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## EXERGOECONOMIC ANALYSIS OF AMMONIA PRODUCTION FROM RESIDUAL BAGASSE GASIFICATION

Rodrigo Oliveira Telini  
Daniel Flórez-Orrego  
Silvio de Oliveira Junior

Department of Mechanical Engineering, Polytechnic School, University of Sao Paulo, Sao Paulo, Brazil  
rodrigotelini@usp.br; daflorez@usp.br; soj@usp.br

**Abstract.** *This work aims to evaluate the potential to produce synthetic nitrogen fertilizers from sugarcane bagasse in São Paulo state. An ammonia synthesis plant with biomass gasification at atmospheric pressure is fed with the residues of a sugarcane mill in order to produce more valuable products than only electricity surplus and to partially or totally decarbonize the production of these compounds. Two scenarios were analysed, one considering a bagasse surplus from the mill and the other with no bagasse surplus, i.e. using it only to generate electricity to the grid. The analysis also includes a preliminary assessment of the collection and transportation of all the surplus bagasse to the ammonia plant. As a result, a maximum potential of ammonia production of about 1240 t<sub>NH<sub>3</sub></sub>/day would be possible, considering a radius of 20 km around the city of Pradópolis, in a scenario that would involve only the consumption of the surplus bagasse from two sugarcane plants. Moreover, the net revenues obtained were fourfold when using residual bagasse to produce ammonia, compared to the case in which only electricity surplus is sold by the sugar cane mill cogeneration plant. This fact is explained by a more profitable biomass upgrading and diversification of the marketable products. Particularly, the highest revenue corresponds to an ammonia plant configuration that uses residual bagasse as feedstock and natural gas as utility fuel in a combined cycle at the chemical ammonia plant utility system. Finally, the lowest unit exergy costs of ammonia and CO<sub>2</sub> produced correspond to the configuration that imports electricity from the grid to drive the processes of the ammonia chemical plant.*

**Keywords:** ammonia, bagasse, gasification, exergy, CO<sub>2</sub>

### 1. INTRODUCTION

The fertilizer industry is a fundamental economic activity, reportedly responsible for approximately half of the yield of global crops (ABISOLO, 2017). Brazil mostly imports the nitrogen fertilizers that it consumes (60%), which leaves the country more susceptible to variations of international prices of non-renewable resources, such as oil and gas, as well as to logistical and transportation costs at the ports (ABISOLO, 2018; PETROBRAS, 2014; HERNANDEZ et al., 2011). As the main compound for producing nitrogen fertilizers, currently, ammonia is mainly manufactured at large scale from the steam reforming process of natural gas. However, the utilization of inexpensive biomass has recently attracted attention, due to the potential use of residual biomass from agricultural and forestry industries.

Several studies have proposed the gasification process of biomass in order to use renewable syngas in the ammonia production, and so, reduce the greenhouse gas emissions (GHG) by 65%, compared to the conventional route (GILBERT, 2014). Actually, the use of biomass in ammonia production can even render the overall emissions negative, depending on the extent of the control volume analyzed (GILBERT, 2014; AHLGREN, 2008; SARKAR, 2011; TOCK, 2014). Different types of biomass, such as wood (GILBERT, 2014; SARKAR, 2011; TOCK, 2014; ARORA, 2017; ANDERSON, 2014), sugarcane bagasse (FLÓREZ-ORREGO, 2018), straw from cereal production and short rotation willow (*Salix*) coppice (AHLGREN, 2008), along with african palm rachis (BARRIOS, 2017) have been reported as suitable feedstock for producing ammonia from renewable resources in order to decarbonize the fertilizers sector.

Notwithstanding, since biomass residues are typically spread through a large area, as well as they have a low energy content per unit of volume produced, as well as a large moisture content, it is important to determine the most adequate location in order to avoid costly logistics and transportation. In this regard, the Southeast region of Brazil has a great potential for capitalizing on biomass wastes, as long as it concentrates about 65% of the sugarcane milling capacity of the country, being the Sao Paulo state the highest producer of sugar cane (CONAB, 2018). Sao Paulo state also counts on the existence of the Brazil-Bolivia gas pipeline (GASBOL), extending from the Mato Grosso do Sul state to the Parana state, which could be relevant for developing a gradual transition strategy from non-renewables to renewables energy resources in the foreseen ammonia production plants. For instance, an ammonia plant cogeneration system located in this scenario may consume electricity, natural gas or syngas (derived from bagasse gasification process). Accordingly, this work aims

to perform an exergoeconomy analysis of the ammonia production process at one or more ammonia production plants supplied with residual bagasse from nearby sugarcane mills and transported to the place where the ammonia plant settles.

## 2. METHODOLOGY

This section is divided into three main subsections. The first subsection describes the configurations chosen for the sugarcane mill cogeneration facilities. The second subsection refers to the discussion of the transportation stage of the residual bagasse from the cities where the sugar cane mill(s) settle to the place where the ammonia plant is localized; and the last section describes the process occurring at the ammonia unit operations.

### 2.1 Sugarcane mills and cogeneration setups

The first aim of the study was the obtainment of reliable data about the milling rate and localization of the sugarcane mills in the Sao Paulo state. To this end, data about the total sugarcane milling rates per city in the crop year 2018-19 was adopted, according to the report of the RCGI & GBIO (2019), whereas the location and number of the sugarcane mills per city was obtained from PROCANA (2016). Based on this data, an average sugarcane milling rate per plant and per city has been calculated, and the representative number of active facilities were classified in ten groups according to their range of milling capacity, as it is shown in Fig. 1.

