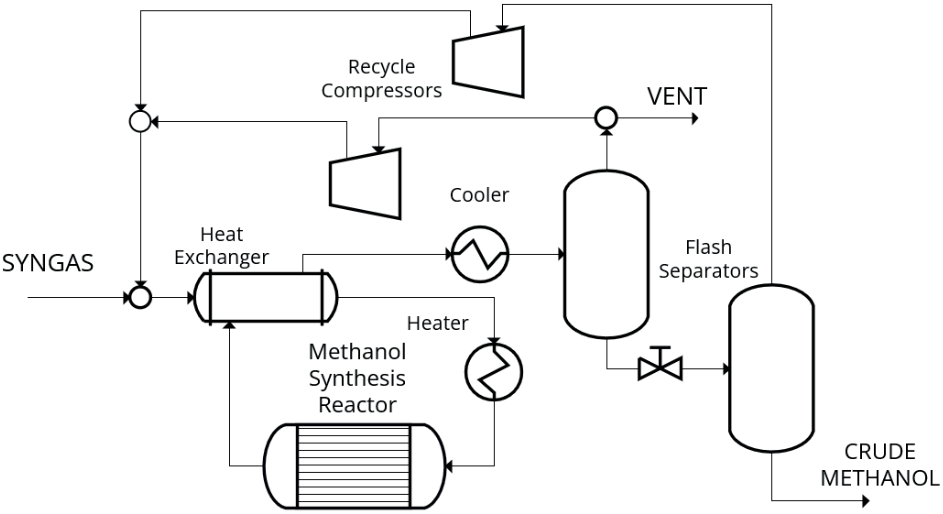

Figure 7 – Methanol synthesis loop flowsheet.

Methanol is synthesized from syngas by the hydrogenation reactions of carbon monoxide and carbon dioxide, while the water-gas shift (WGS) reaction can also occur, as described in Eq. (13) and (14), respectively.

$$CO_{(g)} + 2\,H_{2\,(g)} \leftrightharpoons CH_3OH_{(g)} \qquad (13)$$

$$CO_{2\,(g)} + 3\,H_{2\,(g)} \leftrightharpoons CH_3OH_{(g)} + H_2O_{(g)} \qquad (14)$$

The synthesis reactions are exothermic and non-equimolar, as the number of compounds produced is less than the number of reactants. These types of properties indicate that the methanol reaction is favored at low temperature and high pressure. Therefore, the reactions are carried out in catalytic beds to achieve higher conversion rates. The CuO/ZnO/Al_2O_3 catalyst is the most commonly used in industry for the conversion of syngas to methanol (Bozzano *et al.*, 2016).

The kinetics of methanol conversion is directly influenced by the content of H_2 and carbon oxides in the reaction system. One of the most widely used kinetic models in the literature is the model developed by Vanden Bussche & Froment (1996). The kinetics consists of two independent reactions: the hydrogenation of carbon dioxide and the water-gas shift reaction, presented above in Eqs. (13) and (14), respectively. The expressions utilized in this model for the kinetic reaction rates of CO_2 hydrogenation and the WGS reaction, in mol s^{-1} $kgcat^{-1}$, are described in Eqs. (15) and (16):

$$r_{CO2} = \frac{k_1 P_{CO2} P_{H2}\left(1 - \frac{1}{K_{eq1}} \frac{P_{H2O} P_{CH3OH}}{P_{CO2} {P_{H2}}^3}\right)}{1 + K_1 {P_{H2}}^{0.5} + K_2 P_{H2O} + K_3 \frac{P_{H2O}}{P_{H2}}} \tag{15}$$

$$r_{WGS} = \frac{k_2 P_{CO2}\left(1 - \frac{1}{K_{eq2}} \frac{P_{H2O} P_{CO}}{P_{CO2} {P_{H2}}^3}\right)}{1 + K_1 {P_{H2}}^{0.5} + K_2 P_{H2O} + K_3 \frac{P_{H2O}}{P_{H2}}} \tag{16}$$

