Material and Energy Balance Analysis for Urea Production from Biomass via Methane Steam Reforming

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Received: 28 Jan 2021;
Received in revised form: 03 Mar 2021;
Accepted: 14 Apr 2021;
Available online: 09 May 2021
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Keywords — Balance Energy, Biomass, Biogas, Urea.

Abstract — The urea industry often requires the use of fossil fuels or natural gas. This study raises the possibility of producing urea from biogas, a more environmentally friendly alternative. The purpose of this work is a block flow diagram for a passage process; also, the material in terms of molecular flow and energy balances has been resolved for some process units, considering the main theoretical chemical reactions that are involved in these processes. From the material balance analysis, it is possible to estimate a biogas ratio for urea of 14.8. Thus, it is possible to verify the relevance of the recovery and reuse of non-reactive products for increasing urea production. Therefore, the energy balance analysis, the endothermic and exothermic characteristics of the chemical reactions involved are necessary to estimate the thermal load of each unit studied.

1. INTRODUCTION

Urea is an essential product in agriculture due to its nitrogen (46%), necessary to cultivate roots, sprouts, and fruits of plants. Thus, all fertilizer produced consumes approximately 90% of the Urea (SERGEEV et al., 2020).

Three process steps are the main routes for urea synthesis. They are: (1) decomposition of methane gas (CH₄), under high temperatures, into hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂); (2) reaction between hydrogen formed and nitrogen (N₂) to synthesize ammonia (NH₃) and finally (3) the reaction between ammonia and carbon dioxide (CO₂) to form ammonium carbamate (NH₂COONH₄) and decomposed into urea ((NH₂)₂CO) and water (H₂O) (DAVEY et al., 2010).

The gas mixture composed of H₂ and CO, resulting from methane decomposition, is known as synthesis gas (syngas). It is the only economically viable route for converting methane into a higher added-value chemical product. Among the chemical ways for obtaining syngas are (a) steam reform, (b) dry reform, and (c) partial oxidation (YORK et al., 2003).

Syngas, ammonia, and urea production often originate from coal or natural gas with other materials and CO₂ (GUO, 2013). The present work reinforced the use of biogas, a gaseous mixture rich in CH₄ and CO₂ produced by bacterial decomposition of organic wastes, as a plausible feedstock for urea obtention.

The stimulation of biogas production is essential since methane is one of the significant constituents of biogas.
Also, since methane is one of the greenhouse gases, its use for hydrogen production is beneficial. The first step in the synthesis of urea reduces environmental impacts. Still, it offers an efficient destination for using this resource (biogas), with the advantages of having low cost and excellent availability (CHAO et al., 2008).

Thus, this work proposes a better understanding of urea's production from biogas through a process block flowchart. This flowchart aims to simplify and facilitate understanding of this process's basic structure and demonstrate the realization of the fundamentals of material flow analysis (molecular) and energy balance. These tools represent a gold standard feature of chemistry. Also, to processing systems and playing an essential role in efforts to support operational plants.

II. GENERAL DESCRIPTION OF THE PROCESSES

A. Methane Steam reforming

The first patents on steam methane reform (SMR) date back to 1926, with the first reform plant built in the 1930s. However, large-scale production only started in the 1960s, following the discovery of large fields of gas in Europe, which made it possible to change the raw material from coal to natural gas, and today, the SMR method is responsible for 80% - 85% of global hydrogen production (KOROBITSYN et al., 2000; ALHAMDANI et al., 2017).

Two main reactions can describe the steam methane reforming (SMR) process. (Eq. 1 and Eq. 2) (KOROBITSYN et al., 2000):

\[
\text{CH}_4(g) + H_2O(g) \leftrightarrow 3H_2(g) + CO(g) \\
\Delta H_{298}^0 = 206.0 \text{kJ/mol} \tag{1}
\]

\[
\text{CO}(g) + H_2O(g) \leftrightarrow H_2(g) + CO_2(g) \\
\Delta H_{298}^0 = -41.0 \text{kJ/mol} \tag{2}
\]

The first reaction (Eq. 1) is the reform reaction itself, while the second reaction (Eq. 2) is known as the water-gas shift reaction (WGS). SMR is an endothermic reaction and requires steam as an oxidizing agent to produce syngas with an H₂/CO ratio of 3 (Eq. 1). Despite the stoichiometric regent ratio H₂O/CH₄ of 1, steam is usually fed in excess with H₂O/CH₄ ratio around 2.5–3 (VASCONCELOS & LAVOIE, 2018).

