

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

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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.

I. 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).

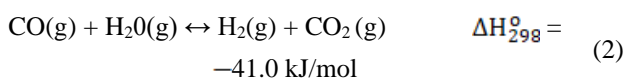
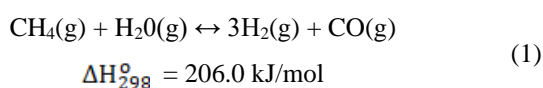
Thus, this work proposes a better understanding of urea's production from biogas through a process block flowchart. This flowchart aims to simplify and facilitate understanding of this process's basic structure and demonstrate the realization of the fundamentals of material flow analysis (molecular) 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):



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 reagent 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.).

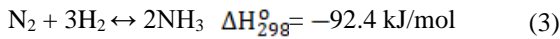
Regardless of being a well-established technology, several studies propose improvements for the methane steam reforming process, including catalysts (MORAL et al., 2018; AMJAD et al., 2019; KATHERIA et al., 2019) and process designs (EYALARASAN et al. 2013; KHUSAIBI & RAO, 2016; NGUYEN et al., 2019).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



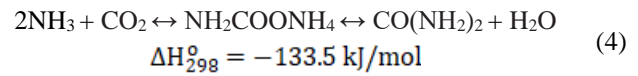
Usually, the reaction occurs on an iron catalyst with pressure in the range of 150 to 250 bar, and temperatures in 350 °C to 550 °C. Moreover, at the usual common reaction operating conditions, the conversion achieved per pass is limited from 20% to 30%; consequently, the precise removal of synthesized 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).



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 prevented from the synthesis reactor must be concentrated to a urea melt for conversion to a solid piled 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.

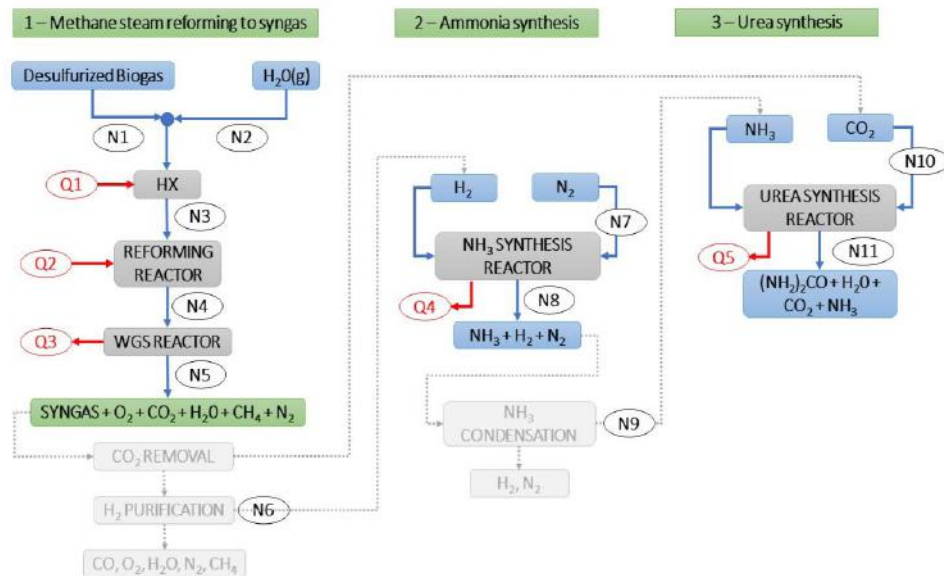


Fig.1: Brief process block flow diagram to produce urea from biogas. The molecular flows are represented by the letters "N," and the heat flows are represented by the letters (Q).

