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Magali Christe Cammarota
Ofélia de Queiroz Fernandes Araújo

PRODUCTION, PROCESSING, DISTRIBUTION AND USE OF GAS WITH HIGH CO_2 CONTENT:

BIOGAS and Pre-Salt NATURAL GAS

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UNIVERSIDADE FEDERAL DO RIO DE JANEIRO

INSTITUTO NACIONAL DE TECNOLOGIA
INT
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FAPERJ
Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro

Atena
Editora
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Production, processing, distribution and use of gas with high CO^2 content: biogas and pre-salt natural gas

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The authors acknowledge the institutions that contribute to the maintenance and infrastructure of the laboratories involved in this book: Federal University of Rio de Janeiro, and National Institute of Technology.

The authors acknowledge the technical team from the laboratories and undergraduate students who contributed to carrying out the studies reported in this book.

Natural Gas is a determining component in the security of the Brazilian energy matrix. From their supporting role in the energy matrix in a scenario dominated by hydraulic energy to the situation where thermoelectric power plants are operating at full capacity, plants powered by natural gas stand as a solution with less environmental impact to support the transition to a low-carbon economy and sustainable development.

The increasing availability of natural gas in Brazil following the discovery of the Pre-Salt reserves justifies the role of gas-fired power plants as a bridge technology in the energy transition, supplying the expansion in energy demand while renewable sources scale up. Projections indicate that the situation should change in the following 10 years. Between 2020 and 2030, 41.5 GW of natural gas thermoelectric capacity would come into operation. Thus, natural gas thermoelectric capacity would jump from 9 GW to 55 GW in 2030, representing 19% of the total installed capacity (LOSEKANN et al., 2012)[1]. However, it must be added that the typical natural gas associated with oil from the Pre-Salt, in the largest exploration and production projects, has a high CO_2 content, that is, ranging from 8% to above 40% CO_2 in mol. Upgrading the Pre-Salt natural gas (PS-NG) poses technology challenges to ensure economic separation of large volumes of CO_2.

Like PS-NG, raw biogas has a high CO_2, averaging 40% mol of CO_2. It is produced by natural phenomena in swamps, oceans and fresh water, and by anthropogenic sources, such as flooded rice plantations, wastewater treatment, livestock waste treatment and landfills. In the low-carbon economy model for the energy industry, biogas produced by the anaerobic digestion of organic matter already has an important role in several countries (e.g., Germany, Sweden and the Netherlands). Biogas production, in addition to recovering energy from agricultural, industrial, and urban waste, offers the environmental benefits of mitigating the impact of the final disposal of solid waste and wastewater discharge into water bodies.

The traditional biogas pretreatment is the removal of hydrogen sulfide to use in boilers, and direct use in a power generator set adapted for use with diesel. However, without an advanced purification, its use in more sophisticated equipment (e.g., vehicle engines and microturbines) leads to a significant reduction in the useful life of the equipment, recently related to the presence of contaminants not regulated in the natural gas compliance specification.

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[1] Losekann, L.; Marreiro, G.A.; Ramos-Real, F.J.; Almeida, E.F. Efficient Power Generating Portfolio in Brazil: Conciliating Cost, Emissions and Risk. Discussion Paper 001l2012. http://www.ie.ufrj.br/images/pesquisa/pesquisa/textos_sem_peq/texto1505.pdf.

Upon upgrading, CO_2 is removed to produce biomethane, a biofuel licensed for use in equipment and installations that use processed natural gas (CO_2 content < 3%) as fuel. In developed economies, biogas is recognized as an effective way of dealing with excreta and waste, and plays a significant role in improving the energy structure, environment and health by replacing the use of fossil fuels, therefore reducing fossil carbon emissions in the atmosphere.

Therefore, the project was structured to meet the challenges of the biogas (renewable natural gas – RNG) and Pre-Salt natural gas (PS-NG) production chains, exploring synergies, aiming at co-digestion, co-processing and co-distribution and resulting in interchangeable use of RNG and PS-NG for the end user. The main challenge in using RNG and PS-NG is the separation and disposal of CO_2, the primary contaminant of these gases.

The project received the Support Program for Centers of Excellence (PRONEX). It used the existing chemical analysis infrastructure for monitoring CO_2 separation processes for PS-NG, located at the Center of Excellence in Natural Gas (CEGN), located in the UFRJ Technology Park. CEGN's central research groups in CO_2 separation for PS-NG conditioning are the H2CIN Laboratory (School of Chemistry/UFRJ, coordinated by professors José Luiz de Medeiros and Ofélia Q.F. Araújo), and the PAM (Chemical Engineering Program/ COPPE/UFRJ, coordinated by professors Alberto Cláudio Habert and Cristiano Piaseck Borges).

In this project, H2CIN and PAM recognize the chemical similarity of raw biogas and raw Pre-Salt natural gas, notably in aspects related to CO_2 removal for product specification – respectively RNG and PS-NG – and expand CEGN's lines of interest to include the production, processing and utilization of biogas (RNG), sharing the available laboratory infrastructure. The project combines the excellence achieved in CO_2 processing and separation (Professors José Luiz de Medeiros, Alberto Cláudio Habert, Cristiano Piaseck Borges and Ofélia Q. F. Araújo) with process dynamics and control (Professor Argimiro R. Secchi) in the context of natural gas, in addition to the experience in waste biodigestion acquired by the Environmental Technology Laboratory (coordinated by Professor Magali C. Cammarota) and the Air Pollution Control Laboratory (coordinated by Professor Claudinei de Souza Guimarães) of the School of Chemistry at UFRJ, and to the recognized competence from the National Institute of Technology (INT) in gas analysis and certification, and in the development of methane and CO_2 conversion technologies (Dr. Fabio Bellot Noronha). Added to this unique arrangement of excellence is the participation of the Center for Research in Engineering Systems and Management (GESTORE/ Polytechnic School/ UFRJ), coordinated by Dr. Cláudia Morgado, contributing to the development of sustainability indicators. Additionally, the project integrates three emerging research groups, namely researchers from: (i) Xerém Campus at UFRJ (Xerém/UFRJ); (ii) Federal Institute of Rio de Janeiro (IFRJ), and (iii) Federal University of São Paulo (UNIFESP). As a result of the added competencies, the Project was conceived in three vertical and two transversal research lines.

VERTICAL LINE 1: RNG production – pretreatment and biodigestion

This line of research is based at the Environmental Technology Laboratory of the School of Chemistry at UFRJ, and emerging researchers from Xerém/UFRJ, IFRJ and UNIFESP. The research activities in this line are presented in Figure 1.

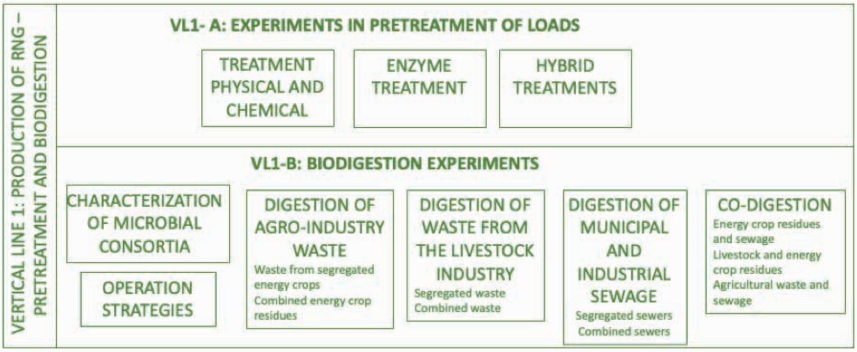

Figure 1 - Vertical line 1: RNG production – pretreatment and biodigestion.

VERTICAL LINE 2: Conditioning of RNG and PS-NG with high CO_2 content

Vertical Line 2 has its nucleus at CEGN, through the actions of the H2CIN and PAM research groups, which have pilot plants for CO_2 separation by chemical absorption, separation by permeation in membranes and contactors. Figure 2 presents the research activities in the line, aimed at developing PS-NG and RNG conditioning technologies, using an experimental (pilot plants) and computational (modeling and simulation) approach. In the computational approach, models of special CO_2 separation operations are developed – membranes, contactors, absorption columns and CRIODEX – on the MATLAB platform with calibration via literature data and pilot plants, in addition to the development of extensions to commercial simulators (ASPEN HYSYS).