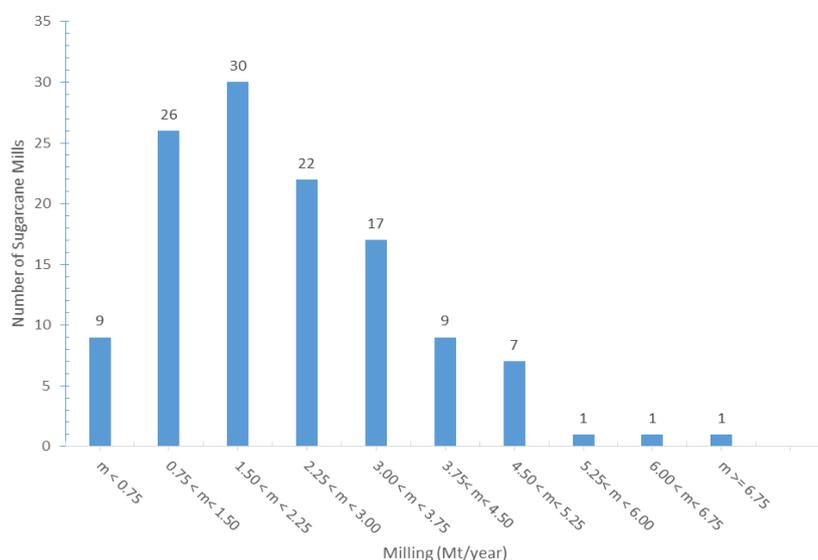


Figure 1. Number of representative sugar cane mills classified by milling capacity.

Next, the most common and other breakthrough configurations of cogeneration systems, pertaining to sugarcane mill facilities, were briefly reviewed. According to a literature survey of actual and simulated configurations, the steam pressure and superheated temperature conditions to the steam turbine may vary from 22 bar and 300°C up to supercritical water conditions (ENSINAS, 2009; PELLEGRINI, 2009). Considerable low pressure steam consumption at 2.5 bar (~196-250 t/h of steam for a typical 500t/h sugar cane milling capacity) is also required in order to meet the heating demands of the sugarcane mill. Pellegrini (2009) performed different simulations of sugarcane mill cogeneration plants based on either 42 bar/400°C, 67 bar/480°C or 100 bar/520°C steam conditions. The process steam consumption, considering thermal integration of the milling plant achieved 392 kg of vapor per ton of cane processed; whereas power consumption, without considering electrification but typically mechanically-driven plant components, reached 30 kWh per ton of processed cane. Two cogeneration layouts were studied: the first one is composed of a backpressure steam turbine (BPST) system and other relies on a condensing-extraction steam turbine (CEST), aiming to increase the amount of surplus electricity sold to the grid. Modesto (2016) proposed a condensing-extraction steam turbine operating at 80 bar and 500 °C. Pina et al (2017) compared various energy integration approaches used in two types of sugarcane mills (annexed and autonomous facilities), assuming superheated steam conditions as high as 100 bar and 530 °C in a backpressure steam turbine. Meanwhile, Guerra (2014) compared the advantages of using either reheating or regeneration systems in condensing-extraction steam turbines operating at 67bar/480°C and 100bar/520°C. Finally, according to CALDEMA (2019), most of the boilers in operation in sugarcane mills located in the Sao Paulo state operates at pressures varying between 42 bar and 67 bar, and superheated steam temperatures ranging from 420 to 530°C.

Based on these upper and lower bounds of the operation parameters of the cogeneration systems in sugarcane mills found in the literature, the suite Steam Pro® of the Thermoflow® software has been used to simulate ten different

configurations of cogeneration system, referring to each scale of the classification shown in Fig. 1. Thermoflow® is one of the most reliable and widespread tools, chiefly thanks to its comprehensive library of commercially available turbomachinery, and its capabilities of simultaneously performing thermodynamic, equipment sizing and economic assessments from simple gas turbine to complex Rankine and combined cycles, operating at both nominal and partial load.

It is worthy to notice that, depending on the aim of the overall production system, the totality of the bagasse derived from the milling process in the sugarcane mill could be used only to produce surplus electricity to the grid, as it is currently performed. However, in order to analyze the thermodynamic, environmental and economic benefits of upgrading the residual bagasse to value-added products (*e.g.* fertilizers), it may be rather considered that the residual bagasse (*i.e.* after the sugarcane mill energy demands have been already met) could be destined not to produce surplus electricity, but transported and fed to a gasification upgrading process in one or more ammonia production plants. For instance, according to Flórez-Orrego et al (2015), in a typical 500 t/h sugarcane mill, up to 5.3% of the total sugar cane mass flow rate entering the mill would end up as residual bagasse, available for biomass waste upgrading, such as biofuels production purposes, as discussed further in Nakashima et al (2020).

Thus, in this work, two setups were considered. In the first one, the sugarcane mill cogeneration system was based on the works of Pellegrini (2009) and Burin *et al* (2015), and it considers a condensing steam turbine working in parallel with a backpressure steam turbine, as shown in Fig. 2. A bubbling fluidized bed biomass boiler (BFBBB), fuelled with 50% wet sugarcane bagasse, was used to generate superheated steam at 67 bar and 480°C. In this system, the total power generated is the sum of the sugarcane mill demand (30 kWh/tc) and the surplus electricity exported to the grid. Certainly, if all the bagasse from the mill is consumed at the BFBBB to generate the maximum electricity surplus, no residual sugarcane bagasse will be available for ammonia production, and, therefore, the latter scenario will be considered the reference case, *i.e.* when no biomass waste capitalization is intended.

In contrast, a second scenario considers that sugarcane bagasse is used only in an amount enough for attending both demands of process steam (392 kg<sub>steam</sub>/tc) and power (30 kWh/tc) of the sugarcane mill, whereas the remainder bagasse is exported for ammonia production purposes. As a result, the power generated for electricity export will be at the minimum. The simplified layout of this cogeneration unit is shown in Fig. 3 (PELLEGRINI, 2009; FLÓREZ-ORREGO et al, 2015).