The expressions for the kinetic parameters presented for the kinetic reaction rates above are described as follows:

$$k_1 = 1.07 \exp\left(\frac{36696}{\mathrm{R\,T}}\right) \tag{17}$$

$$k_2 = 1.22 \exp\left(\frac{-94765}{\mathrm{R\,T}}\right) \tag{18}$$

$$log_{10} K_{eq1} = -10.592 + \frac{3066}{T} \tag{19}$$

$$log_{10} K_{eq2} = 2.029 - \frac{2073}{T} \tag{20}$$

$$K_1 = 0.499 \exp\left(\frac{17197}{\mathrm{R\,T}}\right) \tag{21}$$

$$K_2 = 6.62 \times 10^{-11} \exp\left(\frac{124119}{\mathrm{R\,T}}\right) \tag{22}$$

$$K_3 = 3453.38 \tag{23}$$

in which P_i is the partial pressure of component i, in bar, k_1 (mol s^{-1} kg_{cat}^{-1} bar^{-2}) and k_2 (mol s^{-1} kg_{cat}^{-1} bar^{-1}) are reaction kinetic constants, K_{eq1} (bar^{-2}) and K_{eq2} (dimensionless) are equilibrium constants and K_1 ($bar^{-0.5}$), K_2 (bar^{-1}) e K_3 (dimensionless) are adsorption constants.

After the catalytic conversion to methanol in the synthesis reactor, the stream of unreacted gases needs to be separated from the stream containing the final product. As the conversion per pass in the reactor is low, a recycle is used to increase the overall conversion. The recycled gases are separated from the liquid stream in gas-liquid separators.

The bottom product of the first separator is a crude methanol stream, consisting mostly of methanol (approximately 85%). This stream also contains water and small amounts of dissolved gases. Part of the stream recycled after the separator is purged to prevent the accumulation of inert gases, such as methane and nitrogen, and to control the loop pressure. This purge gas can be used as fuel for the reformer or can be sent to a PSA unit to use the excess hydrogen to improve the syngas quality (Bertau *et al.*, 2014).

After depressurization to the operating pressure level of the distillation unit, a second separator vessel is used to separate the gas phase formed at this lower pressure level. This second separator reduces the demand on the distillation columns and increases the overall efficiency of the process.

For methanol to have commercial applications, the raw methanol stream, product of the synthesis loop, must be sent to purification unit. This unit is composed of distillation columns in series, the number of equipment depending on the desired degree of purity and the composition of water and other impurities in the raw methanol stream (Bozzano *et al.*, 2016).

2.7. CASE STUDIES

To evaluate the potential of these technologies, case studies were carried out simulating the described biogas sustainable technology routes: case A represents the ammonia-urea route, and case B represents the methanol route. For these studies, a biogas feed stream of 1000 kmol/h was taken as a base for every case study. The simulations were carried out using the commercial simulator Aspen Plus (version 12.1) and models developed in the Python environment, based on conventional industrial operating conditions found in technical and scientific literature.

Considering the non-polar characteristics of the compounds present in the simulated systems, the Peng-Robinson (PR) thermodynamic model was chosen as the equation of state for calculating the system's physical properties and state variables for the ammonia and methanol synthesis plants, while the Soave-Redlich-Kwong (SRK) thermodynamic equation of state model with the Schwartzenruber and Renon (SR-Polar) mixing rule was utilized for the urea synthesis plant.

2.7.1. Case A – Ammonia-Urea

The models for the ammonia-urea plant were developed individually for each product and then integrated to synthesize the nitrogen fertilizer. Both plants were simulated using the basic flowsheet available in the Aspen Plus software. Figure 8 shows the ammonia synthesis process flowsheet.