The steam reform reaction is favorable at high temperatures and low pressures. At first, reforming proceeded at atmospheric pressure, but, as it was found that increased pressure can save compression energy in the downstream synthesis stage, Process conditions are increased to pressures up to 30 bar and temperatures up to 1000°C (KOROBITSYN et al., 2000). ZHOU et al. (2011) studied thermodynamic equilibrium models for methane reforming processes and found that steam reforming is not favorable at temperatures less than 630 °C and from their models, it was also shown that CO and H₂ production reach a maximum near 850 °C, which is also the CH₄ maximum conversion.

Following the SMR, the H₂ / CO ratio of the synthesis gas produced can be increased utilizing the water-gas displacement reaction (WGS) at lower temperatures. Besides, carbon monoxide is converted to carbon dioxide, which can be used later in the synthesis of Urea (Vasconcelos & Lavoie, 2018; COPPLESTONE & KIRK, n.d.).

Regardless of being a well-established technology, several studies propose improvements for the methane steam reforming process, including catalysts (MORAL et al., 2018; AMIAD et al., 2019; KATHERIA et al., 2019) and process designs (EYALARASAN et al., 2013; KHUSAIBI & RAO, 2016; NGUYEN et al., 2019).

Such studies play a significant role in the achievement of reforming plants with lower investments and operational costs (FERREIRA-APARICIO et al., 2005).

Among the suggestions is using a novel feedstock instead of coal and natural gas for hydrogen generation. In that respect, the anaerobic bacterial digestion of different residual streams (e.g., wastes in landfills) allows the obtention of a methane-rich gas called biogas. Biogas is mainly applied for heat and power generation employing its direct combustion. However, the interest in the valorization of landfill biogas has led to its use to produce valuable chemicals of industrial relevance. Thus, the biogas conversion into syngas could be considered to develop such valorization technology (MORAL et al., 2018).

Raw biogas composition often corresponds to the fraction of 40-75% of methane (CH₄); 15-65% of carbon dioxide, and trace amounts of other gases as hydrogen sulfide (H₂S), carbon monoxide (CO), hydrogen (H₂) and nitrogen (N₂). From those components, H₂S must be removed since it is a toxic and corrosive gas. Thus, biogas' desulphurization is a requirement for its use for energy and hydrogen generation (RYCKEBOBCH et al., 2011). According to Moral et al. (2018), It can apply several alternatives to provide raw biogas for its further use as raw material for producing biofuels and or chemicals. Regarding H₂S removal, Ryckeboch et al. (2011) review distinct methods such as biological filter, membranes, and chemical absorption, reaching 100% removal efficiency.
B. Ammonia Synthesis

One of the reagents for urea reaction synthesis, ammonia (NH₃), has been known for over 200 years when it was first isolated in gaseous form, in 1774, by the English chemist Joseph Priestley. Nevertheless, the feasible reaction for producing commercial quantities of ammonia was first described by the German chemist Fritz Haber, that synthesized ammonia in the laboratory from N₂ and H₂ (PATTABATHULA & RICHARDSON, 2016), as shown in the reaction (Eq. 3):

\[ \text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3 \quad \Delta H_{298}^\circ = -92.4 \text{ kJ/mol} \quad (3) \]

Usually, the reaction occurs on an iron catalyst with pressure in the range of 150 to 250 bar, and temperatures in 350 °C to 550 °C. Moreover, at the usual common reaction operating conditions, the conversion achieved per pass is limited from 20% to 30%; consequently, the precise removal of synthesized ammonia is essential. It is accomplished via mechanical refrigeration or absorption/distillation (MAXWELL, 2004).

Most of the global production of ammonia is based on steam reforming of natural gas (PATTABATHULA & RICHARDSON, 2016), and it has a direct impact on the costs for ammonia production since natural gas prices can vary according to many factors (e.g., region and government controlling) (MAXWELL, 2004). In this sense, many studies in recent years have recognized the potential of ammonia production from the biomass gasification route (ARORA et al., 2016), supporting the use as mentioned above of biogas to hydrogen generation.