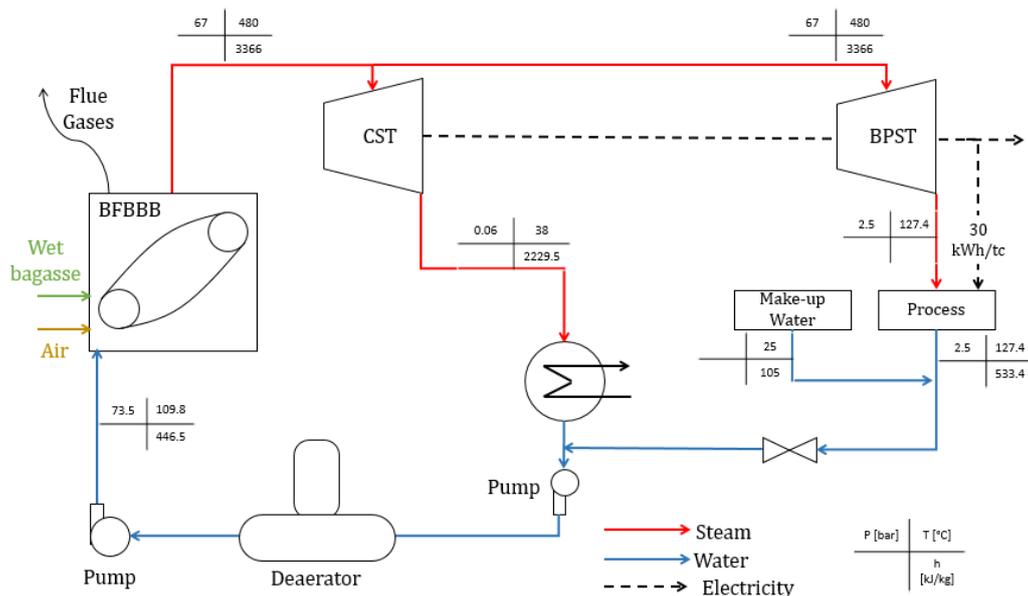


Figure 2. Sugarcane mill cogeneration system with a condensing steam turbine (CST) and a backpressure steam turbine (BPST) with superheated steam conditions at 67 bar/480°C, employed in a “no surplus bagasse” scenario.



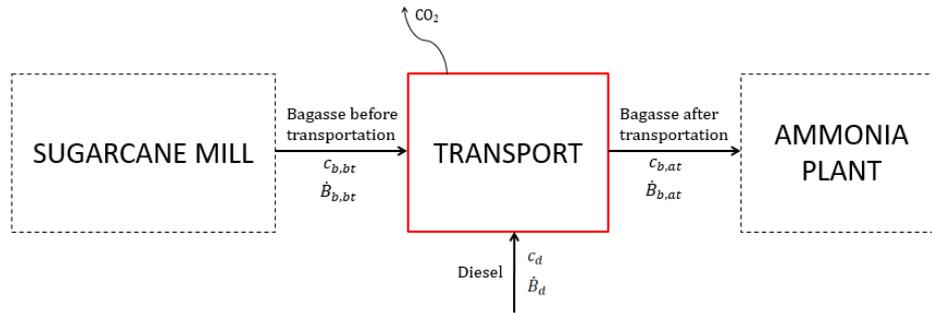


Figure 4. Control volume for the transportation stage of residual bagasse.

By performing the balance of exergoeconomic costs ( $C = c \times B$ , in kW) of the transportation stage, and recognizing that the useful exergy of the transported biomass does not virtually change with the transportation service (*i.e.*  $B_{b,at} = B_{b,bt}$ ), all the terms at both sides of the cost balance can be divided by  $B_{b,at}$ , so that the unit exergy cost of the transported bagasse ( $c_{b,at}$ ) can be calculated according to Eq. 2:

$$c_{b,bt} + c_d \frac{\dot{B}_d}{\dot{B}_{b,at}} = c_{b,at} \quad (2)$$

where the ratio ( $B_d/B_{b,at}$ ) can be defined as the specific exergy consumption ( $r_c$ ) according to the exergoeconomic methodology proposed by (FLÓREZ-ORREGO et al, 2015). This magnitude can be calculated by considering data of the truck (e.g. load, specific fuel consumption, number of travels necessary and number of trucks per travel), the properties of the diesel fuel and bagasse transported, and the distances from the  $i$ -th city to the ammonia power plant location, according to Eq. 3.

$$r_c = \sum_{i=2}^n \frac{\frac{b_{ch}^{diesel} * Spec\_Cons}{b_{ch}^{bagaço}} * Distance_i * N_i^{travel}}{Load * N_i^{truck}} \quad (3)$$

For deducing Eq. (3), it was considered that a truck has to perform a roundtrip, thus  $N^{travel} = 2N^{truck}$ . Moreover, the chemical exergy of bagasse has been calculated based on its moist ultimate composition, namely 46.7% C; 44.95% O; 6.02% H; 0.17% N and 0.02% S; with 50% moisture content (Flórez-Orrego, 2019), as well as through correlations proposed for calculating the moist bagasse lower heating value (LHV) (PARIKH, 2005, MICHAÏLOS, 2016) and the ratio of the specific chemical exergy to the lower heating value ( $\phi = b^{CH}/LHV$ ) (SZARGUT, 1988). All the data regarding the unit exergy costs and chemical exergy of diesel, wet bagasse, natural gas and electricity are shown in Table 2, in agreement with Szargut (1988) apud Flórez-Orrego et al (2014, 2015). Moreover, based on the travelled distance from the ammonia chemical plant to any sugarcane biorefinery, the gross cumulative CO<sub>2</sub> emissions, derived from both the cogeneration of electricity and the bagasse transportation, can be also calculated. However, the CO<sub>2</sub> emissions avoided at the ammonia chemical plant (*i.e.* captured in the syngas purification unit) represent an additional marketable byproduct and not a source of emissions.