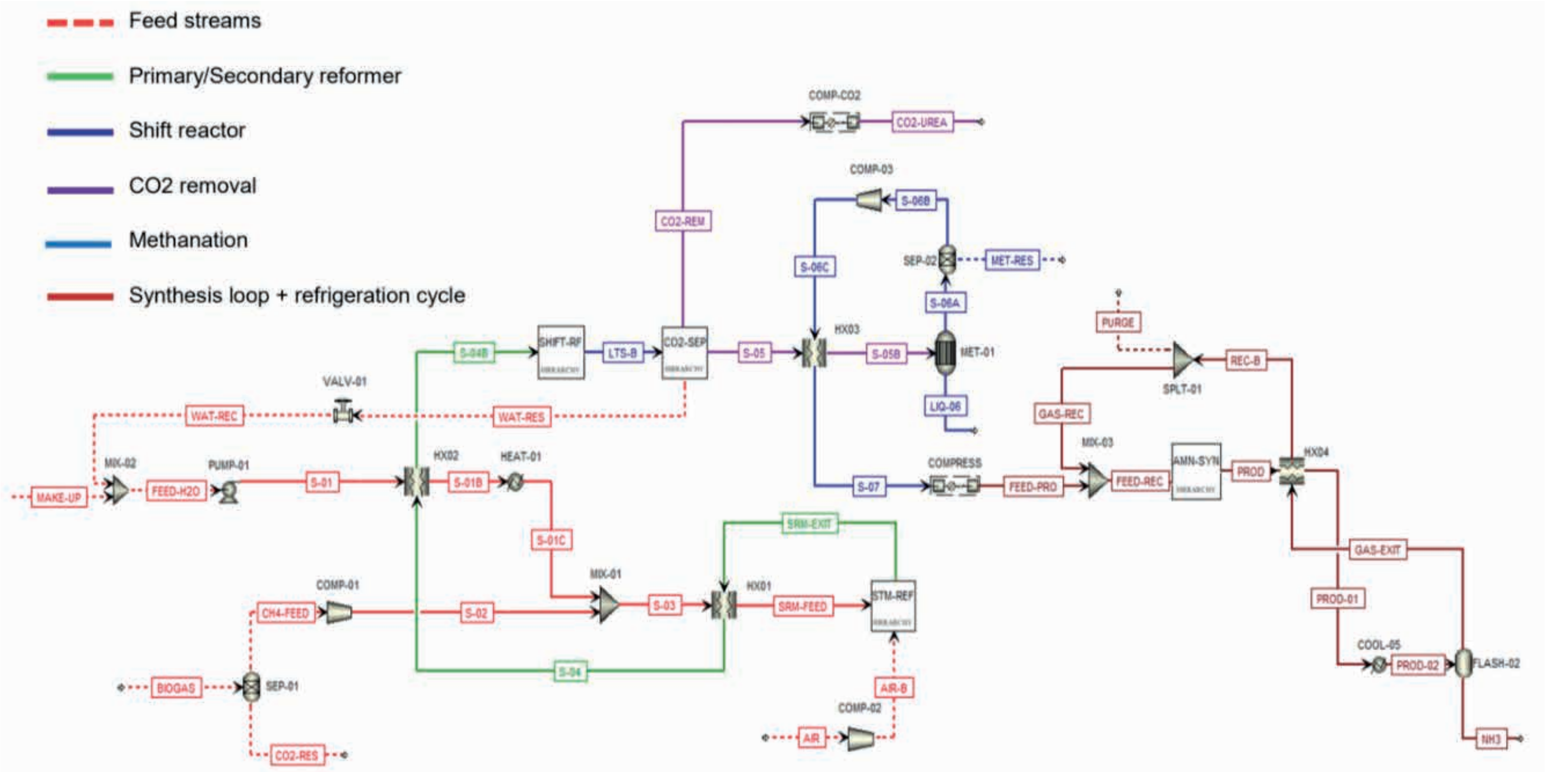

Figure 8 – Ammonia synthesis process flowsheet.

The ammonia plant flowsheet was adapted from the software library (ASPEN TECH, 2008a) and the work performed by Vianna (2017), while the kinetic reaction model implemented was proposed by Dyson and Simon (1969), with the expression developed by Gillespie and Beatie (1930) for calculating the equilibrium constant according to the equations outlined in Section 2.4.

Methane reforming considers the presence of primary and secondary reformers, in which an equilibrium reactor was chosen for the simulation. From this equipment model, it is possible to determine specific stoichiometric reactions and the reaction products in the equilibrium condition. Reactions (1), (2) and (3), described in Section 2.2, were considered for the reactor model, and the equilibrium constant data is available in the software's own database.

After the reformer, syngas is submitted to a two-stage shift reaction: high temperature (LTS) and low temperature (HTS). Shift reactors were also modeled as thermodynamic equilibrium reactors specified by the presence of the reactions highlighted in Section 2.1. The CO_2 removal section was carried to replicate an absorption tower using an amine solution as solvent. This simulation was carried using a tool available in Aspen Plus called Component Separator, consisting of a mathematical approach for separating components based on the specification of flow rates/fractions in the current composition (Vianna, 2017). Finally, the catalytic reactor was simulated as a plug-flow reactor, consisting of catalytic beds coupled with intermediate heat exchangers (Carvalho, 2016; Cheema *et al.*, 2018; Paixão, 2018).