C. Urea Synthesis

The commercial production of urea is based on the reaction of ammonia (NH₃) and carbon dioxide (CO₂) at high pressure (150 to 160 bar) and temperature (180 °C to 190°C) to form ammonium carbamate, which is dehydrated into urea and water, according to the reaction described in Eq. 4. Such reaction (Eq. 4) was discovered in 1868 by a Russian chemist, Alexander Ivanovich Bazarov. Nowadays, global urea production reaches 229 million tons/year (SOLIMAN, 2019; MAXWELL, 2004; SERGEEV et al., 2020).

\[ 2\text{NH}_3 + \text{CO}_2 \leftrightarrow \text{NH}_2\text{COONH}_2 \leftrightarrow \text{CO}((\text{NH}_2)_2) + \text{H}_2\text{O} \]
\[ \Delta H_{298}^\circ = -133.5 \text{ kJ/mol} \quad (4) \]

The synthesis of urea is purely a thermal reaction and does not require any catalyst (MacDOWELL et al., 2010). The ammonium carbamate formation is fast, highly exothermic, and goes essentially to completion under normal industrial processing conditions, while urea formation is slow and endothermic. Moreover, ammonia is usually feed in excess, and therefore the reaction conversion is described in terms of carbon dioxide reacting percentage (SOLIMAN, 2019).

The significant difference among the existing urea production technologies is how urea is separated from the reactants and how ammonia and carbon dioxide are recycled. Concerning the urea separation, the urea solution prevenient from the synthesis reactor must be concentrated to a urea melt for conversion to a solid pilled or granular product. (MAXWELL, 2004).

III. PROCESS BLOCK FLOW DIAGRAM FOR UREA PRODUCTION FROM BIOGAS

The above-mentioned theoretical approach of the three steps for urea production is proposed a short process flow diagram for urea production from biogas. In addition, material and energy balances involved in such a process are estimated, aiming to add to the development of such potential methods and improve process efficiencies.

The proposed process block flow diagram for such a process is presented in Fig. 1.
Fig. 1: Brief process block flow diagram to produce urea from biogas. The molecular flows are represented by the letters "N," and the heat flows are represented by the letters (Q).

From Figure 1, the proposed block diagram for urea production from biogas is a three steps process. At the first step, saturated steam and methane streams are mixed and preheated in a heat exchanger (HX) before flowing into the reforming reactor. At the outlet reform reactor, the produced steam of gases is directed to the water-gas shift reactor. Then the gases of interest (H₂ and CO₂) leaving the WGS reactor must be purified to be used at further steps. The non-reacted reagents at the end of step 1 (CH₄ and H₂O) can be reutilized after cleansing. At the second step, hydrogen purified from step 1 reacts with nitrogen to yield ammonia (NH₃). At the third step, the ammonia separated from step 2 reacts with carbon dioxide (CO₂) (which part of the necessary amount was produced at step 1) to solve molten urea.

A. Molecular Species and Energy Balances

Material balances are essential to support a process design since they can determine the quantities of raw materials required and products produced in stream flows and compositions. The material balance for any process, given by the mass conservation law, can be written as shown in Eq. 5 (CLARK, 2009):

$$\frac{d}{dt}(\nu \Sigma c_{sys}) = \sum_{i=1}^{N} P_{in,i} c_{in,i} - \sum_{j=1}^{N} P_{out,j} c_{out,j} 
$$

Where $\nu$ is the volume of the system, $c_{sys}$ is the average concentration of the component of interest; $\nu$ is the volume of the system, $c_{sys}$ is the average concentration of the component of interest in the system.

Considering steady-state conditions, the time derivative in Eq.5 is equal to zero, and $Q$ values are constants. Hence, Eq. 5 turns into Eq. 6:

$$\sum_{i=1}^{N} Q_{in,i} c_{in,i} = \sum_{j=1}^{N} Q_{out,j} c_{out,j} 
$$

For systems involving chemical reactions, a molecular balance for each species should be done, considering the terms of consumption and generation. Thus, the general molecular balance equation for a reactive steady-state system is given by Eq. 7:

$$\text{input} + \text{generation} = \text{output} + \text{consumption} \quad (7)$$

From the proposed process block flow diagram for urea production from biogas (Figure 1), desulphurized biogas is the process feedstock. Thus, to realize molecular balance, it is

Table 1. Biogas composition considered for the study

| Species | mol Fraction, Yi (%) | MM (kg / k mol) | Biogas MM* (kg / k mol) |
|---------|----------------------|-----------------|------------------------|
| CH₄     | 56.00                | 16.04           | 8.98                   |
| CO      | 3.00                 | 28.00           | 0.84                   |
| CO₂     | 37.00                | 44.01           | 16.28                  |
| N₂      | 1.00                 | 28.01           | 0.28                   |