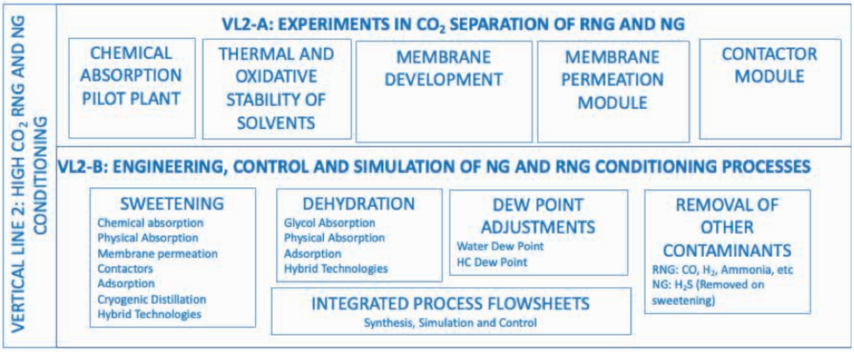

Figure 2 - Vertical line 2 – Conditioning of RNG and PS-NG with high CO_2 content.

VERTICAL LINE 3: Use of CH_4 and CO_2 as raw materials

Vertical Line 3 explores alternative CO_2 conversion routes on the experimental front (conducted at INT) and process engineering front using the ASPEN HYSYS simulator (developed at CEGN). The activities of Vertical Line 3 are shown schematically in Figure 3.

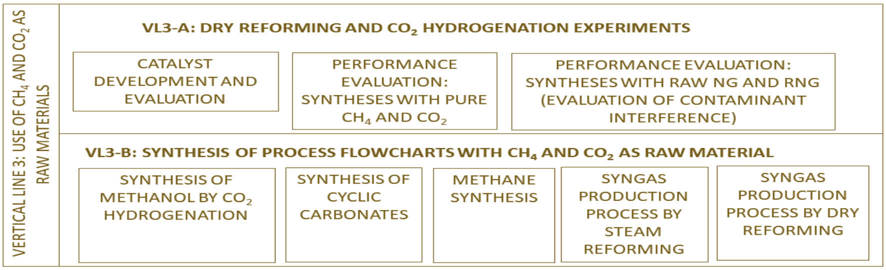

Figure 3 - Vertical line 3 – Use of CH_4 and CO_2 as raw materials.

TRANSVERSAL LINE 1: Characterization of PS-NG, RNG and process streams

The activity of developing inferential estimators for monitoring and controlling processes in the RNG and PS-NG production chain is carried out at the Software Development Laboratory for Process Optimization and Control (LADES) (Prof. Argimiro R. Secchi) and at CEGN (Prof. José Luiz de Medeiros, Survey of correlations between online primary measurements and offline measurements). The activities of Transversal Line 1 are presented in Figure 4.

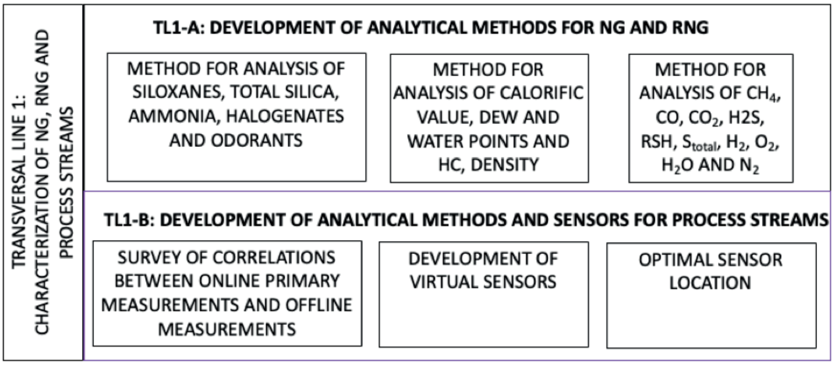

Figure 4 - Transversal line 1 –Characterization of PS-NG, RNG and process currents

TRANSVERSAL LINE 2: Integration and sustainability of RNG and PS-NG production chains

Transversal Line 2 employs environmental analysis tools such as Remote Sensing and Geographic Information System (GIS) and Life Cycle Analysis (LCA), combined to provide integrated methodologies capable of providing information and results to determine implementation strategies for energy crops aimed at reducing energy consumption and greenhouse gas (GHG) emissions. The activities of Transversal Line 2 are presented in Figure 5.

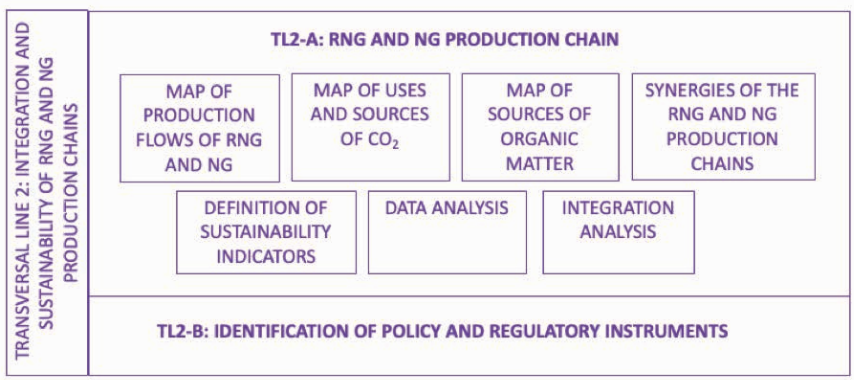

Figure 5 - Transversal Line 2 – Integration and sustainability of RNG and PS-NG production chains

The main objective of this edition is to disseminate studies conducted during the project in different lines of research. It aims to contribute to advancing scientific and technological knowledge and educating human resources in technologies for the production, processing, and use of biogas and natural gas, in addition to stimulating the energy potential of biomass and its conversion into biogas, as well as the development of emerging groups in the area of biogas and natural gas.

Our thanks to Editora Atena and to the authors who contributed to this edition.

Ofélia de Q. F. Araújo
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SUMMARY

CHAPTER 1

PRETREATMENT METHODS OF MICROALGAE BIOMASS FOR BIOGAS PRODUCTION

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ABSTRACT: Interest in the production of biofuels from microalgae biomass is growing. The benefits of microalgae and cyanobacteria over terrestrial plants are that they help reduce CO_2 emissions, can grow in nutrient-rich wastewater, have simple nutritional requirements, and have high productivity. However, low cell concentration in cultivation and the recalcitrance of raw algae biomass hinder methane yields. Most species of microalgae and cyanobacteria have a rigid cell wall made of layers of cellulose, hemicellulose, pectin, peptidoglycan, sporopollenin, and other resistant polymers. Many pretreatment methods have been proposed to break down complex cell wall polymers into smaller, soluble, and biodegradable molecules. However, the relationship between biomass solubilization and methane yield is not well defined. Furthermore, most studies do not provide an assessment of the energy balance of working conditions, with energy demand being a key challenge for biomass pretreatments. Mechanical, thermal, chemical, and thermochemical are all energy-intensive methods, either due to the energy required for heating biomass or the energetic cost of producing chemicals, or both. An in-depth analysis of the effects of chemical and thermochemical pretreatments of algal biomass for methane production suggests that less severe conditions should be preferred for microalgae biomass. Only enzymatic pretreatment and a few thermal pretreatments result in a positive energy balance. The large-scale implementation of pretreatment methods requires technological innovations to reduce energy consumption and its integration with other processes in wastewater treatment plants.

KEYWORDS: biogas, biomethane, microalgae, pretreatment.

1. INTRODUCTION

Climate change caused by increased greenhouse gas emissions, especially CO_2, has driven the search for alternative energy sources that could replace fossil fuels (Singh *et al.*, 2016). According to the IPCC (Intergovernmental Panel on Climate Change), global warming needs to be limited to 1.5 °C by 2030, or well below 2 °C by 2050, so that the impacts on Earth's ecosystems and human life are as minimal as possible (IPCC, 2018). Due to its dependence on fossil fuels, the energy sector is one of the biggest contributors to the release of CO_2 into the atmosphere. The Global Carbon Budget report revealed that in 2018, 36.6 Gton of CO_2 was emitted because of the use of fossil fuels (Friedlingstein *et al.*, 2019; Peters *et al.*, 2020). Thus, a transition to a low-carbon economy must happen in the next few years, which requires increasing the share of renewable energy sources in the global energy mix (Jackson *et al.*, 2019).