Table 1. Unit exergy costs and specific chemical exergy of the various chemicals and feedstock involved.

	Natural Gas	Electricity	Diesel	Bagasse	Ammonia	Carbon dioxide
<b>Specific chemical exergy (kJ/kg)</b>	51,600	-	44,850	19,142	19,876	451
<b>Unit exergy cost<sup>1</sup></b>	1.1167	1.7956	1.0308	1.1610	--	--

<sup>(1)</sup> The unit exergy costs of the electricity, the diesel consumed in the truck, as well as the residual bagasse that leaves the sugarcane biorefinery are known by previous exergoeconomic analysis of the Brazilian energy and electricity mixes (FLOREZ-ORREGO et al, 2014, 2015). The unit exergy cost of the value-added products, namely ammonia and CO<sub>2</sub>, will depend on the configurations studied and the extent of decarbonization of the ammonia the chemical plant.

### 2.3 Ammonia plants configurations

The various ammonia plant configurations shown in Fig. 5 rely on the concepts developed by Flórez-Orrego (2018). The author compared different scenarios for producing ammonia either by using the conventional steam methane

reforming route or, alternatively, by means of the bagasse gasification route. However, since the objective is to evaluate the potential of partially or totally decarbonizing the fertilizers production, in this work, biomass is considered as the main feedstock for ammonia production purposes. Nonetheless, other energy resources, consumed in the utilities system of the ammonia plant, may comprehend both natural gas and electricity from the grid (Fig.5a and b). Actually, even though the syngas produced from the bagasse gasification processes is mainly intended as feedstock for the ammonia production plant, syngas could be also used as fuel in the cogeneration system thereof. Thus, one of the various ammonia production processes studied (see Fig. 5c) entirely depends only on the bagasse as energy resource. Moreover, likewise the cogeneration plant of the sugarcane mills, the utility system of the ammonia plant could be based on two different technologies, namely a Rankine and a combined cycle. In this regard, Figs. 5a-c summarize the five concepts of ammonia synthesis and utility systems studied: (a) biomass consumed as feedstock and natural gas used to fuel either a Rankine or combined cycle; (b) biomass consumed as feedstock, while the electricity from the grid is used to balance the power generated by a Rankine cycle, which also supplies the heating requirements by recovering the waste heat available along the chemical plant; (c) only bagasse is used as energy resource, so that the syngas produced can be used both as feedstock for ammonia synthesis and for fuelling either a Rankine or a combined cycle. In all the cases, ammonia is the main product of the bagasse upgrading process and carbon dioxide can be marketed for producing other chemicals (methanol, urea, food, polymers, enhanced oil recovery); whereas the purge, rich in hydrogen, nitrogen and methane could be further processed, flared or consumed as fuel for district heating purposes.

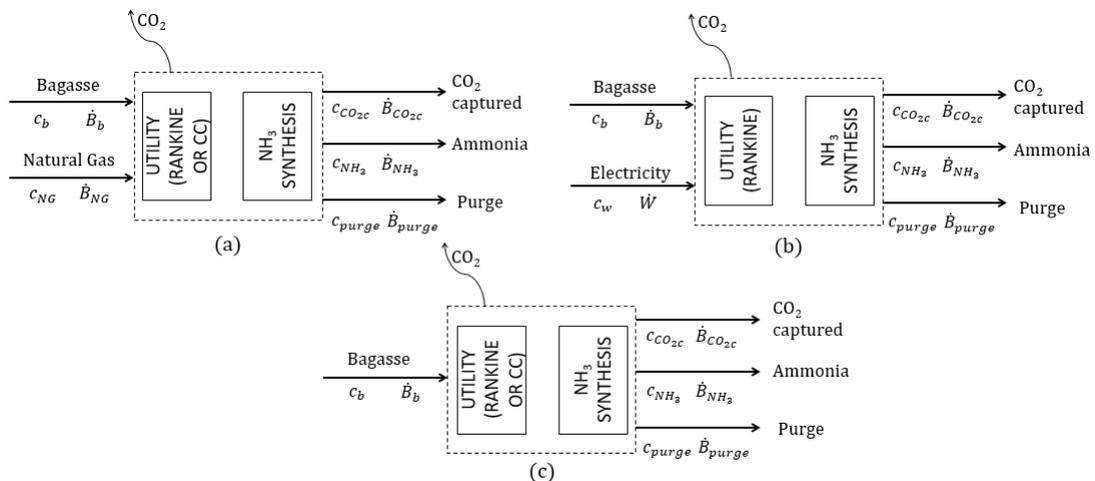


Figure 5. Different scenarios of ammonia chemical plants and their utility systems depending on the feedstock and fuel energy resources used: (a) bagasse and natural gas; (b) bagasse and electricity; and (c) bagasse only.

A closer look at the ammonia synthesis plant is given in Fig. 6. Therein, the bagasse has to be dried up to about 10% moisture content before it is chipped and fed to an indirectly heated gasifier operating at atmospheric pressure. Henceforth, a gaseous mixture (raw syngas) needs to be conditioned in order to adjust the  $N_2:H_2$  ratio to 1:3, suitable for ammonia production. The first step is a water scrubbing process, followed by an autothermal reformer and two high and low temperature water gas shift reactors (FLÓREZ-ORREGO, 2018). Next, the syngas goes through a purification process based on the physical absorption of  $CO_2$  by using a solution of dimethyl ether polyethylene glycols (DEPGs) at high pressure ( $\sim 30$  bar) (GUO, 2012). Finally, the  $CO_2$  is exported and the purified syngas is further compressed up to 200 bar and enters into the ammonia loop, wherein ammonia is produced via the Haber-Bosch process. In this process, the hydrogen-nitrogen mixture passes through a sequence of catalytic reactor beds with intercooling, whose main products are ammonia and purge gas. The former is condensed by using cooling water and a compression refrigeration system, while the latter can be further recovered due to its high  $H_2$  content ( $\sim 54\%$ ) (ISALSKI, 1982; KENT, 2012).