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Besides biogas composition, some reasonable assumptions important for molecular balance were taken: (a) H₂O/C ratio for steam reform reaction equal to 4 (SHAGDAR et al., 2020); (b) methane conversion at steam reform reaction equal to 90% (SHAGDAR et al., 2020); (c) H₂ conversion at ammonia synthesis reaction equal to 26% (MAXWELL, 2004); (d) CO₂ conversion into urea equal to 60% and NH₃/CO₂ ratio for urea synthesis of 2.95 (MAXWELL, 2004).

Given the concepts and assumptions for molecular balance applied in the present study and knowing that molecular flow determination plays an essential role in the energy balance, the current work's energy balance concepts and beliefs are now presented.

Energy balance equations were used to confirm the first law of thermodynamics for each system of the blocks presented in Fig. 1 as a control volume under the steady-state operation. From the first law of thermodynamics, the energy balance for a stationary open system with no kinetic, potential energy, and volume variation is given by:

\[ Q = \Delta H = n_{\text{output}} \dot{H}_{\text{output}} - n_{\text{input}} \dot{H}_{\text{input}} \]  

(8)

\( Q \) Value is the heat transfer rate going into or out of the system, \( n \) and \( \dot{H} \) values are the molecular flow and specific enthalpies of the components going into (reagents) and out (products) of the system, respectively.

Specific enthalpy values for each component at the inlet and outlet streams of each process were calculated taking into consideration the relationship between the standard enthalpy of formation (\( \Delta H_f^\circ \)), heat capacity \( (C_p) \), and temperature \( (T) \) variation:

\[ \dot{H}_{\text{specie}} = \Delta H_f^\circ + \int C_p \, dT \]  

(9)

Finally, heat capacity \( (C_p) \) values for each component at the inlet and outlet streams were estimated as described in Felder (2016), as presented in Eq. 10, and the coefficient values, as well as standard enthalpy values, are shown in Table 2 (Felder, 2016).

### Table 2. Coefficient values for heat capacity equation and Standard Enthalpy of Formation \( (\Delta H_f^\circ) \)

| Species          | a   | b    | c    | d       | \( \Delta H_f^\circ \) (kJ/mol) |
|------------------|-----|------|------|---------|---------------------------------|
| CH₄              | 3.43E-02 | 5.47E-05 | 3.66E-09 | -1.10E-11 | -74.84                         |
| CO               | 2.90E-02 | 4.11E-06 | 3.55E-09 | -2.22E-12 | -110.52                        |
| CO₂              | 3.61E-02 | 4.23E-05 | -2.89E-08 | 7.46E-12  | -393.51                        |
| N₂               | 2.90E-02 | 2.20E-06 | 5.72E-09 | -2.87E-12 | 0                               |
| H₂               | 2.88E-02 | 7.65E-08 | 3.29E-09 | -8.68E-13 | 0                               |
| O₂               | 2.91E-02 | 1.16E-05 | -6.08E-09 | 1.31E-12  | 0                               |
| H₂Oliq           | 7.54E-02 | -     | -     | -285.84             |                                |
| H₂Ogas           | 3.45E-02 | 6.88E-06 | 7.60E-09 | -3.59E-12 | -241.83                        |
| NH₃              | 3.52E-02 | 2.95E-05 | 4.42E-09 | -6.69E-12 | -67.20                         |
| (NH₂)₂C₀        | 9.00E-02 | -     | -     | -333.39             |                                |

The temperature is Celsius °C.

### IV. RESULTS AND DISCUSSIONS

#### A. Molecular balances

Table 3 shows the molecular flow in the inlet and outlet streams of the steam reforming reactor. As it can be seen, it was established 1 mol of methane (corresponding to 1.77 mol of biogas) and four mols of water vapor...
flowing into the system. From the steam reform stoichiometry equation (Eq. 1), it is observed that water is fed in excess with the H$_2$O/CH$_4$ ratio of 4.