Anaerobic digestion is a complex biochemical process carried out by a mixed microbial population of anaerobic methanogenic archaea and bacteria that degrade organic matter. This consolidated technology for the biological treatment of waste and wastewater is applied to a wide range of organic materials (Khanal, 2008).

The anaerobic digestion process does not require high temperature or pressure. Its advantages include i) the ability to process a wide range of organic materials, solids, and liquids (concentrated or diluted); ii) the possibility of recycling or recovering nutrients from digestate; and iii) the possibility of recovering energy in the form of methane after biogas purification. The disadvantages include i) the requirement of skilled professionals to design, construct, and operate the reactor; ii) the need to control the temperature, pH, and other operational parameters; and iii) the sensitivity of methanogenic archaea to chemical compounds present in the raw material and imbalances in the reactor.

Anaerobic digestion has also gained prominence as a bioenergy production route because the biogas generated in the process could be used as a source of thermal and/or electrical energy. Thus, many biomasses, including algae biomass, have become as candidates for anaerobic digestion. For energy conversion, the main components of the biomass must be carbohydrates, proteins, fats, cellulose, and hemicellulose. Angelidaki and Sanders (2004) estimated that the methane potential from anaerobic digestion of lipids, proteins, and carbohydrates corresponds to 1,040 mL CH_4/g VS (volatile solids), 496 mL CH_4/g VS, and 415 mL CH_4/g VS, respectively.

Biogas is a colorless and, depending on its composition, odorless gas. Its typical composition is 50 to 75% methane (CH_4) and 25 to 45% carbon dioxide (CO_2), with smaller amounts of hydrogen (H_2), nitrogen (N_2), hydrogen sulfide (H_2S), oxygen (O_2), ammonia (NH_3), and carbon monoxide (CO). The energy component of biogas is methane, which, after biogas purification, can be used as fuel for industries, households, or transportation. The percentage of methane in biogas varies according to the chemical composition of the digested material. Operating parameters and imbalances in the anaerobic reactor also affect methane production.

To increase the methane yield from the anaerobic digestion of different biomasses, several authors have proposed pretreatment methods to solubilize recalcitrant molecules present in the biomass (Rodriguez *et al.*, 2015). Thermochemical pretreatment, using acidic or alkaline reagents, is a widely used method done prior to the energy conversion of raw materials such as lignocellulosic biomass (Amin *et al.*, 2017), algae biomass (Bohutskyi; Betenbaugh; Bouwer, 2014; Candia-Lomeli *et al.*, 2022), and waste activated sludge (Kim; Yu; Lee, 2013; Torres; Lloréns, 2008). Despite aiding biomass degradation and enhancing the availability of organic matter to the digesting microorganisms, there is no correlation between the increase in biomass solubilization and the increase in methane yield resulting from pretreatment. Therefore, a deeper investigation is needed of traditional and novel biomass pretreatments that benefit the anaerobic digestion, not only solubilization. The aim of this chapter is to present the most employed pretreatment methods and their effect on microalgae and cyanobacteria biomass (here called algae biomass, excluding macroalgae).

2. BIOMASS PRETREATMENTS

Although anaerobic digestion is a mature biotechnology to convert organic matter into biogas, most biomasses explored as energy sources are resistant to degradation. This results in less methane yield than the theoretical methane potential presented by those biomasses. To tackle this issue, many pretreatment methods have been investigated to enhance biomass biodegradability by microorganisms in anaerobic digestion (Córdova; Passos; Chamy, 2019; de Carvalho e*t al.*, 2020; Kannah *et al.*, 2021).

The main goal of the pretreatment is to disorganize the rigid structure of the cell wall responsible for the biomass recalcitrance. Microalgae have a complex cell wall often comprised of highly polymerized polysaccharides. Thus, most pretreatment methods seek to solubilize hemicellulose, depolymerize cellulose into smaller sugars, decrease crystallinity, and/or modify cellulose microfibrils by increasing its surface area. Other organic constituents like proteins can also be affected by the pretreatment, releasing smaller, easily degradable molecules.

Even though researchers have intensively studied some methods and implemented them at an industrial scale, like chemical and hydrothermal pretreatments, a universal pretreatment method for biomass does not exist. Cell wall composition varies greatly between the different microalgae species (Table 1). Some microalgae and cyanobacteria lack a rigid cell wall, having only a cell membrane, while others have many external layers protecting the cell (de Carvalho *et al.*, 2020; D’Hondt *et al.*, 2017; Kahnnah *et al.*, 2021). Additionally, most pretreatment methods are unspecific, which can lead to the formation of undesirable products that hamper methane production.

Table 1 – Cell wall components of biotechnologically relevant microalgae.

Microalgae Species	Cell Wall Components	References
Scenedesmus	Peptide-glycan layer; sporopollenin layer; fibrillar layer made of cellulose and hemicellulose; cell membrane.	de Carvalho *et al.*, 2019 Oliveira; Bassin; Cammarota, 2022 D'Hondt *et al.*, 2017 Spain; Funk, 2022 Weber *et al.*, 2022
Nannochloropsis	Sporopollenin layer; cellulose layer; fibrillar layer; cell membrane.	
Chlorella	Sporopollenin layer; fibrillar layer (cellulose and hemicellulose); cell membrane.	

Some research attempting to determine microalgae cell wall composition relies on sequential pretreatments to depolymerize polysaccharides and polypeptides, in addition to releasing lipidic layers protecting the cell wall. Although cellulose and hemicellulose are regarded as part of the cell wall of *Chlorella vulgaris*, little is known about the chemical structure of its other components. Aside from cellulose, Weber *et al.* (2022) found the presence of chitin- and pectin-like polysaccharides in the cell wall of *C. vulgaris*. These polyssacharides release monosaccharides like galactose, mannose, rhamnose, glucosamine, and uronic acids, identified in *C. vulgaris* hydrolysates (Weber *et al.*, 2022). Glucose, rhamnose, and mannose monomers were released from the cell wall of *Scenedesmus* sp. after enzymatic pretreatment (Spain; Funk, 2022). The cell wall of microalgae can be comprised of proteins, lipids, glycoproteins, and inorganic material (Ye *et al.*, 2023). In addition, the arrangement of those complex macromolecules within the cell wall layers may increase the complexity and recalcitrance of microalgae biomass.

No pretreatment method and/or condition is suitable for all biomasses. Furthermore, a pretreatment is unlikely to promote simultaneously all the desired results because it exerts different effects on the cell wall components (da Silva *et al.*, 2013). Thus, choosing a pretreatment is still a challenging step for the energetic conversion of biomass. This chapter presents and describes some of the most common pretreatments applied to algae biomass aimed at improving methane yields, with special attention given to chemical, thermochemical, and enzymatic pretreatments. Figure 1 is an overview of the classification of biomass pretreatment methods.

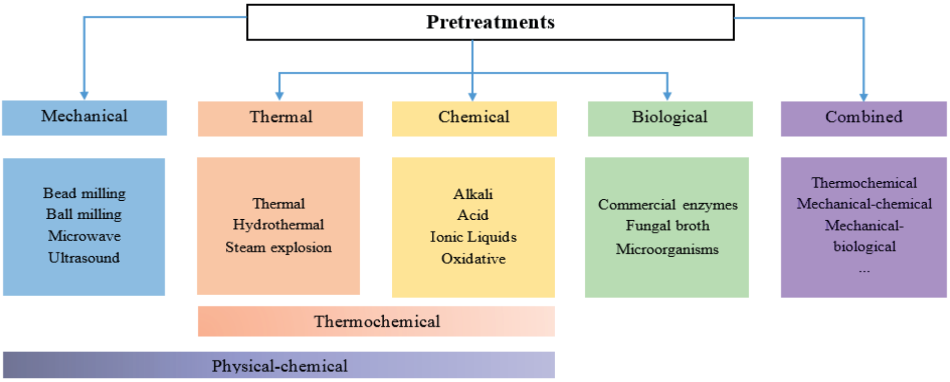

Figure 1 – Biomass pretreatment methods

2.1 MECHANICAL PRETREATMENTS

Mechanical pretreatment methods can rupture the cell wall structure by physical damage mainly. Bead milling is a simple mechanical pretreatment for microalgae and cyanobacteria cell wall disintegration. In this method, an algae suspension is added to a grinding chamber filled with ceramic beads (Schwenzfeier; Wierenga; Gruppen, 2011). Cell wall rupture by bead milling can release intracellular content, enhancing the availability of organic matter for anaerobic digestion.