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 (H_2 and CO_2) leaving the WGS reactor must be purified to be used at further steps. The non-reacted reagents at the end of step 1 (CH_4 and H_2O) can be reutilized after cleansing. At the second step, hydrogen purified from step 1 reacts with nitrogen to yield ammonia (NH_3). At the third step, the ammonia separated from step 2 reacts with carbon dioxide (CO_2) (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):

$$\frac{d}{dt}(VC_{sys}) = \sum_{i=1}^N F_{in,i} C_{in,i} - \sum_{j=1}^M F_{out,j} C_{out,j} \quad (5)$$

F Values are mass flows going into or out of the system; C values are mass concentrations of some component of

interest; V 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 derivate in Eq.5 is equal to zero, and QC values are constants. Hence, Eq. 5 turns into Eq. 6:

$$\sum_{i=1}^N Q_{in,i} C_{in,i} = \sum_{j=1}^M Q_{out,j} C_{out,j} \quad (6)$$

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:

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

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)
CH ₄	56.00	16.04	8.98
CO	3.00	28.00	0.84
CO ₂	37.00	44.01	16.28
N ₂	1.00	28.01	0.28

H ₂	1.00	2.02	0.02
O ₂	2.00	32.00	0.64
TOTAL	100.00	-	27.05

*MM = MOLECULAR MASS

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:

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{output}x\hat{H}_{output} - \dot{n}_{input}x\hat{H}_{input} \quad (8)$$

\dot{Q} Value is the heat transfer rate going into or out of the system, \dot{n} and \hat{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 (ΔH_f°), heat capacity (C_p), and temperature (T) variation:

$$\hat{H}_{specie} = \Delta H_f^\circ + \int C_p dT \quad (9)$$

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 (ΔH_f°)

Species	a	b	c	d	ΔH_f° (kJ/mol)
CH ₄	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
CO ₂	3.61E-02	4.23E-05	-2.89E-08	7.46E-12	-393.51
N ₂	2.90E-02	2.20E-06	5.72E-09	-2.87E-12	0
H ₂	2.88E-02	7.65E-08	3.29E-09	-8.68E-13	0
O ₂	2.91E-02	1.16E-05	-6.08E-09	1.31E-12	0
H ₂ Oliq	7.54E-02	-	-	-	-285.84
H ₂ Ogas	3.45E-02	6.88E-06	7.60E-09	-3.59E-12	-241.83
NH ₃	3.52E-02	2.95E-05	4.42E-09	-6.69E-12	-67.20
(NH ₂) ₂ C O	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 H₂O/CH₄ ratio of 4.

Table 3 Number of species (mol) in inlet and outlet streams at methane steam reforming

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.

Table 4. Number of species (mol) in inlet and outlet streams at water-gas shift reactor (step 1)

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 (H₂) value was higher compared to the inlet stream. Carbon dioxide (CO₂) value was also higher, which can be desirable since such species can be purified and further utilized for urea synthesis. The consumption of H₂O 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).

$$XR_{H_2O} = \frac{N_{H_2O}^{in} - N_{H_2O}^{out}}{N_{H_2O}^{in}} \tag{11}$$

Where $N_{H_2O}^{in}$ and $N_{H_2O}^{out}$ are the amount of H₂O in the inlet and outlet streams of steam reforming reactor, respectively.

Thus, the amount of H₂O 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 H₂ and CO₂ 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).

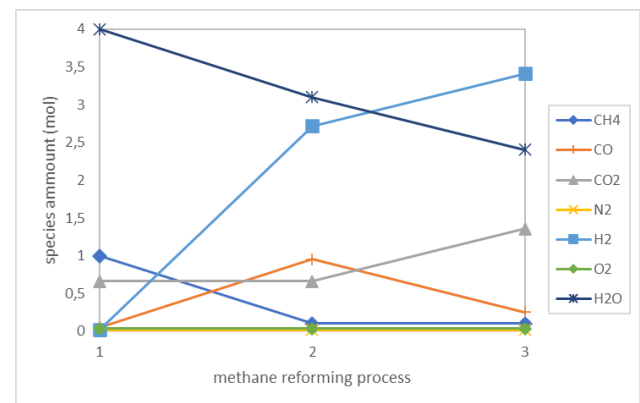


Fig.2: Amount (mol) of each species involved in methane steam reforming was at the x-axis, 1 = reagents input (N1 + N2 = N3); 2 = amount (mol) of each species at the steam reforming reactor outlet stream (N4), and 3 = amount (mol) of each specie at the water-gas shift reactor outlet stream (N5)