| Species | Inlet | Consumption | Generation | Outlet |
|---------|-------|-------------|------------|--------|
| CH$_4$  | 1.000 | 0.900       | 0.000      | 0.100  |
| CO      | 0.054 | 0.000       | 0.900      | 0.954  |
| CO$_2$  | 0.661 | 0.000       | 0.000      | 0.661  |
| N$_2$   | 0.018 | 0.000       | 0.000      | 0.018  |
| H$_2$   | 0.018 | 0.000       | 2.700      | 2.718  |
| O$_2$   | 0.036 | 0.000       | 0.000      | 0.036  |
| H$_2$O  | 4.000 | 0.900       | 0.000      | 3.100  |

Table 4 shows the calculated values of each species in the inlet and outlet streams of the WGS reactor.

| Species | Inlet | Consumption | Generation | Outlet |
|---------|-------|-------------|------------|--------|
| CH$_4$  | 0.100 | 0.000       | 0.000      | 0.100  |
| CO      | 0.954 | 0.698       | 0.000      | 0.256  |
| CO$_2$  | 0.661 | 0.000       | 0.698      | 1.358  |
| N$_2$   | 0.018 | 0.000       | 0.000      | 0.018  |
| H$_2$   | 2.718 | 0.000       | 0.698      | 3.415  |
| O$_2$   | 0.036 | 0.000       | 0.000      | 0.036  |
| H$_2$O  | 3.100 | 0.698       | 0.000      | 2.403  |

It can be noticed that the inlet values are the same presented, like outlet values from steam reforming reaction. Also, as expected, after the WGS reaction (outlet stream), the amount of carbon monoxide (CO) was lower, while the hydrogen (H$_2$) value was higher compared to the inlet stream. Carbon dioxide (CO$_2$) value was also higher, which can be desirable since such species can be purified and further utilized for urea synthesis. The consumption of H$_2$O was calculated applying the concept of the extent of reaction (XR) since WGS is a strongly reversible reaction and thus requires the quantification of how far the reaction goes in terms of a fractional consumption of a specified reactant (MORRIS, 2011).

\[
XR_{H_2O} = \frac{N_{H_2O}^I - N_{H_2O}^O}{N_{H_2O}^O}
\]  

(11)

Where \(N_{H_2O}^I\) and \(N_{H_2O}^O\) are the amount of H$_2$O in the inlet and outlet streams of steam reforming reactor, respectively.

Thus, the amount of H$_2$O reacting in the WGS reactor was obtained multiplying \(XR_{H_2O}\) (0.23) times the amount available after steam reforming is complete (3.1 mols). A noticeable point concerns the reaction’s extent of the reaction being less than one, supporting that the chemical reaction in question is reversible and does not have a limiting reactant. When equilibrium is reached, there is still some reactant present (MORRIS, 2011).

The consumption and generation behavior for each species involved in step 1 can be observed in Fig. 2. It is worth highlighting H$_2$ and CO$_2$ curves considerably rising during the process when CO is generated (point 1 to 2, on the x-axis) and later consumed (point 2 to 3, on the x-axis).

For this theoretical approach, it was considered that all the amount of hydrogen generated in step 1 is fed into step 2, as can be seen in Table 5. From the stoichiometry equation of ammonia synthesis (Eq. 3), the amount of N$_2$ required is on third of the H$_2$ amount in the inlet stream. On the consumption column, it is observed that 26% of H$_2$ conversion (0.888 of 3.417 mols) on the outlet column is considered. It can be observed the amount of NH$_3$ generated and non-reacted reagents leaving the reactor.
Table 5. Number of species (mol) in inlet and outlet streams at ammonia synthesis reaction

| Species | Inlet | Consumption | Generation | Outlet |
|---------|-------|-------------|------------|--------|
| H2      | 3.415 | 0.888       | 0.000      | 2.527  |
| N2      | 1.138 | 0.296       | 0.000      | 0.842  |
| NH3     | 0.000 | 0.000       | 0.592      | 0.592  |

It is important to reiterate that at the present work, it has been considered that the amount of ammonia formed is achieved by a single pass through the reactor. Thus, the amount of non-reactant products in the outlet stream is high, corroborating the data about such procedure not being of commercial interest. It must be considered a recycling system for more ammonia, as was firstly proposed by Fritz Haber (PATTABATHULA & RICHARDSON, 2016).

In Fig. 3 it is shown the consumption and generation behavior for each species involved in step 2. It can be clearly observed that, as the H₂ conversion is low, the amount of non-reactant products (H₂ and N₂) is higher than the amount of the product of interest (ammonia, NH₃) in the outlet stream (point 2, on the x-axis).