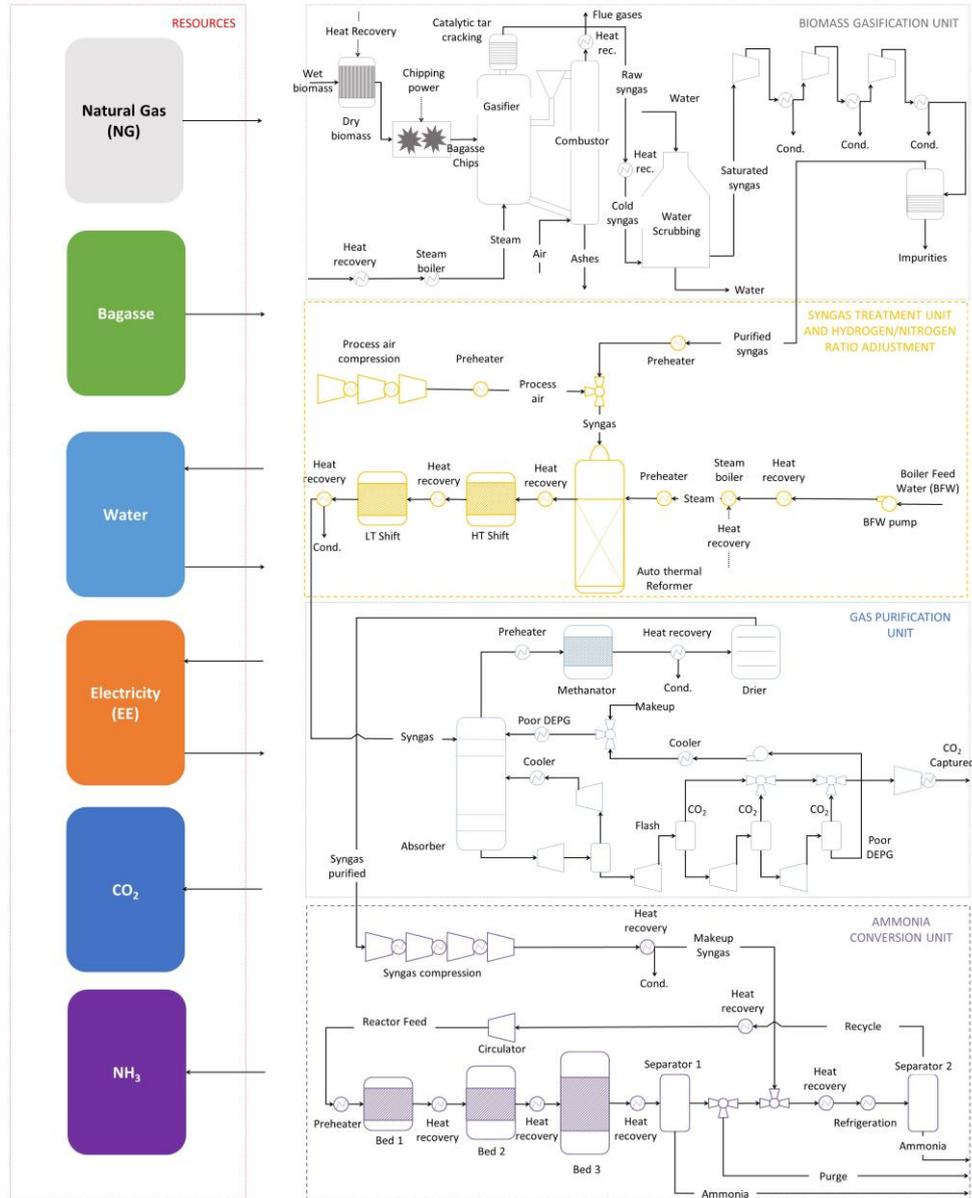


Figure 6. Process flowsheet of an ammonia production plant using bagasse gasification. Adapted from Flórez-Orrego et al (2019).

The unit exergy costs of the products of the ammonia chemical plant were calculated based on the equality partition criterion, which assigns the same cost to the main product (ammonia) and byproducts (marketable CO<sub>2</sub> captured and purge gas) (KOTAS, 1995; OLIVEIRA JUNIOR, 2013), according to Eq. 4. Meanwhile, the rational exergy efficiency of the ammonia plant, Eq. 5, is expressed in terms of the exergy consumed (bagasse as feedstock, electricity and natural gas as utility streams) and the ammonia plant products and byproducts.

$$c_{NH_3} = c_{CO_{2c}} = c_{purge} = c = \begin{cases} \frac{c_b \dot{B}_b + c_{NG} \dot{B}_{NG}}{\dot{B}_{NH_3} + \dot{B}_{CO_{2c}} + \dot{B}_{purge}} \\ \frac{c_b \dot{B}_b + c_w \dot{W}}{\dot{B}_{NH_3} + \dot{B}_{CO_{2c}} + \dot{B}_{purge}} \\ \frac{c_b \dot{B}_b}{\dot{B}_{NH_3} + \dot{B}_{CO_{2c}} + \dot{B}_{purge}} \end{cases}$$

(4)

$$\eta_{ex,NH_3 plant} = \frac{B_{NH_3} + B_{CO_2capt} + B_{purge}}{B_{feedstock} + B_{utility}} \quad (5)$$

Meanwhile, the prices of marketable CO<sub>2</sub> and ammonia, as well as the costs of the natural gas, electricity from the grid and bagasse were assumed according to Hotza (2008), Santos (2016), Flórez-Orrego (2017) and Marques (2009) apud Flórez-Orrego (2018). The price of electricity generated from bagasse was found in Lorenzon (2020). Those reference values are summarized in Table 2.