Like the ammonia plant, the urea synthesis section was implemented based on the available flowsheet within the Aspen Plus software (2008b) and work by Chinda (2015). Changes were made for the kinetic model and simulation strategy of the urea conversion reactor, with this equipment being modeled as a sequence of 10 continuous stirred tank reactors (CSTR) with the same volume of 20 m³ (Chinda, 2015; Hamidipour *et al.*, 2005; Rasheed, 2011). Furthermore, it was considered that the carbamate condenser contributes directly to urea synthesis in the overall performance of the plant (Chinda, 2015; Rasheed, 2011).

2.7.2. Methanol Plant – Case B

The models for the methanol synthesis plant, as well as the parameters and specifications required to the simulation of the entire process were developed based on the work of Santos *et al.* (2018). Figure 9 illustrates the process flowsheet considering the configuration used for each of the steps (reforming, upgrading and synthesis).

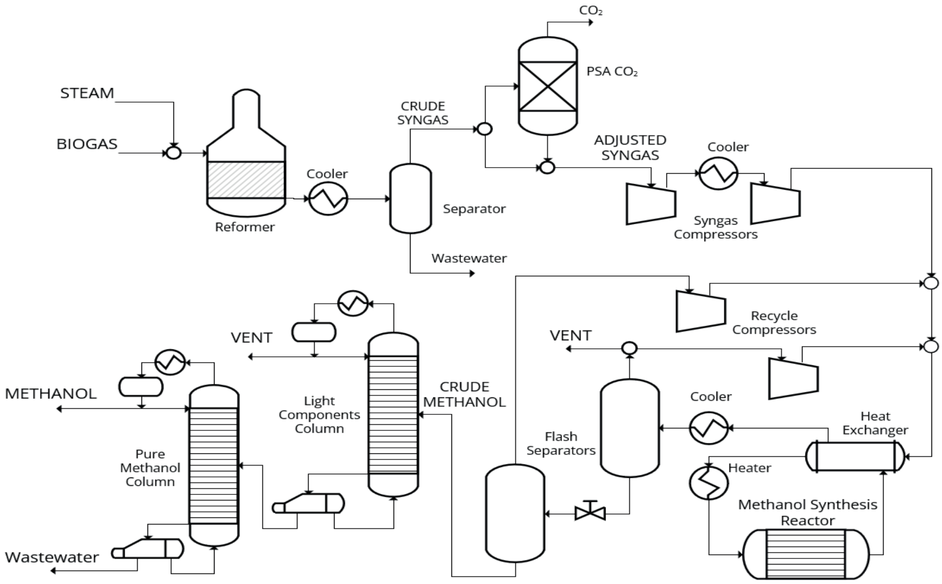

Figure 9 – Methanol synthesis process flowsheet.

For the reforming stage, only the presence of a single reformer was considered, based on the conventional primary reformer, with a steam/biogas ratio of 1.5 and a temperature of 850 °C. The PSA unit has a removal efficiency of 90% of CO_2. The synthesis reactor was modeled as a fixed bed multitubular PFR, which uses a countercurrent cooling jacket, operating at 80 bar and a feed temperature of 230°C. The distillation columns were modeled using interpolation tables, constructed from data obtained from simulations developed in the Aspen HYSYS software and based on specifications proposed by Blumberg et al. (2017). All equipment models were developed in a Python environment, except for the distillation columns.

3. RESULTS AND DISCUSSION

3.1. AMMONIA-UREA PLANT

As previously discussed, a flow of 1000 kmol/h containing 60 and 40% CH_4 and CO_2 was used as a benchmark. It was established that methane is completely separated from the CO_2 stream, which is a direct by-product of the process with a flow rate of 400 kmol/h (~ 422 ton/day). The biogas and water feed rates are intended to maintain the H_2O/CH_4 molar ratio close to 3 to increase the useful life of the catalysts used in methane reforming. Trying to keep this relation, the plant operates continuously with a total water vapor flow rate of 1800 kmol/h. The total amount is composed of a make-up stream and the wastewater stream coming from the CO_2 removal section. The second one aims to eliminate excess water vapor from next process stages and promote the recirculation of process reactants. This water stream is separated and recirculated past the shift reactors with a total flow rate of 835 kmol/h, while the make-up water stream provides a continuous feed of 964 kmol/h.