Ball milling is conducted on either dry or wet biomass in a rotary drum filled with balls of different sizes and materials. This method reduces the particle size and significantly decreases the crystallinity of cellulose (da Silva *et al.*, 2013). Amorphous cellulose is more susceptible to degradation than the crystalline form; thus, the biomass becomes easier to digest after ball milling treatment.

Ultrasound breaks the cell wall from the inside out due to the cavitation produced by magnetic waves that penetrate the cells (Jankowska; Sahu; Oleskowicz-Popiel, 2017; Rodriguez *et al.*, 2015). Microwave pretreatment promotes an increase in the kinetic energy of water dipoles, causing the rupture of hydrogen bonds of the macromolecules, altering their structures and ultimately damaging the cell wall (Rodriguez *et al.*, 2015).

2.1.1 Advantages and disadvantages of mechanical pretreatments

Mechanical methods often produce a rise in temperature sufficient to break intermolecular bonds between polysaccharides. Thus, in addition to mechanical forces, the locally increased temperature contributes to cell wall weakening, resulting in increased biomass degradability. In the case of ball or bead milling, the temperature rises as a side result of the friction between the spheres and the biomass. In microwave pretreatment, the heating from the electromagnetic waves is enough to break hydrogen bonds.

The main disadvantage of mechanical pretreatments is the energy demand. To become economically feasible, the methane yield must compensate for the energetic and economic cost of the pretreatment. A balance between the energy demand and the recovered energy is hard to achieve for most pretreatments because mechanical equipment consumes extensive amounts of electricity. Since recalcitrant algae species usually need pretreatments with higher power input, those methods become economically unattractive to implement at large scales. Research has indicated that ultrasound is not recommended for protein-rich microalgae species because it may cause aggregation of proteins. Therefore, the overall recalcitrance of biomass is not eliminated (Oleszek; Krzemińska, 2021).

2.2 THERMAL PRETREATMENTS

Thermal pretreatments usually occur in temperatures ≤ 100 °C (thermal pretreatment) or very high temperatures with increased pressure (hydrothermal pretreatment) at different times (Rodriguez *et al.*, 2015). High temperatures solubilize organic matter and partially hydrolyze macromolecules, including carbohydrates, lipids, and proteins. Most studies on thermal pretreatment of algae biomass have been conducted with a temperature range from 55 to 170 °C (Kendir Çakmak; Ugurlu, 2020; Passos; García; Ferrer, 2013).

Wilson and Novak (2009) studied the effect of temperature on the degradation of carbohydrates, lipids, and proteins by applying thermal pretreatment to starch, cellulose, fatty acids, and albumin. The authors found that above 150 °C the degradation of proteins is accompanied by the generation of ammonia; unsaturated fats are converted to volatile fatty acids, such as acetic and propionic acid; and saturated fats form long-chain fatty acids (Wilson; Novak, 2009). These observations prove that high temperatures produce inhibitory compounds for the metabolism of anaerobic microorganisms. This reduces the digestibility of biomass treated under harsher temperatures compared to milder conditions (Mendez *et al.*, 2014).

Hydrothermal pretreatments are usually done at temperatures ≥ 160 °C. In these conditions, hemicellulose autohydrolysis takes place. Water at a high temperature disrupts the chemical bonds between the hemicellulose polymeric chain and its ramifications. Thus, acetic acid is formed locally and contributes to further hemicellulose depolymerization. Moreover, hydrothermal pretreatment can be catalyzed by adding chemicals like HCl, H_2SO_4, SO_2, and CO_2. Acid catalysts promote the hydrolysis of the hemicellulose fraction, increasing the yield of soluble sugars. Nevertheless, in addition to corrosion problems, acid catalysts can react with solubilized monomeric sugars to form inhibitors. More drawbacks related to adding chemicals will be discussed in the section on chemical pretreatments.

The chemical reactions that take place in steam explosions are very similar to hydrothermal pretreatment. Temperatures usually range between 160 and 220 °C, and biomass is hydrolyzed in the presence of steam. Steam explosion also relies on physical mechanisms to disrupt biomass constituents. As the temperature rises, there is also an increment in pressure. At the end of residence time, the reactor is then suddenly depressurized so that the quick pressure drop destroys the cell wall fibers and enhances biomass porosity.

The main factors affecting hydrothermal and steam explosion pretreatments are temperature, residence time, and the addition of catalysts. In hydrothermal pretreatment, the reactor heating and cooling steps should be as fast as possible to guarantee that most chemical reactions occur at the desired temperature. Duration of thermal pretreatment usually compensates for temperature, as higher temperatures demand shorter residence times and vice versa (Oliveira; Bassin; Cammarota, 2022). Biomass thermal hydrolysis can be improved by the addition of chemical catalysts, which also reduce the duration of pretreatment. Thermochemical pretreatments will be discussed in another section.

2.2.1 Advantages and disadvantages of thermal pretreatments

The main advantages of thermal pretreatments include high biomass solubilization and efficient release of monomeric sugars; previous biomass size reduction is not mandatory; the addition of chemicals is optional; and it is easy to implement at industrial scales.

At high temperatures, the degradation of lipids and proteins can lead to the accumulation of long-chain fatty acids and ammonia, respectively, both of which inhibit the metabolism of methanogenic microorganisms (Wilson; Novak, 2009). High temperatures also favor Maillard reactions between amino acids and reducing sugars, forming new complex molecules and decreasing protein solubility. Thus, the formation of inhibitory and recalcitrant compounds accounts for the lower digestibility of biomass pretreated at high temperatures, indicating the need to prioritize milder temperatures for thermal pretreatments (Solé-Bundó *et al.*, 2017). Other drawbacks include the economic costs derived from the intense consumption of heat and/or electricity for reactor heating.

Table 2 shows the increase in methane yield after the mechanical and thermal pretreatments of algae biomass.

Table 2 – Methane yields after mechanical and thermal pretreatments of microalgal biomass

Microalgae species	**Pretreatment method**	**Pretreatment conditions**	**Methane yields (NmL CH$_4$/g VS)**			**Reference**
			Without PT	With PT	Variation (%)	
Scenedesmus obliquus	Thermal	155 °C, 30 min	159	233	47	Ometto *et al.*, 2014
		165 °C, 30 min		259	63	
	Hydrothermal	155 °C, 5 bar, 30 min		242	52	
		165 °C, 7 bar, 30 min		384	141	
	Ultrasound	100 W, 10 MJ/kg TS, 8 min		243	53	
Chlorella sorokiniana	Thermal	145 °C, 30 min	169	206	22	
		165 °C, 30 min		173	2	
	Hydrothermal	120 °C, 2 bar, 30 min		173	2	
		165 °C, 7 bar, 30 min		318	88	
	Ultrasound	100 W, 20 MJ/ kg TS, 10 min		164	-3	
		100 W, 35 MJ/ kg TS, 20 min		244	44	
Scenedesmus sp.	Ultrasound	80 W, 129 MJ/ kg TS, 30 min	82	154	88	González-Fernandes *et al.*, 2012
	Thermal	80 °C, 25 min		129	57	
Chlorella sorokiniana	Ultrasound	220 W, 30 min	318	458	44	Córdova, Passos, Chamy, 2018
	Thermal	80 °C, 20 min		375	18	
Mixed microalgae biomass	Microwave	900 W, 64.4 MJ/kg TS, 3 min	118	210	79	Passos *et al.*, 2013
Mixed microalgae biomass	Microwave	900 W, 3 min, 70 MJ/kg VS	170	270	58.8	Passos *et al.*, 2014
Chlorella sp.	Thermal	65 °C, 4 h	211	297	41	Scarcelli *et al.*, 2020
Chlorella vulgaris	Hydrothermal	160 °C, 6 bar, 10 min		256	64	
Acutodesmus obliquus	Ultrasound	20 MJ/kg TS	156	174[a]	50	Gruber-Brunhumer *et al.*, 2015
	Bead milling	20 min		198[a]	72	
	Thermal	100 °C, 60 min		149[a]	29	

[a] Nm^3 CH$_4$/g COD (chemical oxygen demand)

2.3 CHEMICAL AND THERMOCHEMICAL PRETREATMENTS

Chemical methods have already been implemented on a large scale to pretreat waste activated sludge and organic wastes prior to anaerobic digestion. Thus, many researchers have been trying to adapt those methods for algae biomass.