Table 6. Amount of (mol) in inlet and outlet streams at urea synthesis reaction (step 3)

| Species   | Inlet | Consumption | Generation | Outlet |
|-----------|-------|-------------|------------|--------|
| NH₃       | 0.592 | 0.240       | 0.000      | 0.352  |
| CO₂       | 0.201 | 0.120       | 0.000      | 0.080  |
| (NH₂)₂CO  | 0.000 | 0.000       | 0.120      | 0.120  |
| H₂O       | 0.000 | 0.000       | 0.120      | 0.120  |

Figure 4 illustrates the consumption and generation behavior for each species involved in step 3. It must be kept in mind that in the present work, for investigating purpose, it was considered that the reaction of conversion of CO₂ and NH₃ into (NH₂)₂CO occurs in the sense of complying with the ideal chemical equation (Eq. 4), not taking into consideration the intermediates and undesirables compounds formation.

To summarize, it was assumed that the process described in the present work was fed with 1.77 moles of biogas (representing 1.00 moles of methane, 56%) and four moles of water vapor. At the end of the process, following the reactions presented and discussed. It was obtained 0.120 mol of urea, resulting in a CH₄ / (NH₂)₂CO ratio of 8.31. This proportion can be reduced when considering an industrial process by recycling unused reagents, for example. In relation to the single-pass procedures adopted in the present work, the quantities of species not consumed are:
0.100 mol of CH₄; 0.256 mol of CO; 0.036 mol of O₂; 1.238 mols of CO₂; 2.527 mols of H₂; 0.860 mol of N₂; 0.351 mol of NH₃; and 2.403 mols of H₂O.

It must be emphasized that the time unit of choice can give the basis of calculation regarding inlet material flow (1 mol of CH₄). According to the international system of units, it was assumed that the methane feed flow mentioned above corresponds to one second, which means that all material flows were also considered in terms of one second (mol/s).

Finally, the molecular composition of each stream (following Fig. 1) is shown in Table 7. It is worth noticing the molecular composition is (a) N5 stream, which is the WGS reactor output, presenting high content of H₂ (45.042%); (b) N8 stream, which is the NH₃ synthesis reactor output, presenting higher content of non-reactants (H₂ and N₂) than product (NH₃) and thus evidencing the low conversion rate achieved by a single pass and (c) N11 stream, which is the urea synthesis reactor output, presenting a similar condition to the previously described.

| Specie | N1 | N2 | N3 | N4 | N5 | N6 |
|--------|----|----|----|----|----|----|
| CH₄    | 56.00 | - | 1.32 | 1.32 | 1.32 | - |
| CO     | 3.00  | - | 12.57 | 12.57 | 3.38 | - |
| CO₂    | 37.00 | - | 8.71 | 8.71 | 17.90 | - |
| N₂     | 1.00  | - | 0.24 | 0.24 | 0.24 | - |
| H₂     | 1.00  | - | 35.83 | 35.83 | 45.02 | 100.00 |
| O₂     | 2.00  | - | 0.47 | 0.47 | 0.47 | - |
| H₂O    | - | 100.00 | 40.87 | 40.87 | 31.67 | - |
| NH₃    | - | - | - | - | - | - |
| (NH₄)₂CO | - | - | - | - | - | - |

| Specie | N7 | N8 | N9 | N10 | N11 |
|--------|----|----|----|-----|-----|
| CH₄    | - | - | - | - | - |
| CO     | - | - | - | - | - |
| CO₂    | - | - | - | 100.00 | 11.94 |
| N₂     | 100.00 | 21.26 | - | - | - |
| H₂     | - | 63.79 | - | - | - |
| O₂     | - | - | - | - | - |
| H₂O    | - | - | - | 17.91 | - |
| NH₃    | - | 14.94 | 100.00 | - | 52.24 |
| (NH₄)₂CO | - | - | - | - | 17.91 |

**B. Energy balances**

The energy balance analysis was carried out to estimate the amount of heat required to be transferred to or removed from the units presented in Figure 1: heat exchanger (HX), reforming reactor, and WGS reactor, Q1, Q2, and Q3, respectively, on step 1; NH₃ synthesis reactor, Q4, on step 2 and urea synthesis reactor, Q5, on step 3.