It is also worth highlighting that CO_2 removal section is responsible for cleaning the gaseous effluent that will be sent to the synthesis loop. Therefore, a concentrated CO_2 stream of 655 kmol/h is produced as a direct by-product of the shift stage and can be sent directly to the urea synthesis section but is not completely absorbed by the urea plant.

Furthermore, atmospheric air flow is introduced directly into the secondary reforming stage to supply the necessary nitrogen for ammonia synthesis and enough oxygen demand for the partial combustion of methane. All syngas preparation steps work together to promote the adjustment of the H_2/N_2 molar ratio in stoichiometric proportions for the synthesis loop. Therefore, considering this parameter as a key performance indicator, the atmospheric air flow rate required is approximately 900 kmol/h to guarantee that operating condition before the gas stream enters the synthesis loop. Table 1 contains the main data regarding operational parameters of syngas preparation section, detailing raw material flow rates.

At the end of the syngas preparation process, the inlet stream of synthesis loop has as its majority molar composition the presence of the reactants N_2 and H_2, corresponding to a value close to 96%. The remaining percentage is made up of reactants recirculated after leaving the last stage of the main reactor.

The main reactor strategy involves the existence of three catalytic beds coupled with heat exchangers. Ammonia synthesis presents complex operating conditions due to the exothermic and reversible characteristic of the reaction, limiting the conversion rate due to thermodynamic equilibrium. A gradual decrease profile in the molar fraction of reactants and an increase of products in the molar fraction due to the reaction progress is observed, as expected in the literature. Consequently, there is an increase in temperature inside the catalytic bed. Considering the exothermic characteristics and adiabatic operation of the reactors, there is a need to cool down the outlet streams of the intermediate beds. The goal is to maximize conversion considering the restriction imposed by thermodynamic equilibrium. It is verified that the outlet temperature in each catalytic bed does not exceed 500 ºC and a temperature difference above 100 ºC between outlet and inlet streams seeks to be avoided, according to the established operational safety rules (Azarhoosh *et al.*, 2014; Carvalho, 2016; Cheema *et al.*, 2018; Paixão, 2018; Yoshida *et al.*, 2021).

Table 1 – Syngas preparation section main results

Variables	Values
Air flow rate (kmol/h)	903
CO_2 flow rate (kmol/h)	1056[a]
Water steam flow rate (kmol/h)	1800
H_2O/CH_4 molar ratio	3
H_2/N_2 molar ratio	3

[a] Sum of residual CO_2 purification stream and CO_2 removal section.

A daily production of 508 ton/day (~1240 kmol/h) of ammonia with a purity of 98.6% on a molar basis is observed after the refrigeration cycle, with the remainder of the composition consisting of unreacted gases (N_2 and H_2) and inert gases (Ar and CH_4). The purge/recycle ratio is relevant because it promotes the recycle of unconverted gases and control of the concentration of inert compounds present in the feed stream of the first catalytic bed. Therefore, the value of 0.05 was defined because it is possible to reconcile a value for the global reactor conversion close to 27% and the product stream conditions (flow and purity) desired to supply the demand coming from the urea synthesis section. It is worth highlighting that values lower than 0.05 for the purge/recycle ratio promote an increase in the inerts concentration in the reactor feed stream and, consequently, a decrease in the overall conversion of the process and in the purity of the ammonia product stream (Carvalho, 2016; Paixão, 2018).

Table 2- Ammonia synthesis main results

Variables	Values
Purge/recycle ratio	0.05
Pressure (atm)[a]	200
NH_3 production (ton/day / kmol/h)	508 / 1240
Purity (% mol/mol)	98.6
Conversion (%)	27.2

[a] Loop synthesis and refrigeration cycle pressure.

According to the logical sequence of the process, the two raw materials necessary for urea synthesis are fully supplied by the ammonia plant. The CO_2 and NH_3 feed flow rates were 620 and 1.220 kmol/h, respectively, following a stoichiometric NH_3/CO_2 molar ratio close to 2. Table 3 contains the main results regarding to urea synthesis section.