Table 2. Selling price and purchase cost of the various energy resources studied (Euro to Dollar: 1.14, Brazilian real to Dollar: 5.35, July 17<sup>th</sup>, 2020).

NH <sub>3</sub> (EUR/kWh)	CO <sub>2</sub> capt (EUR/kWh)	NG (USD/GJ)	EE from bagasse (BRL/MWh)	Bagasse (USD/t <sub>bagasse</sub> )
0.098	0.0084	9.7	200	20

### 3. RESULTS AND DISCUSSIONS

Figure 7 shows the results of the exergy efficiency of the cogeneration plants pertaining to the sugarcane mills at both “no residual bagasse” and “residual bagasse” scenarios for the different sugarcane milling capacities. For the sake of clarity, the right axis also shows the efficiency difference between the two scenarios. As it can be seen, the exergy efficiency for the “no residual bagasse” scenario ranges from 11.47% to 13.00%, whereas for the “residual bagasse” scenario, the exergy efficiency of the sugarcane mill cogeneration plant varies from 13.63% to 14.73%. In other words, as more residual bagasse is exported, the exergy efficiency of the cogeneration system of the sugarcane mill increases about 1.7-2.2%, this increase being higher at lower milling capacities.

As it has been implied earlier, the amount of residual sugarcane bagasse can be obtained from the efficiency of the cogeneration system at the “residual bagasse” scenario as being about 11.3-11.7% of the total sugarcane milling capacity, much higher than the value of 5.3% residual bagasse reported by Flórez-Orrego et al (2015), mainly due to the lower pressures and temperatures employed in that work for the superheated steam conditions (22 bar/ 300°C). Accordingly, an enhancement of the operating conditions (67 bar/480°C) is found to be capable of doubling the amount of residual bagasse, while still maintaining the supply of the process steam and power demands of the sugarcane mill. Moreover, since the potential of ammonia production considers a linear relation between residual bagasse and NH<sub>3</sub> produced, it is expected that the chemical plant yield will also double.

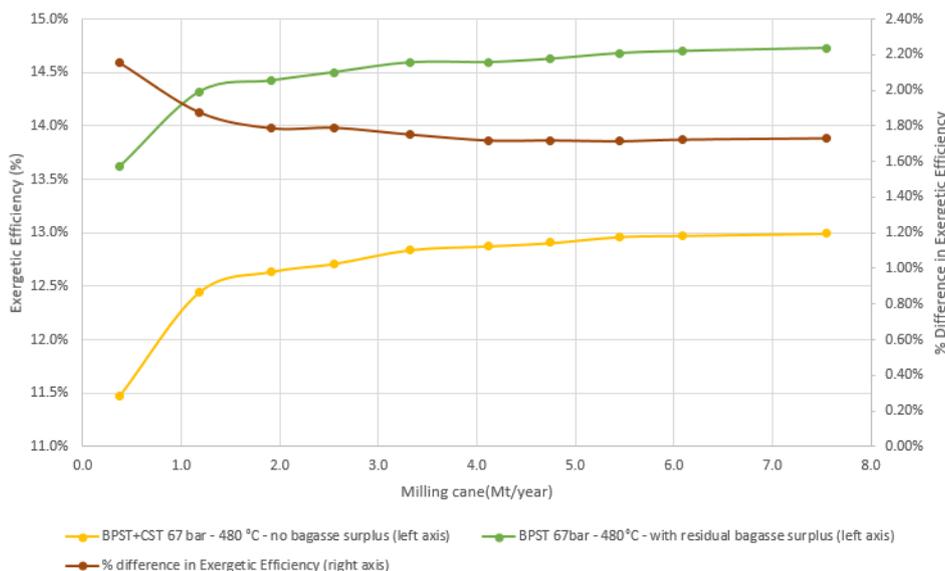


Figure 7. Exergy efficiencies of the cogeneration plants pertaining to the sugarcane mill for both the “no residual bagasse” and “residual bagasse” scenarios (left axis) and the difference (right axis) considering the total milling capacity of the sugarcane mill.

As earlier stated, the “no residual bagasse” scenario does not involve any bagasse transportation and gasification upgrading processes as its main product is electricity export to the grid. On the other hand, for the “residual bagasse” scenario, Fig. 8 shows the calculated ammonia production potential and percentage increase of the unit exergy cost of the residual bagasse transported as a function of the radius of transportation. The city of Pradópolis was chosen as the location

for installing the ammonia plant since it houses the sugarcane mill with the largest processing capacity in the world (SÃO MARTINHO, 2020).

In this way, for a conservative radius of 20 km around Pradópolis, the maximum potential of ammonia production is 1,235 t<sub>NH<sub>3</sub></sub>/day, with a percentage increase of only 0.01% of the unit exergy cost for the transported bagasse. This potential is equivalent to that proposed in the work of Flórez-Orrego (2018) and close to that used by Arora et al (2017). Notably, this result involves the bagasse transportation from only two sugarcane mills. The widening of this radius up to 100 km (HAMELINCK, 2005) or even 50-250 km (SUURS, 2002; JUNQUEIRA & WATANABE, 2017) may lead to a very high potential of ammonia production. Moreover, the percentage growth in the unit exergy cost of the transported bagasse is lower than 1% until 100 km, and reaches 4.75% when the radius is increased to 200 km. certainly, as the number of involved mills increases, many challenges related to the strategies of residual bagasse management may also arise. Thus, in this work, ammonia production potential for a scenario of radius of 20 km has been considered.