For such purpose, the assumptions taken were that ambient temperature, i.e., initial temperature for biogas, was 25 °C, and water flowing into the system was as saturated steam at 100 °C. Moreover, the inlet temperature for the mixture of biogas and water (vapor) for the steam reaction was determined to be 400 °C, seeing that, usually, the reaction mixture before a methane reformer is preheated to 400 to 600 °C (PASHCHENKO, 2019). The reform reactor temperature was established to be 850 °C since it was demonstrated that, at this temperature, methane conversion reaches its maximum (ZHOU et al., 2011). After reforming the reaction, the gaseous mixture is cooled to 340-370 °C before charging in the shift converter (EYALARASAN et al., 2013). Therefore 370 °C was chosen as inlet temperature for the water-gas shift reactor. Also, it was established 630 °C as WGS reaction outlet temperature (EYALARASAN et al., 2013). Dioxide carbon present at WGS reaction product is subsequently absorbed, and the treated gas exits the process at 40 °C (MOLBURG & DOCTOR, 2003).

For the ammonia synthesis, it was considered that H₂ and N₂ inlet temperature is five °C. Moreover, it was established that the ammonia synthesis reactor and the gases are heated to 400 °C. The outlet gas from the ammonia synthesis reactor is cooled at 30 °C, so ammonia is condensed and separated (COPPLESTONE & KIRK, n. d.).

For the urea synthesis, it was considered the inlet CO₂ stream temperature of 40 °C, the same temperature after being recovered at step 1, and the condensate NH₃ stream, from step 2, at 30 °C. In the rectors, the temperature reaches 185 °C (MAXWELL, 2004).

Considering that each unit's heat duty can be calculated by considering the total input and output enthalpies of the species, such thermodynamic property was calculated. It was considered the unit of material flow (the basis of calculation) to be of mol/s. Consequently, the unit for calculated enthalpies takes a second (kJ/s). Table 8 presents the enthalpy values considering inlet temperature equal to 25 °C for biogas and 100 °C for H₂O steam and outlet temperature (T) equivalent to 400 °C. It can be
noticed that \( \text{N}_2 \), \( \text{H}_2 \), and \( \text{O}_2 \) initial enthalpy values were calculated as zero since, at 25 \( ^\circ \text{C} \), such elements are in their standard states.

| Table 8. Inlet and outlet Enthalpies (H) for species at heat exchanger before methane steam reform (Q1) |
| Species | Hin (kJ/s) | Hout (kJ/s) |
|---------|------------|------------|
| \( \text{CH}_4 \) | -74.84 | -57.61 |
| CO | -5.92 | -5.32 |
| \( \text{CO}_2 \) | -260.00 | -249.20 |
| \( \text{N}_2 \) | 0.00 | 0.20 |
| \( \text{H}_2 \) | 0.00 | 0.19 |
| O\( _2 \) | 0.00 | 0.42 |
| \( \text{H}_2\text{O} \) | -956.83 | -923.34 |
| **TOTAL** | -1297.59 | 1234.65 |

In Table 9, the calculated enthalpy values of each species in the inlet (\( T = 400 \) \( ^\circ \text{C} \)) and outlet (\( T = 850 \) \( ^\circ \text{C} \)) streams of the reforming reactor are shown. A significant variation in the values of the species being consumed (\( \text{CH}_4 \) and \( \text{H}_2\text{O} \)) and generated (\( \text{H}_2 \) and \( \text{CO} \)) is observed. It is also noticed the higher value presented by the outlet stream (-950.56 kJ/s) compared to the inlet stream (-1234.65 kJ/s).

| Table 9. Inlet and outlet Enthalpies (H) for species at methane steam reformer (Q2) |
| Species | Hin (kJ/s) | Hout (kJ/s) |
|---------|------------|------------|
| \( \text{CH}_4 \) | -57.61 | -4.47 |
| CO | -5.32 | -91.51 |
| \( \text{CO}_2 \) | -249.20 | -244.28 |
| \( \text{N}_2 \) | 0.20 | 0.26 |
| \( \text{H}_2 \) | 0.19 | 36.68 |
| O\( _2 \) | 0.42 | 0.55 |
| \( \text{H}_2\text{O} \) | -923.34 | -647.78 |
| **TOTAL** | -1234.65 | -950.56 |