Alkalis and acids are traditional reagents for chemical and thermochemical pretreatments; therefore, the solubilization of organic matter from multiple biomass sources by those methods has been extensively studied. Oxidizing agents and ionic liquids have gained attention as an alternative to traditional chemicals. The most influential factors in the chemical and thermochemical pretreatment of algae biomass are the concentration of the reagent, the concentration of the biomass, the temperature, and the contact time between the biomass and the chemicals (Oliveira; Bassin; Cammarota, 2022).

Table 3 shows the increase in methane yield after chemical and thermochemical pretreatments of algae biomass. For acid and alkaline pretreatments, temperatures above 100 °C usually allow good solubilization for 20 min to 2 h. At mild temperatures, the contact time seems to have little influence on the solubilization result (Solé-Bundó *et al.*, 2017; Mahdy *et al.*, 2014a).

Regardless of the type of alkali or acid chosen for the pretreatment, some authors have observed that the solubilization of biomass tends to stabilize or even decrease after a certain concentration of reagent (Du *et al.*, 2020; Penaud; Delgenès; Moletta, 1999). The solubilization increases as the pH moves toward higher values of either acidity or alkalinity. Species with a rigid cell wall, like *Chlorella* and *Nannochloropsis*, usually demand harsher pretreatment conditions. In this case, thermochemical pretreatment is preferable over chemical pretreatment at room temperature. On the other hand, chemical pretreatment seems to be indifferent for the anaerobic digestion of microalgae species with no cell wall because they are already easy to digest (Bohutskyi; Betenbaugh; Bouwer, 2014).

Table 3 – Methane yields after chemical and thermochemical pretreatments of microalgal biomass

Microalgae specie	Pretreatment method	Pretreatment conditions	Methane Yields (mL CH_4/g VS)			Reference
			Without PT	With PT	Variation (%)	
Oscillatoria tenuis	acid	H_2SO_4 4M, pH 2; room temp.	191	210	10	Cheng *et al.*, 2018
Microalgae biomass after lipid extraction	acid	HCl, pH 1, room temp.	104[c]	217[c]	109	Sposob *et* al., 2020
Mixed biomass of *Chlorella* sp. and *Monoraphidium* sp.	acid - thermochemical	HCl 0.05% m/m, pH 1, 80 °C, 2 h	78	142	82	Passos *et al.*, 2016
Isochrysis galbana	acid - thermochemical	H_2SO_4 0.2% v/v, 40 °C, 16 h	9	16	72	Santos *et al.*, 2014
Scenedesmus obtusiusculus	acid - thermochemical	HCl 3% m/m, 105 °C, 1.7 h	234	296	26	Rincón-Pérez *et al.*, 2020
Scenedesmus sp.	acid - thermochemical	H_2SO_4 0.1% v/v, 150 °C, 1 h	131	253	93	Marques *et al.*, 2018
Mixed microalgae biomass of *Desmodemus opoliensis* (47%) and others	acid - thermochemical	HCl 2 M, pH 0.3, 121 °C, 1 h	216	250	20	Juárez *et al.*, 2018
Spirulina platensis	alkali	NaOH 0.8 g/L, room temp., 12h	279	290	4	Du *et al.*, 2020
	alkali	NaOH 1.6 g/L, room temp., 12h		298	7	
	alkali	NaOH 4.0 g/L, room temp., 12h		295	6	
Thalassiosira weissflogii	alkali	NaOH 20 g/L, pH 13, room temp.	unavailable		20	Bohutskyi; Betenbaugh; Bouwer, 2014
Mixed microalgae biomass	alkali	530 mg N-NH_3/L, pH 9.5, 22°C, agitation (300 rpm)	136	162	19	Wang; Park, 2015
Mixed biomass of *Chlorella* and *Scenedesmus*	alkali - thermochemical	CaO 4% m/m, pH 12, 72 °C, 24 h	260	287	10	Solé-Bundó *et al.*, 2017
Scenedesmus obtusiusculus	alkali - thermochemical	NaOH 4 M, pH 10, 120 °C, 20 min	155	227	46	Candia-Lomeli *et al.*, 2022

[a] NmL CH_4/g COD.

a) Acid pretreatment

Acid pretreatment is a common pretreatment method for lignocellulosic biomass, and many researchers have adapted this type of pretreatment to microalgal biomass (Ariunbaatar *et al.*, 2014). Hemicellulose is an amorphous polymer susceptible to the attack of hydrogen protons during acid hydrolysis. The detailed reaction mechanism between the acid reagent and the hemicellulose polymer has been studied and can be found elsewhere (Miguez *et al.*, 2023).

The most common reagents for acid pretreatment are hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). Especially in the case of anaerobic digestion, accumulation of Cl^- and SO_4^{-2} may be harmful to the methanogenic microorganisms, and concentrated acid should be avoided. The conditions of acid pretreatment should be carefully chosen and monitored to minimize the formation of undesired degradation products. Severe pretreatment conditions may lead to a reaction between the acid and the released sugars. This decreases the number of available sugars after pretreatment and results in the formation of inhibitory compounds, especially when concentrated acid is applied.

The main inhibitory products formed during acid hydrolysis are furfural (FF), which originates from xylose degradation, and 5-hidroximetilfurfural (HMF) due to glucose degradation (Amin *et al.*, 2017; Bohutskyi; Betenbaugh; Bouwer, 2014). Inhibition of microbial growth and methanogenic activity has been reported at 2 g/L of FF or HMF in mesophilic or thermophilic anaerobic digestion (Ghasimi *et al.*, 2016). Acid pretreatment of mixed algae biomass of *Chlorella* and *Monoraphidium* sp. with HCl 1.25% at 80 °C for 2 h led to the formation of 3.8 mg/L of FF. When HCl concentration increased to 2.0%, FF concentration rose to 6.9 mg/L, and 1.3 mg/L HMF was also present (Passos *et al.*, 2016a). In this case, the degradation products at these concentrations did not impair anaerobic digestion. However, higher acid concentrations led to more FF and HMF formation.

Apart from the formation of inhibitors, acid pretreatment requires high-quality construction materials for the reactors to avoid corrosion, increasing the economic costs (Rodriguez *et al.*, 2015). Another drawback of this method is the need for pH adjustment before anaerobic digestion, because the anaerobic community is very sensitive to environmental changes and operates within a strict pH range, usually between 6.8 and 7.2.

b) Alkaline pretreatment

Alkaline pretreatment is a conventional method for solubilizing waste activated sludge prior to anaerobic digestion. Therefore, many studies rely on this method to propose a pretreatment for microalgae biomass (Oliveira; Bassin; Cammarota, 2022). Alkaline pretreatment causes saponification of uronic acids and esters from hemicellulose, resulting in the swelling of the fibers and surface area increase (Penaud; Delgenès; Moletta, 1999; Singh; Sharma, 2022). It also decreases the cellulose crystallinity, making it easier to break by hydrolytic enzymes from the microorganisms. Proteins can also be solubilized by alkaline pretreatment (D'Hondt *et al.*, 2017; Mendez *et al.*, 2013). These structural changes in biomass favor the access of the digesting microorganisms to organic matter and enhance methane production (Mahdy *et al.*, 2014a).