Table 3 – Urea synthesis main results

Variables	Values
CO_2 flow rate (kmol/h)	620
NH_3 flow rate (kmol/h)	1200
Urea production (ton/day)	868
Conversion (%)	60

Like the ammonia synthesis loop, urea production process is also conducted under high pressure conditions (135-140 bar). However, operating temperature conditions of the equipment are milder, varying between 150 and 200 ºC. The system is interconnected to promote the recycle of unconverted reagents and benefit from CO_2 as a stripping agent. In this way, the entire process operates under the same pressure condition (140 bar) due to the connection of existing equipment and currents.

The carbamate condenser, also known as pool condenser, is feed from the gaseous stream coming from the stripper (recirculated unconverted reactants) and the liquid stream containing the mixture of fresh ammonia inlet and the carbamate solution processed in the scrubber. This equipment directly participates in the synthesis of urea in the STAC unit. However, information on the specification for both the synthesis of ammonium carbamate and urea is very limited, which makes it difficult to provide a basis for direct comparison even for a qualitative perspective. Thus, a simplified representation was adopted for the pool condenser, considering the intrinsic phenomenology and linking its operation to important operating parameters of the urea reactor such as CO_2 conversion parameter and mass fraction of urea in the liquid stream (Chinda, 2015).

The main equipment of the Stamicarbon process is the urea reactor, modeled and simulated from a sequence of CSTRs reactors in order to reproduce the internal trays existing in the industrial equipment (Chinda, 2015; Hamidipour *et al.*, 2005; Rasheed, 2011; Zendehboudi *et al.*, 2014). The urea reactor has a two-phase operating condition, receiving gaseous reactants (NH_3 and CO_2) and a liquid stream containing ammonium carbamate, urea and water. The inlet (170 ºC) and outlet (185 ºC) temperatures were chosen to emulate the temperature behavior throughout the equipment, assuming a profile of linear increase during the sequence of CSTRs employed (Brouwer, 2009a; Dente *et al.*, 1992; Hamidipour *et al.*, 2005). The evolution of temperature throughout the reactor is explained by the characteristic of the urea synthesis reaction system, since the formation of ammonium carbamate represents a fast and exothermic reaction, while the dehydration of the intermediate for urea synthesis is endothermic and corresponds to the slow step. The CO_2 conversion was 60%, while the mass fraction of urea in the reactor's liquid output was close to 34%, obtaining values in agreement with the literature (Chinda, 2015; Hamidipour, 2005). The flow rate of urea produced in the synthesis section was approximately 868 ton/day.

Figure 10 illustrates the differences between conventional process and new concept using biogas as main feedstock. As described in previous sections, the integrated plant considers full replacement of natural gas by biogas as raw material without modifying existing technologies. Regarding conventional process, the main change is related to raw-material pre-treatment due to the higher concentration of CO_2 in the feed stream. In the naturas gas plant, there is no need for an upgrade process due to the higher methane concentration. Another relevant challenge is to guarantee the continuous supply of the unit fed by biogas since generation occurs through batch processes. Plant's location becomes a relevant aspect to ensure a high availability of biogas production, which requires its own infrastructure of surge tanks and gas pipelines to avoid any supply chain problems.

Furthermore, another relevant topic refers to the large surplus of 400 kmol/h CO_2 from the biogas upgrading. The ammonia plant is capable of fully supplying urea synthesis due to the presence of methane steam reforming, causing CO_2 to become an unwanted waste if it is not sold. Therefore, residual CO_2 monetization would lead to an increase in the total revenue and would directly lead to an improvement in the project economic metrics. This should be important as recurring revenue considering CO_2 is a by-product and should not need a huge additional investment. However, it is worth highlighting that there are challenges which are related to prospect nearby customers and the technical specification required for commercialization.

After pre-treatment of raw material, the new process becomes very similar to the traditional process, without the need to replace technologies due to the technological maturity existing in industry. The integrated ammonia-urea plant demands high energy due to the characteristics of the system, mainly due to the presence of the methane reforming stage and the compression cycles necessary for the unit operation. New alternatives have been studied to reduce energy expenditure and environmental impact, such as the implementation of bi-reforming reactors to replace the traditional steam reforming process (Moura, 2021), integrated plant concepts for the production of urea from of biomass in a fully renewable process (Zhang *et al.*, 2021) and use of wind energy sources and electrolysis to obtain the necessary hydrogen (Carvalho, 2016; Reese *et al.*, 2016). However, there are still technological challenges for these alternative technologies to compete economically with the traditional process in the coming years, requiring greater investment for the gradual establishment of new concepts supported in the context of sustainability for chemical engineering.