Subsequently, Table 10 presents the values of the calculated enthalpy for each species in the inlet (\( T = 370 \) \( ^\circ \text{C} \)) and outlet (\( T = 630 \) \( ^\circ \text{C} \)) streams of the WGS converter. It was not illustrated in the process block flow diagram proposed in Figure 1. Nevertheless, it is implied that after leaving the unit of reforming (and before being fed into the WGS converter), the gas stream must be cooled to reach the desired inlet temperature for the WGS reaction. From Table 10, it can be highlighted the variation in the \( \text{CO}_2 \) enthalpy value, which is formed by the WGS reaction.

| Table 10. Inlet and outlet Enthalpies (H) for species at water gas shift converter (Q3) |
| Species | Hin (kJ/s) | Hout (kJ/s) |
|---------|------------|------------|
| \( \text{CH}_4 \) | -5.93 | -5.89 |
| CO | -95.55 | -26.20 |
| \( \text{CO}_2 \) | -250.16 | -516.50 |
| \( \text{N}_2 \) | 0.18 | 0.14 |
| \( \text{H}_2 \) | 27.20 | 26.29 |
| O\( _2 \) | 0.38 | 0.31 |
| \( \text{H}_2\text{O} \) | -711.01 | -556.40 |
| **TOTAL** | -1034.88 | -1078.25 |

Table 11 shows the calculated enthalpy values for each species in the input and output currents of the ammonia synthesis reactor. It was considered the purified \( \text{H}_2 \) from step 1, which was cooled to 5 \( ^\circ \text{C} \), to be fed into the reactor. The inlet temperature for pure \( \text{N}_2 \) was also considered at 5 \( ^\circ \text{C} \), and the temperature of the outlet current was considered to be 400 \( ^\circ \text{C} \). Thus, the variation in the enthalpy values of inlet and outlet for \( \text{H}_2 \) and \( \text{N}_2 \) observed significantly, corroborating to indicate the influence of temperature on enthalpy values. Furthermore, such variation may be mainly related to the temperature change concerning the fact that the variation in the number of moles of \( \text{H}_2 \) and \( \text{N}_2 \) in the inlet and outlet currents is slight due to the low conversion of the reagents into ammonia given the single passage in the reactor considered in the present work.

| Table 11. Inlet and outlet Enthalpies (H) for species at ammonia synthesis reactor (Q4) |
| Species | Hin (kJ/s) | Hout (kJ/s) |
|---------|------------|------------|
| \( \text{H}_2 \) | -1.97 | 28.97 |
| \( \text{N}_2 \) | -0.66 | 10.36 |
| NH\( _3 \) | 0.00 | -152.48 |
| **TOTAL** | -2.63 | -113.15 |

In Table 12, the calculated enthalpy values of each species in the inlet and outlet streams of the reforming reactor are presented. The inlet temperature for \( \text{CO}_2 \) was 40 \( ^\circ \text{C} \), which is its temperature after the recovery by ammine purification process following its formation at step 1. On the other hand, the inlet temperature for NH\( _3 \) was assumed to be 30 \( ^\circ \text{C} \), indicating that the produced ammonia from step 2 must be previously cooled before fed into the urea synthesis reactor.
V. CONCLUSION

A brief process block flow diagram to produce urea from biogas has been demonstrated. Besides, an analysis of material flow (in terms of molecular composition) and energy balance for the proposed diagram was made. From the material balance, it was possible to present the direction and needed quantity (amount) of reactants and obtained products. Precisely, from 100 kg/s (1.77 mol/s) of biogas, it has been estimated to be obtained approximately 15 kg/s (0.12 mol/s) of urea. The energy balance analysis suggested that input energy is necessary for the heat exchanger unit previously to the methane reforming reactor and for the reforming reactor itself supporting the endothermic character of the reforming reaction. On the other hand, for the remaining units, the heat was shown that heat needs to be removed from the system. Mainly, the purpose of elucidating the potential biogas utilization, which is a nearly endless source, as a feedstock for urea obtention was shown.

ACKNOWLEDGEMENTS

This article is a product of results from a project execution entitled “Management of macrophytes in Barra do Braúna reservoir - control of cyanobacterial blooms using excess biomass for the production of biogas, energy, and urea”. It is financed with resources from the R & D / ANEEL portfolio, from ITIQUIRA ENERGÉTICA SA and BARRA DO BRAÚNA ENERGÉTICA SA companies, code P&D - 06305-0219 / 2020, to which the authors express their thanks.

The authors also would like to thank NECTAR - NUCLEUS DEVELOPMENTS IN SCIENCE, TECHNOLOGY, AND ARTS, to support the management and operationalization of project execution activities.

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