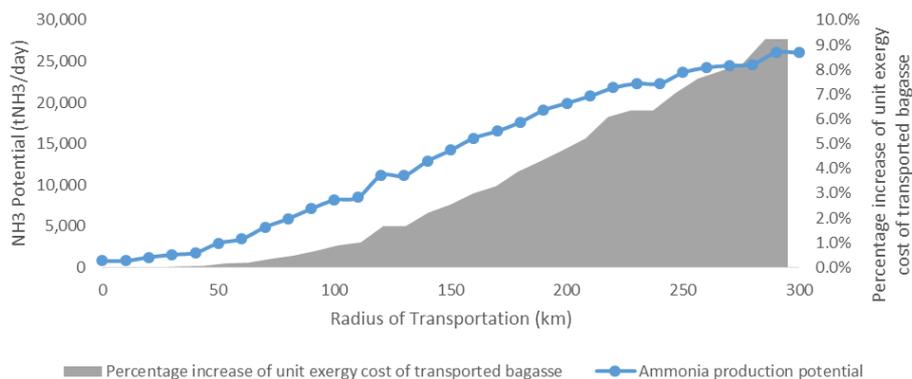


Figure 8. Ammonia production potential and percentage growth in the unit exergy cost of the transported bagasse as a function of the radius of transportation when setting Pradópolis city as the ammonia plant location.

After the residual bagasse has been transported to the location of the ammonia plant, the biomass suffers a series of energy conversion processes, as discussed in section 2.3. Since the exergy embodied in the various energy resources is continuously degraded as the number of unit operations increase, the irreversibility and the energy consumption associated to the ammonia products also increase, leading to a higher cumulative unit exergy cost of those compounds. In Table 3, some performance indicators and other consumption remarks of the ammonia production scenarios are compared with the reference case (no residual bagasse). Accordingly, the highest unit exergy costs were found for the configurations that use only biomass (bagasse as feedstock and syngas as utility fuel), while the lowest figures have been obtained for the configuration that uses bagasse as feedstock and electricity as utility import. This fact occurs mainly due to the nature of energy consumed. Actually, the use of electricity as utility import decreases the exergy destruction compared to the other cases, as the latter requires further energy conversion processes, such as combustion steps and further chemical transformations to supply the combined heat and power demands. Also, the use of syngas in the utility system implies higher usage of bagasse at the gasification step per unit of ammonia throughput in order to produce a syngas fuel with lower LHV compared to that of natural gas. The gasification process, its preparation steps and the syngas compression unit (shown in Fig. 6) are highly power-intensive, accounting for a quarter of the total power consumption of the plant (FLÓREZ-ORREGO, 2018). Furthermore, this specific higher usage of residual bagasse is reflected in the amount of ammonia produced and CO<sub>2</sub> captured. In fact, the total amount of ammonia produced and CO<sub>2</sub> captured when bagasse is used as the only energy input to the ammonia chemical plant is between 9.4 and 18% lower, depending on the utility system adopted (Rankine or combined cycle).

Table 3. Performance indicators and other economic remarks of the ammonia production scenarios compared to the business-as-usual (no bagasse surplus) case.

	Utility fuel	Syngas	Syngas	Electricity	Natural gas	Natural gas
	Cycle	Rankine	Combined	Rankine	Rankine	Combined
<b>Correspondence to Fig. 5</b>		5c	5c	5b	5a	5a
<b>Ammonia plant configuration</b>	<b>Unit exergy cost of products (kJ/kJ)</b>	3.1772	2.7165	2.4492	2.6709	2.4800
	<b>Exergy rational efficiency (%)</b>	36.40	42.65	48.16	43.26	46.72
	<b>NH<sub>3</sub> produced (t/day)</b>	1013	1125	1235	1235	1235
	<b>CO<sub>2</sub>capt (t/day)</b>	2537	2815	3091	3091	3091
	<b>NH<sub>3</sub></b>	10.60	11.80	12.90	12.90	12.90
	<b>CO<sub>2</sub>capt</b>	0.05	0.06	0.06	0.06	0.06
	<b>Natural Gas</b>	-	-	-	-1.40	-0.59
	<b>EE from the grid</b>	-	-	-1.01	-	-
<b>Incomes and Expenditures (USD/tc)</b>	<b>Cost of opportunity of EE surplus from bagasse</b>	-4.91	-4.91	-4.91	-4.91	-4.91
	<b>Diesel cost</b>	-0.01	-0.01	-0.01	-0.01	-0.01
	<b>Incremental revenue</b>	5.73	6.94	7.03	6.64	7.45

The incomes and expenditures of an ammonia production plant located in Pradópolis city are also shown in Table 3 (all values in USD/tc, considering a year of 200 days of production). The maintenance and operations costs, as well as the investment to build a new ammonia plant were not considered, accounting only for the price of the sellable products and costs of the energy inputs. It is noteworthy that, the cane purchase cost (already including the costs of growing the plant, and the use of fertilizer and insecticides on the soil), as well as the incomes from selling the ethanol and sugar produced are common for both scenarios, namely the business-as-usual (power only) and the bagasse upgrading process (ammonia and byproducts). Consequently, the main purpose of the economic analysis was the incremental comparison of revenues, including the cost of opportunity brought about by the electricity surplus that was not generated when ammonia and CO<sub>2</sub> were produced instead. In fact, since the electricity surplus at the cogeneration plant of the sugarcane mill decreased by 25% at the expense of the additional production of ammonia and marketable CO<sub>2</sub>, the “residual bagasse” scenario incur an opportunity cost of 4.91 USD/tc. Notwithstanding, the use of bagasse for waste upgrading purposes opens an opportunity to produce a more diversified, value-added products, considering that the market value of ammonia is much higher than the electricity generated from sugarcane bagasse. Accordingly, positive values for the incremental revenues evince that producing ammonia via bagasse gasification retrieves higher revenues compared to only exporting electricity to the grid, as in the business-as-usual setup.