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 N₂ required is on third of the H₂ amount in the inlet stream. On the consumption column, it is observed that 26% of H₂ conversion (0.888 of 3.417 mols) on the outlet column is considered. It can be observed the amount of NH₃ 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
H ₂	3.415	0.888	0.000	2.527
N ₂	1.138	0.296	0.000	0.842
NH ₃	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).

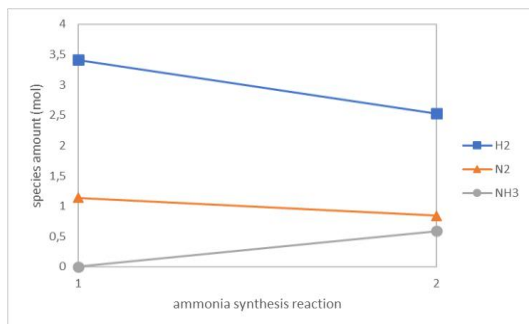


Fig. 3: Amount (mol) of each species involved at ammonia synthesis reaction, where at the x-axis, 1 = reagents input (N6 for H₂ and N7 for N₂); 2 = amount (mol) of each species at the reactor outlet stream (N8).

The synthesized amount of ammonia from step 2 (0.592 mol) is fed into step 3 to react with carbon dioxide and yields urea. The amount value for each species involved in step 3 is shown in Table 6. From the stoichiometry equation of urea obtention (Eq. 4), it is observed that NH₃/CO₂ is two but, as NH₃ is supposed to be fed in excess (ratio of 2.95), the amount of CO₂ in the inlet stream was established to be 0.201 mol (0.592/2.95). Such amount of CO₂ required is lower than the amount produced from step 1, indicating that the surplus amount of CO₂ can be stocked or applied for other purposes. Moreover, the assumed conversion of CO₂ is equal to 60%, justifying the value for CO₂ presented on the

consumption column (0.120 mol). On the outlet column, it is observed that all species are shown in the stream, leaving the process, and the amount of urea produced is equal to the amount of water (0.120 mol).

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

Species	Inlet	Consumption	Generation	Outlet
NH ₃	0.592	0.240	0.000	0.352
CO ₂	0.201	0.120	0.000	0.080
(NH ₂) ₂ CO	0.000	0.000	0.120	0.120
H ₂ O	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.

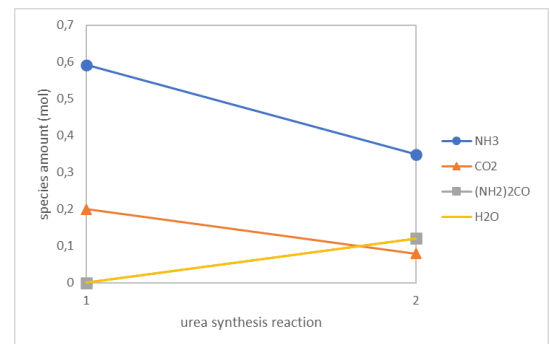


Fig.4: Amount (mol) of each species involved at urea synthesis reaction, where at the x-axis, 1 = reagents input; 2 = amount (mol) of each species at the reactor outlet stream (N11).

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, that 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.