NaOH, KOH, CaO, and $Ca(OH)_2$ are the most commonly employed reagents for alkaline pretreatment. However, according to some authors, monovalent alkalis should be preferred over divalent alkalis, because the latter partially ionize in aqueous media (Oliveira; Bassin; Cammarota, 2022). In a novel approach, Wang *et al*. (2019) achieved positive results, improving methane yield using an ammonia-based alkaline pretreatment.

c) Ionic liquids

Ionic liquids (ILs) are organic salts that are liquid at temperatures < 100 °C. Those liquids are composed of an inorganic anion and an organic cationic counterpart. The thermodynamic and physical-chemical properties (like melting point, viscosity, density, and solubility) of ILs are very particular and vary greatly as a function of their components. Replacing the anionic, cationic, or both ions is enough to change the characteristics of ILs (Holm; Lassi, 2011). This allows for new ILs to be prepared for specific uses.

Since they do not release toxic by-products or dangerous gases, those chemicals have been studied as green solvents for many applications. Furthermore, the ability of cellulose solubilization by some ILs allows biomass pretreatment with the goal of cellulose recovery and further conversion into bioenergy (Hou *et al.*, 2017).

Solubilization of cellulose by ILs is related to the breakage of intra and intermolecular chemical bonds of the cellulose fibrils (da Silva *et al.*, 2013). ILs with chloride or formate anions are suitable for cellulose solubilization, especially because of the hydrogen bonds formed between the chloride anion and the hydroxyl group of cellulose. However, chloride-based ILs require temperatures > 70 °C for biomass pretreatment, while formate-based ILs have low stability (Holm; Lassi, 2011). More stable options are acetate-based or phosphate-based ILs. Regarding the cationic component, Holm and Lassi (2011) found that ILs with small cations are more efficient at dissolving cellulose.

Cellulose solubility in ILs depends on cellulose crystallinity, temperature, pretreatment duration, and initial cellulose concentration (Holm; Lassi, 2011). Moreover, the presence of water in the system may lead to the formation of inhibitory compounds, especially at high temperatures. The chemical structure of cellulose can be altered by chemical reactions, resulting in undesired derivatization. Thus, for biomass pretreatment, the ILs must be water-free and without any impurities (Holm; Lassi*,* 2011). After pretreatment, the cellulose fraction can be recovered by adding a counter solvent, such as water (da Silva *et al.*, 2013; Holm; Lassi, 2011).

Despite the potential for fractionation of microalgae biomass by ILs, they are mainly used for lipid recovery and high-value products. Since microorganisms in anaerobic digestion are not restricted to a class of molecules, the recovery of a specific biomass fraction may not be economically attractive for methane production.

d) Thermochemical

Both acid and alkaline pretreatments of microalgae biomass have been minimally explored at room temperature, with most studies conducted at temperatures around 50 °C and above, including > 100 °C. The combination of an acid or alkaline reagent and temperature makes it possible to disintegrate biomass in less time than chemical pretreatments at room temperature or thermal treatment alone (Bohutskyi; Betenbaugh; Bouwer, 2014; Mendez *et al.*, 2014; Penaud; Delgenès; Moletta, 1999; Solé-Bundó *et al.*, 2017).

Since hydrothermal pretreatment leads to autohydrolysis of hemicellulose, it is sometimes referred to as a thermochemical pretreatment, especially when a chemical catalyst is added. Autohydrolysis was discussed in the Thermal pretreatments section.

2.3.1 Advantages and disadvantages of chemical and thermochemical pretreatments

In general, chemical and thermochemical pretreatments lead to a high degree of biomass solubilization. However, their disadvantages include the cost of reagents, changes in the pH of the digester, accumulation of ions or degradation intermediates that inhibit methanogenic activity, corrosion of equipment, and high energy demand (Oliveira; Bassin; Cammarota, 2022). The disadvantages of ammonia-based pretreatments are mainly related to ammonia recuperation. However, ammonia recovery and recycling are feasible, and this step is crucial for anaerobic digestion because free ammonia may inhibit methanogenic activity.

After pretreatment, the greater organic matter available is expected to increase the methane yield compared to untreated biomass. Anaerobic digestion of different microalgae species after chemical and thermochemical pretreatment resulted in significant increases in methane yield compared to raw biomass (Marques *et al.*, 2018; Santos *et al.*, 2014). However, the scientific literature includes many examples in which increased solubilization of organic matter did not lead to a higher methane yield, especially when harsh conditions were chosen for chemical and thermochemical pretreatments (Bohutskyi; Betenbaugh; Bouwer, 2014; Cho *et al.*, 2013; Passos *et al.*, 2016a).

Therefore, the solubilization of organic matter does not clearly translate into the availability of readily digestible substrates for the anaerobic microorganisms. Most authors attribute this to the occurrence of Maillard reactions between the solubilized molecules, such as amino acids and reducing sugars (Penaud; Delgenès; Moletta, 1999; Solé-Bundó *et al.*, 2017). These reactions are favored by the high temperature and extreme pH of the pretreatments and result in the formation of recalcitrant molecules, leading to decreased biodegradability and low methane production (Penaud; Delgenès; Moletta, 1999).

Because they release the inner moisture of the originally solid biomass, chemical, thermal, hydrothermal, and thermochemical pretreatments result in a biomass slurry. This mixture of liquid and solid fractions does not need further separation for methane production. However, this biomass slurry is a complex mixture of soluble degradable and recalcitrant molecules. After pretreatment, the degree of biomass degradation is usually measured by the rise in soluble COD (chemical oxygen demand), which is chemically unspecific. Some works have assessed the final concentration of soluble sugars released by pretreatment (Passos *et al*., 2016). Other than that, little is known about the chemical composition of biomass slurry. This information could provide new perspectives on the relation between biomass solubilization and methane yields.

2.4 ENZYMATIC PRETREATMENT

Enzymatic pretreatment is an environmentally friendly process due to its low energy costs, high yield of fermentable sugars released from biomass under mild operating conditions, absence of corrosive problems, and few by-products (Yun *et al*., 2014). Since the enzymes target specific substrates, no inhibitory by-products are formed, thus preserving the anaerobic digestion microorganisms. However, it requires a longer residence time, in addition to the high cost of commercial enzymes (Bohutskyi; Bouwer, 2012).

When selecting the enzyme or enzyme mixture to be used, it is necessary to consider i) the chemical composition of the biomass, especially its cell wall; ii) the optimum operating conditions such as pH, temperature, exposure time, and enzyme/substrate ratio; and iii) the costs associated with using the enzymes (Córdova *et al*., 2018). Operating conditions must also be carefully chosen, as unsuitable conditions, especially pH and temperature, can deactivate enzymes due to denaturation. The enzyme/microalgae ratio also directly influences the efficiency of enzymatic activity.

To determine the relative importance of the parameters used for enzymatic hydrolysis, Shokrkar *et al*. (2017) evaluated the effects of microalgae biomass concentration, temperature, pH, and hydrolysis time on the enzymatic hydrolysis of a mixed culture of microalgae using α-amylase and cellulases. They determined that pH was the parameter with the greatest influence on the enzymatic hydrolysis process, followed by substrate concentration, temperature, and hydrolysis time.

The efficiency of enzymatic pretreatment is directly related to the enzymes used and the operating conditions. In the enzymatic hydrolysis of *C. sorokiniana* with cellulase (150 U/mL at 50 °C), Yin *et al*. (2010) reduced the total insoluble solids by about 30% after three hours of pretreatment.

The combined use of enzymes can improve the cell wall degradation of microalgae. In both cases, a cellulase mix can target cellulose and hemicellulose separately. Moreover, the cell wall of many microalgae species has outer layers comprised of biopolymers other than carbohydrates. Thus, a mix of cellulases, proteases, and other types of enzymes can benefit biomass degradation.

The pretreatment of *Chlorella vulgaris* with an enzyme mixture of lysozyme and sulfatase achieved a 98.6% permeability, while the permeability obtained using each enzyme individually was 7.6% for lysozyme; 1.2% for sulfatase (Gerken; Donohoe; Knoshaug, 2013).

Ometto *et al*. (2014) also reported the use of enzymes for the cell wall degradation of *Scenedesmus obliquus* and *Arthrospira maxima.* They found an increase in soluble COD depending on the enzymes used in the process. The use of α-amylase with *S. obliquus* showed no significant differences compared to biomass without pretreatment, while esterase and pectinase increased soluble COD by more than 30 mg/g total solids. The highest release of soluble COD was obtained with enzyme mixture preparations, which indicates that it is preferable to use enzyme cocktails to achieve greater solubilization of the insoluble compounds.