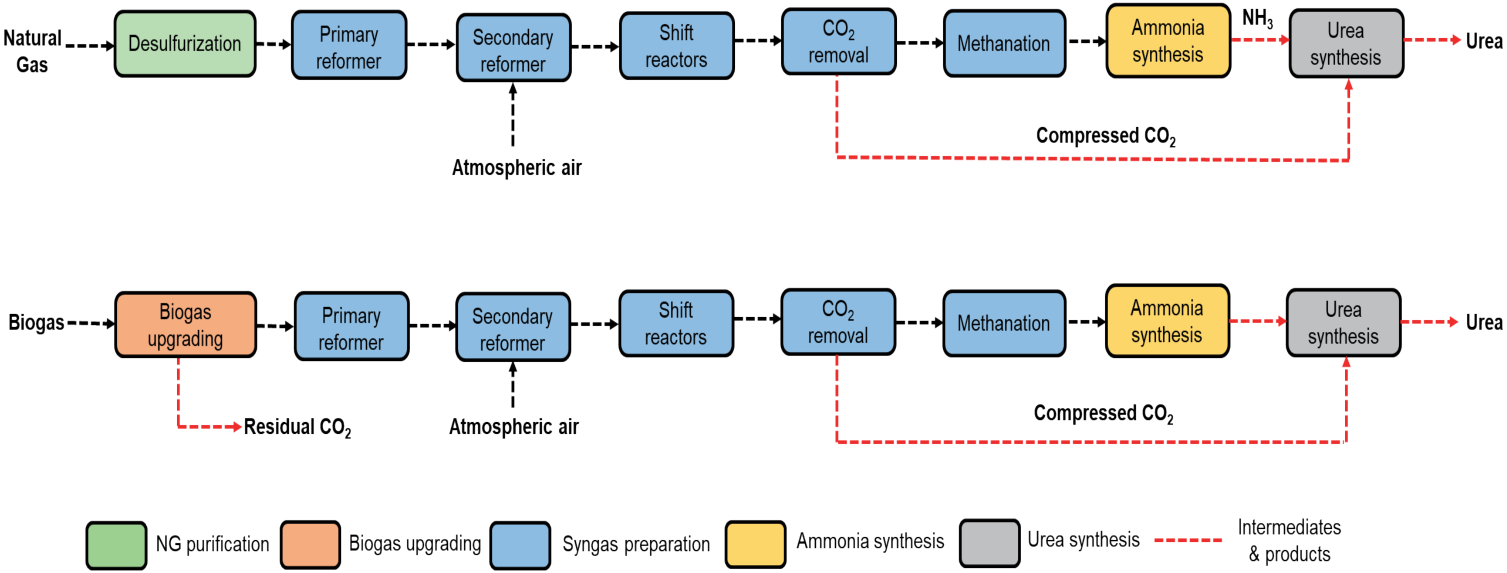

Figure 10 – Conventional and innovative configuration for ammonia and urea synthesis.

3.2. METHANOL PLANT

For methanol synthesis, stoichiometric ratio of the syngas (ratio between the composition of hydrogen and carbon oxides) must be kept close to 2. The steam flow rates, and the CO_2 removal stage are intended to keep this stoichiometric under control. Due to the high temperature at the reformer outlet, steam can be produced from heat integration, supplying the required amount of steam needed at the reformer and reducing the total consumption of utilities.

The amount of CO_2 removed in PSA units corresponds to around 190 kmol/h. This value indicates that more than 50% of the CO_2 present in biogas was consumed in the reforming stage, reinforcing the potential for the use of biogas without the need for preliminary upgrading.

Regarding the methanol synthesis loop, as the conversion per pass in the reactor is low, a recycle is used to increase the overall conversion. Similar to the procedure in the ammonia plant, a fraction of the recycled stream after the separator is purged to prevent the buildup of inert compounds and to control the synthesis loop pressure. This purge gas can be used as fuel for the reformer or can be sent to a PSA unit to utilize spare hydrogen for syngas upgrading.

Due to the exothermic characteristic of the CO and CO_2 hydrogenation reactions, methanol production tends to be favored at lower temperatures. However, operation at lower temperature ranges will directly affect lower kinetic reaction rates. Due to these factors, methanol synthesis in the reactor presents a temperature condition at which maximum conversion can be achieved. For this case study, the optimum supply temperature should remain around 230°C.