Moreover, a comparison between the five ammonia plant cases shows that the highest revenue corresponds to the case in which natural gas is used as utility fuel with a combined cycle. This occurs due to a lower usage of natural gas, compared

to the Rankine cycle configurations. Also, despite the fact that the use of electricity import as utility represents the highest exergy rational efficiency, the revenue in this case is only the second highest, 5.6% lower than the previous case. A similar trend is observed for the combined cycle-powered setup, even when syngas is used as the fuel in the utility system of the ammonia plant. All in all, the combined cycles are among the most attractive technologies for integrating the ammonia plant utility system in terms of incremental revenues.

As it concerns the incremental greenhouse gas emissions, it is worthy to notice that the direct biogenic emissions derived from the bagasse or syngas is consumption in the cogeneration plant of the sugarcane mill and the utility systems of the ammonia, respectively, are considered as neutral, as the carbon embodied in those fuels has been seized by the cane in its growing process. Accordingly, Table 4 shows only the direct (i.e. due to burning) and indirect (i.e. due to the supply chain) emissions of CO<sub>2</sub> for the main energy inputs to the ammonia production plant. The avoided CO<sub>2</sub> (captured at the syngas purification unit) and the incremental CO<sub>2</sub> balance for each ammonia plant configuration are also reported. Strikingly, the avoidance of large emissions at the ammonia production plant was responsible for a net depletion rate (i.e. incremental negative emissions per tc processed) for the whole production process. More interestingly, the incremental CO<sub>2</sub> balance is the best when syngas is used as utility fuel, in agreement with the main aim of this work and other research works, namely, pushing forward the decarbonization of the fertilizer production using readily available agricultural wastes (DOMINGOS et al, 2020, NAKASHIMA et al, 2020).

On the other hand, the direct emissions due to the usage of natural gas are the highest CO<sub>2</sub> emissions values by fuel source, which renders the natural gas as a utility fuel the worst in terms of incremental CO<sub>2</sub> balance. Notwithstanding, the combined cycle-powered ammonia plant configuration using natural gas is still a competitive alternative compared to its Rankine cycle-based counterpart (11% higher incremental CO<sub>2</sub> balance) and with only 7% lower incremental CO<sub>2</sub> balance compared to the scenarios of syngas-fuelled utility systems.

Table 4. Direct and indirect CO<sub>2</sub> emissions, biogenic CO<sub>2</sub> avoided and incremental CO<sub>2</sub> balance for each ammonia plant configuration (in tCO<sub>2</sub>/tNH<sub>3</sub>). EE, electricity; NG, Natural gas.

Ammonia plant configuration	Utility fuel	Syngas	Syngas	Electricity	Natural gas	Natural gas
	Cycle	Rankine	Combined	Rankine	Rankine	Combined
CO <sub>2</sub> emitted - direct		0	0	0	0.368	0.155
CO <sub>2</sub> emitted - indirect - EE import		0	0	0.024	0	0
CO <sub>2</sub> emitted - indirect - NG import		0	0	0	0.034	0.014
CO <sub>2</sub> emitted - direct - Bagasse transportation		0.001	0.001	0.001	0.001	0.001
CO <sub>2</sub> emitted - indirect - Bagasse transportation		2.91E-05	2.62E-05	2.38E-05	2.38E-05	2.38E-05
Biogenic CO <sub>2</sub> avoided		-2.503	-2.503	-2.503	-2.503	-2.503
<b>Incremental CO<sub>2</sub> balance</b>		<b>-2.502</b>	<b>-2.502</b>	<b>-2.478</b>	<b>-2.101</b>	<b>-2.333</b>

Consequently, a comparative assessment of the performance of various configurations in terms of (i) unit exergy cost, (ii) incremental operating revenues and (iii) incremental CO<sub>2</sub> balances, despite the fact of using natural gas as utility fuel in the combined cycle of the ammonia production unit, this scenario still shows the highest incremental revenue and the second lower unit exergy cost of the products. The main drawback of this setup is the incremental CO<sub>2</sub> balance compared to the other scenarios. However it must be born in mind that the overall incremental CO<sub>2</sub> emission balance is still negative, pointing to the fact that it may still compensate the fossil carbon emissions. In contrast, when electricity is used as the main utility import, both the lowest unit exergy cost and a relatively attractive result for incremental CO<sub>2</sub> balance are obtained, compared to the previous case, although the incremental revenue of this scenario was only the second highest. The proximity between these performance indicators suggests that both configurations could represent the most viable paths to produce ammonia via gasification, in order to simultaneously mitigate the CO<sub>2</sub> emissions and reduce the operating costs. These results also evidence the relevance of searching for new ways to improve both the efficiency and the environmental impact of the Brazilian electricity mix, as well as to explore more innovative approaches for the nitrogen fertilizers industry, considering that almost 60% the domestic fertilizer consumption still must be imported (FLOREZ-ORREGO et al, 2019). Actually, the sector is responsible for the highest deficit in bulk chemicals production in Brazil, which radically impacts the production and food security, and the economic sovereignty. Certainly, further developments on the biomass gasification process at large scale are still required, due to the complexity of this technology. Anyhow,

the biomass gasification is a promising route in order to generate more economically viable products, especially in the case of tropical countries with a still underexploited biomass valorization potential.

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