Table 4 shows the increase in methane yield after enzymatic pretreatment of different algae biomasses. Pretreatment of mixed biomass of *Chlorella* and *Scenedesmus* sp. by Avila *et al*. (2020) resulted in greater solubilization with an enzyme dose of 2%; however, anaerobic digestibility was lower than with pretreatments at a lower dose (1%). On the other hand, Mahdy *et al*. (2014c) found that decreasing enzyme dosages in *Chlorella* pretreatment concomitantly decreased hydrolysis efficiency and methane production.

Regarding biofuel production, Ciudad *et al*. (2014) observed an increase of approximately 100 mL CH_4/g VS after *Botryococcus braunii* pretreatment for 24 h with an enzyme extract. Hom-Diaz *et al*. (HOM-DIAZ *et al.*, 2016) evaluated the increase in biogas production by enzymatic pretreatment of a mixed microalgal biomass (predominantly *Oocystis* sp.). The authors evaluated the performance of commercial laccase and an enzymatic extract produced by *Trametes versicolor* fungi, both at a dose of 100 U/L. Results showed that when using commercial enzymes, methane yield increased by 20%, while pretreatment with fungal broth increased methane yield by 74% compared to non-pretreated biomass. The difference in results may be associated with the presence of other enzymes, radicals, and other mediators produced by *T. versicolor* in culture, achieving greater solubilization of the cells.

In addition to increasing the availability of soluble matter, enzyme mixtures can provide higher methane yields. Gruber-Brunhumer *et al*. (2015) obtained a 30.3% increase in methane yield after pretreating *Acutodesmus obliquus* with an enzyme mixture. Ehimen *et al*. (2013) found that an enzyme mixture of lipase, xylanase, α-amylase, cellulase, and protease, in the pretreatment of *Rhizoclonium*, resulted in the highest methane yield, with an increase of 31%. Passos *et al*. (2016a) achieved an 8–15% increase in methane yield from microalgae biomass after pretreatment with an enzyme mixture including cellulase, glucohydrolase, and xylanase.

Some studies have indicated that proteins play a crucial role in algae biogas production, since proteins account for 40–60% of the dry weight of algae. The addition of protease increased the solubilization of the substrate and had an incremental effect on the methane yield (Magdalena; Ballesteros; González-Fernández, 2018). The enzymatic pretreatment of *Chlorella vulgaris* and *Scenedesmus* sp. with protease increased the methane yield by 71% and 62%, respectively, compared to the pretreatment using a carbohydrase mixture (Mahdy; Ballesteros; González-Fernández, 2016). Similarly, pretreatment with *Porphyridium cruentum* protease increased solubilization (32.3%) more than the mixture of cellulase and carbohydrase, with a maximum methane yield of 230 mL CH_4/g VS, which showed an improvement of 77% (Kendir Çakmak; Ugurlu, 2020). A total biogas yield of 42.73 mL/g VS was obtained from the pretreatment of *Spirulina subsalsa* BGLR6 with a multi-enzyme mix containing protease, cellulase, and hemicellulase at a dosage of 10% for 24 hours (Dar; Phutela, 2020).

Apart from the high economic cost of commercial enzymes, the main challenge of this method is the diversity of microalgae cell walls. Some species of industrial importance are well known, e.g., Chlorella genus. However, little data is available about the chemical composition and ultrastructure of other species that have a potential for energetic uses and biorefinery platforms. Therefore, investigation is needed on various enzymes and their suitability for different types of microalgae (Bohutskyi; Betenbaugh; Bouwer, 2014; Bohutskyi; Bouwer, 2012).

Table 4 – Methane yields after enzymatic pretreatment of algae biomass

Microalgae Species	**Pretreatment Conditions**	**Methane Yield (NmL CH_4/g VS)**			**References**
		Without PT	**With PT**	**Variation (%)**	
Chlorella sp. and *Scenedesmus*	Mix of commercial enzymes, 1% E/S, 0.5 h, 37 °C, 100 rpm	124.2	447.5	260	Avila *et al.*, 2021
	Mix of commercial enzymes, 1% E/S, 0.5 h, 37 °C, 100rpm	124.2	640.9	416	
	Poligalacturonase, 1% E/S, 0.5 h, 37 °C, 100 rpm	124.2	652	425	
Chlorella vulgaris	Protease, 0.585 U/g TS, 3 h, 80 °C, 130 rpm	160.4	255.6	59	Mahdy *et al.,* 2014c
Acutodesmus obliquus	Enzymatic cocktail (cellulase, protease, β-glucanase, and xylanase), 10% E/S, 24 h, 37 °C	191.2	218	14	Gruber-Brunhumer *et al.,* 2015
Arthrospira máxima	Lipomod™ 957 (esterase, protease), 24 h, 50 °C	200[a]	1545[a]	672	Ometto *et al.*, 2014
Oocystis sp.	Cellulase, 1%, 37 °C, 6 h	188.6	203	7.6	Passos *et al.*, 2016
Oocystis sp.	Enzymatic cocktail (cellulase, glucohydrolase, and xylanase), 1%, 37 °C, 6 h	188.6	217.3	15.2	Passos *et al.*, 2016
Oocystis sp.	Commercial laccase, 100 U/L, 25 °C, 25 min, 100 rpm	83	100	20	Hom-Diaz *et a*l., 2016
Oocystis sp.	Laccase from *Trametes versicolor,* 100 U/L, 25 °C, 25 min, 100 rpm	83	144	74	
Scenedesmus obliquus	Depol™ 40 L (cellulase, endogalactouronase), 24 h, 50 °C	283.3[a]	1425[a]	403	Ometto *et al.*, 2014
Botryococcus braunii	Enzymatic extract of *Anthracophyllum discolor* 1000 U/L, room temperature, 24 h, 200 rpm	325.6	521	60	Ciudad *et al.*, 2014

[a] biogas yield, VS = volatile solids, TS = total solids, E/S = enzyme/substrate ratio.

2.4.1 Advantages and disadvantages of enzymatic pretreatments

Enzymatic pretreatment is a very promising method for cell wall disruption before anaerobic digestion. Some results show an increase of more than 100% in methane production from enzymatically treated microalgae. Moreover, since enzymes are substrate-specific, the formation of inhibitory molecules or undesired by-products, such as complex recalcitrant glycopeptides, is much less likely to occur. However, this same feature of substrate-specificity requires a tailored choice of enzymes or enzyme mix for a given microalgae species. For example, a single enzyme type may be insufficient for microalgae with lipid capsules or pectin layers. Due to the scarce information about the cell wall composition of microalgae, enzyme selection may take several tests to achieve the ideal choice and operation conditions. Thus, more research is needed to better understand this pretreatment.

Additionally, commercial enzymes are expensive, which hinders their application at demonstrative and industrial scales. Alternative methods should be developed to decrease the enzyme production costs. Residual agricultural biomass can be used for enzyme preparation through fermentative biotechnologies.

3. TECHNICAL AND ECONOMIC OBSTACLES TO ANAEROBIC DIGESTION OF MICROALGAE

Interest in the production of third-generation biofuels from microalgae and cyanobacteria biomass is growing. Microalgae biomass is very versatile for the production of high-value-added biochemicals and biofuels. Biogas/biomethane, biodiesel, bioethanol, biohydrogen, and biobutanol can be obtained from microalgae biomass depending on the route employed (Cavinato *et al.*, 2017; Wang *et al.*, 2022).

Microalgae and cyanobacteria have additional benefits over terrestrial plants. As photosynthetic microorganisms, they help reduce CO_2 emissions. Their ability to grow in nutrient-rich wastewater allows them to be cultivated without clean water or fertilizers (Rusten; Sahu, 2011; SALAMA *et al.*, 2017). Other advantages of algae biomass include their simple nutritional requirements and high productivity, since under suitable conditions, they grow 5 to 10 times faster than terrestrial biomasses (Kröger; Müller-Langer, 2012).