After depressurization to the operating pressure of the distillation unit, a second separator vessel is used to separate the gaseous phase formed at this lower pressure. This second separator reduces the demand on the distillation columns, as well as increasing the overall efficiency of the process.

Table 4 describes the main operational parameters obtained for the methanol plant.

Table 4 – Methanol synthesis main results

Variables	Values
Steam/Biogas ratio	1.5
PSA stream inlet ratio	0.6
Reactor inlet temperature (ºC)	230
Purge/recycle ratio	0.05
Methanol production (ton/day)	500
Overall conversion (%)	65

The energy demand profile of methanol plant is illustrated in Figure 11. The largest source of energy consumption is the generation of heat necessary for the operation of reformer, due to the high endothermic nature of the reforming reactions. Consumption for cold utilities is approximately twice that of hot utilities, due to the high thermal cooling load in the reforming stage and in the synthesis loop. Electricity consumers, represented by compressors and pumps, correspond to around 6% of the plant's total consumption.

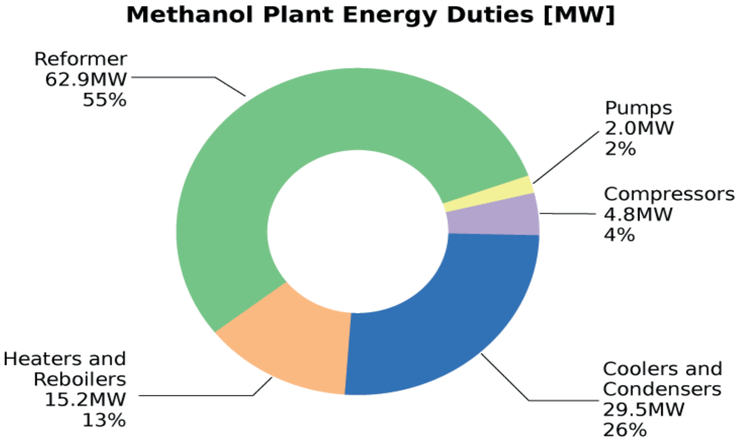

Figure 11 – Energy demand profile of methanol plant.

Comparing the biogas-to-methanol process to the conventional pathway based on natural gas as feedstock, there are few changes to the plant configuration: a higher steam/carbon ratio in the reformer is used to eliminate the need for a CO_2 removal step. Table 5 shows the simulations results for both conventional and biogas technologies.

Table 5 – Comparison of methanol synthesis technologies

Feedstock	Biogas	Natural Gas
Steam/Biogas ratio	1.5	3.0
PSA stream inlet ratio	0.6	0.0
Methanol production (ton/day)	500	630
Overall Conversion (%)	65	82
Total Energy Demand (MJ / kg_{MeOH})	19.8	24.0

The methanol yield from the conventional process is higher, since most of the carbon source is utilized inside the plant while a significant part of the carbon from biogas is lost in the CO_2 purge in the syngas upgrading step. However, the higher amount of required steam and higher flow rates of syngas and crude methanol accounts to a larger energy demand for the reformer, compressors, condenser and reboilers, respectively. Thus, the biogas-to-methanol plant was found to be less energy intensive than the conventional process

CONCLUSIONS

Brazil has a huge potential to explore biogas as a sustainable raw material to produce products with greater added value, promoting the use of this compound beyond electrical energy generation. In terms of the process, the main change required is related to ensuring a continuous supply of biogas for the plant.

It is possible to conclude that the proposal of integrating plants has relevant potential, mainly due to the ease of adapting the existing industrial structure to a new structure considering biogas as the main raw material. Both processes studied reveal technical feasibility, having the capacity to produce the desired products while maintaining an overall conversion close to existing industrial processes.

Furthermore, due to the high CO_2 content in the biogas feed, there is an excess percentage of this byproduct that cannot be fully absorbed by the urea plant or the methanol plant. Therefore, it is necessary to evaluate different strategies for monetizing residual CO_2 to increase the plant economic feasibility. The main challenges are related to plant's location regarding the discovery of potential customers and the technical specification required in the application. Another alternative involves upgrading CO_2 into methane, recycling it and enhancing the overall efficiency of the processes. While an existing biochemical pathway for this conversion is found in literature, additional research is required before this technology can be considered viable.

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