Table 7. Streams molecular composition (%) at each process step

STREAMS							
Specie	N1	N2	N3	N4	N5	N6	
CH ₄	56.00	-	1.32	1.32	1.32	-	
CO	3.00	-	12.57	12.57	3.38	-	
CO ₂	37.00	-	8,71	8.71	17.90	-	
N ₂	1.00	-	0.24	0.24	0.24	-	
H ₂	1.00	-	35.83	35.83	45.02	100.00	
O ₂	2.00	-	0.47	0.47	0.47	-	
H ₂ O	-	100.00	40.87	40.87	31.67	-	
NH ₃	-	-	-	-	-	-	
(NH ₂) ₂ CO	-	-	-	-	-	-	

STREAMS						
Specie	N7	N8	N9	N10	N11	
CH ₄	-	-	-	-	-	
CO	-	-	-	-	-	
CO ₂	-	-	-	100.00	11.94	
N ₂	100.00	21.26	-	-	-	
H ₂	-	63.79	-	-	-	
O ₂	-	-	-	-	-	
H ₂ O	-	-	-	-	17.91	
NH ₃	-	14.94	100.00	-	52.24	
(NH ₂) ₂ CO	-	-	-	-	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 rector, 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 N₂, H₂, and O₂ initial enthalpy values were calculated as zero since, at 25 °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)
CH ₄	-74.84	-57.61
CO	-5.92	-5.32
CO ₂	-260.00	-249.20
N ₂	0.00	0.20
H ₂	0.00	0.19
O ₂	0.00	0.42
H ₂ 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 °C) and outlet (T = 850 °C) streams of the reforming reactor are shown. A significant variation in the values of the species being consumed (CH₄ and H₂O) and generated (H₂ and 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)
CH ₄	-57.61	-4.47
CO	-5.32	-91.51
CO ₂	-249.20	-244.28
N ₂	0.20	0.26
H ₂	0.19	36.68
O ₂	0.42	0.55
H ₂ 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 °C) and outlet (T = 630 °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 CO₂ 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)
CH ₄	-5.93	-5.89
CO	-95.55	-26.20
CO ₂	-250.16	-516.50
N ₂	0.18	0.14
H ₂	27.20	26.29
O ₂	0.38	0.31
H ₂ 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 H₂ from step 1, which was cooled to 5 °C, to be fed into the reactor. The inlet temperature for pure N₂ was also considered at 5 °C, and the temperature of the outlet current was considered to be 400 °C. Thus, the variation in the enthalpy values of inlet and outlet for H₂ and N₂ 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 H₂ and N₂ 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)
H ₂	-1.97	28.97
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 CO₂ was 40 °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 NH₃ was assumed to be 30 °C, indicating that the produced ammonia from step 2 must be previously cooled before fed into the urea synthesis reactor.

Table 12. Inlet and outlet Enthalpies (H) for species at ammonia synthesis reactor (Q5)

Species	Hin (kJ/s)	Hout (kJ/s)
CO ₂	-78.86	-31.12
NH ₃	-39.68	-21.51
CO(NH ₂) ₂	0.00	-38.41
H ₂ O	0.00	-28.44
TOTAL	-118.53	-119.47

After an estimate of the total enthalpy values of entry and exit for the units, the heat rate can be estimated, and the values are shown in Table 13.

As shown in Table 13, Q1 and Q2 values are positive, indicating that heat must be provided to the unit. Considering that the methane steam reforming reaction is endothermic and, therefore, it demands energy to be carried out, the obtained data is following the expected. A similar consideration can be done regarding Q3, Q4, and Q5 values: as the reactions taking place in the units are exothermic, i. e., release heat, those calculated values are negative, indicating that heat must be removed from the unit. It is essential to point out that the total inlet and outlet stream enthalpies, and therefore the unit heat duty is strongly related to the conversion of the reactants since if this parameter is low, the species enthalpy is accounted for both inlet and outlet streams. Such a situation can be noticed when taking into consideration the Q5 value, for instance: although the urea synthesis reaction presents a well-defined exothermic characteristic, the calculated amount of heat (per second) that must be removed from the unit is minimal (-0.94 kJ) when compared to the other units.

Table 13. Heat duty values calculated for the units of the process block flow diagram to produce urea from biogas

HEAT DUTY	VALUE (kJ/s)
Q1	62.93
Q2	284.10
Q3	-43.36
Q4	-110.51
Q5	-0.94

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.

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