The first study of anaerobic digestion of microalgae was carried out by Golueke et al. (1957) who achieved a methane yield of 0.17–0.32 L CH_4/g VS from the microalgae *Chorella vulgaris* and *Scenedesmus*. Bench and pilot experiments, as well as theoretical calculations, have demonstrated the enormous potential of anaerobic digestion of microalgae for methane production, with a higher specific yield than other biomass sources (Mussgnug *et al.*, 2010; Zamalloa; Boon; Verstraete, 2012).

However, technical and economic obstacles to the anaerobic digestion of this type of biomass remain. Low cell concentration in cultivation and the recalcitrance of raw algae biomass hinder methane yields (Bohutskyi; Betenbaugh; Bouwer, 2014; Zabed *et al.*, 2020). Inhibition of anaerobic digestion may occur due to the accumulation of volatile fatty acids from lipid degradation or free ammonia from protein degradation.

In general, the concentration of cells in the cultures is low, less than 1 g/L in open ponds and between 2 and 6 g/L in closed photobioreactors (Roselet *et al.*, 2019). In practice, the low cellular concentration in culture media means that only a small part of the raw material is organic matter available to be converted to methane. This demands the adoption of harvesting technology to recover the cells, since they do not stick together due to electrostatic repulsion (Chatsungnoen; Chisti, 2019; Vandamme; Foubert; Muylaert, 2013).

The ions present in the culture medium surround the cells, forming a stable suspension. Therefore, separation strategies based on sedimentation of the biomass result in low efficiency. However, processes based on centrifugation, filtration, and membrane separation are generally more efficient but costly (Chatsungnoen; Chisti, 2019; Milledge; Heaven, 2013). According to some calculations, biomass harvesting can represent 30% or more of the total biomass production cost, making the process economically unviable (Sharma; Stal, 2013). There is an imperative need for cheap and easily scalable microalgae harvesting technology to upscale methane production from this biomass.

The methane yield from the mesophilic anaerobic digestion of various species of microalgae and cyanobacteria varies considerably from species to species and is affected by the chemical composition of the biomass and the rigidity of the cell wall. Some species have no cell wall and show high yields, for example, *Dunaliella salina* (325 mL CH_4/g VS, Mussgnug *et al*., 2010). Others, such as *Chlamydomonas reinhardtii*, have a cell wall composed mostly of glycoproteins, which is easily degradable and allows for good methane yields (263 mL CH_4/g VS, Mahdy *et al*., 2014b).

However, most species have a rigid cell wall made of layers of cellulose, hemicellulose, pectin, peptidoglycan, and sporopollenin, among other resistant polymers (D’Hondt *et al*., 2017; de Carvalho *et al*., 2020). These polymers make it difficult for anaerobic microorganisms to degrade the cells, consequently reducing methane yield, such as from *Scenedesmus obliquus* (130 mL CH_4/g VS, Zamalloa *et al*., 2012). Although microalgae cell wall composition is a key feature to choose the best operational conditions for pretreatments, chemical characterization of the cell wall is a complex task, especially given the number of microalgae species suitable for energy conversion. Thus, information in the literature is very scarce, but some efforts have been made with converging results.

Finally, a key challenge for biomass pretreatments is the energy demand. Most studies do not provide an energy balance assessment of the working conditions. Authors have collected data available in scientific literature to compare different methods (Oliveira; Bassin; Cammarota, 2022; Marques; Araújo; Cammarota, 2019). Mechanical, thermal, chemical, and thermochemical are all energy-intensive methods, either due to the energy required for biomass heating or the energetic cost of chemical production, or both.

Table 5 offers a comparison of the pretreatments discussed in this chapter. Oliveira *et al.* (2022) conducted an in-depth analysis of the effects of chemical and thermochemical pretreatments of algal biomass for methane production. The results suggest that less severe conditions are preferable for microalgae biomass. Considering the energetic cost of the assessed pretreatments, only enzymatic pretreatment and a few thermal pretreatments result in a positive energy balance (Oliveira; Bassin; Cammarota, 2022).

Table 5 – Characteristics of different pretreatment methods for methane production

Pretreatment	**Changes biomass composition**	**Substrate specific**	**Formation of inhibitors**	**Energy-intensive**	**Corrosive**	**Post-treatment adjustments***
Acid	+	-	+	-	+	+
Alkaline	+	-	+	-	-	+
Ionic Liquids	+	+	-	-	-	+
Ball Milling	-	-	-	+	-	-
Bead Milling	-	-	-	+	-	-
Microwave	+	-	-	+	-	-
Ultrasound	+	-	-	+	-	-
Thermal	+	-	+	+	-	-
Hydrothermal	+	-	+	+	-	-
Steam Explosion	+	-	-	+	-	-
Thermochemical	+	-	+	+	-	+
Enzymatic	+	+	-	-	-	-

*pH adjustment, biomass washing, chemicals recovery ...

+ = yes; - = no

CONCLUSIONS

Mechanical pretreatments are inefficient from the energy perspective because the energy generated from anaerobic digestion often does not offset the energy required for the pretreatment step. Thermal pretreatments are more efficient but energy-intensive and can lead to the formation of inhibitory and recalcitrant compounds with lower digestibility, indicating that milder temperatures are more suitable for thermal pretreatments.

Chemical and thermochemical pretreatments lead to a high degree of biomass solubilization but have high energy demand and result in the formation of inhibitors of methanogenic activity, in addition to the cost of reagents and corrosion of equipment. Although chemical pretreatments with NaOH are widely used, the efficiency of this method for algae biomass is questionable because most of the studies analyzed obtained an increase in methane yield of less than 20%. In contrast, there is a lack of data on acid pretreatment at room temperature.

In both chemical pretreatments at room temperature and thermochemical pretreatments, an increase in the solubilization of organic matter does not necessarily lead to a higher biogas yield, especially if the conditions applied in the pretreatment are more severe. The pretreatment conditions in which greater solubilization is achieved may be different from those that contribute to a higher methane yield. In other words, the relationship between increased solubilization and methane yield has not been well defined.

Enzymatic pretreatment is a very efficient method for cell wall disruption. However, the selection of enzymes depends on the cell wall composition of microalgae, requiring several tests to achieve the ideal enzyme blend and operation conditions. Furthermore, enzymatic pretreatment requires different types of enzymes and the production of enzyme complexes at a lower cost than commercially available enzymes.

Although algae biomass is a promising raw material for methane production, most species are resistant to degradation. Thus, some pretreatment methods have been intensively studied to provide a solution to the recalcitrance of biomass. Although some chemical and hydrothermal pretreatments have been implemented at an industrial scale, there is no universal biomass pretreatment method. It is impossible to name a pretreatment method and/or condition suitable for all biomasses. Thus, the pretreatment choice is still a challenging step for the energetic conversion of microalgae biomass, and more studies are needed to establish a viable pretreatment condition that uses algae biomass to obtain biogas/methane.

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CHAPTER 2

PRETREATMENT OF SECONDARY SLUDGE WITH COMMERCIAL ENZYMES AND MULTIENZYME EXTRACT FROM SOLID-STATE FERMENTATION BEFORE ANAEROBIC DIGESTION

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ABSTRACT: Anaerobic sludge digestion is an efficient and environmentally sustainable technology to produce heat, electricity, and vehicle fuel. Pretreatment of sewage sludge before its anaerobic digestion has been studied to optimize the hydrolysis, limit the steps in the anaerobic digestion process, reduce the sludge particle size, release simpler compounds for the later steps, and boost methane generation. Thermal, biological, physical, chemical methods, or a combination of these can be applied to pretreat the sludge, which will later undergo anaerobic treatment. Enzymatic hydrolysis is conducted by extracellular enzymes produced by the sludge biomass. However, this step of the anaerobic digestion process can be improved by adding exogenous enzymes to accelerate decomposition and using organic compounds to generate biogas. Commercial enzyme mixtures are more efficient in sludge hydrolysis; however, their application increases the cost of sludge treatment. On the other hand, the use of enzyme extracts obtained by solid-state fermentation is low cost, and filamentous fungi synthesize a wide range of enzymes from varied raw materials. Studies are still needed to understand the mechanism of action of enzymes in sludge degradation and obtain the best conditions for applying enzymes in the pretreatment of sewage sludge.

KEYWORDS: anaerobic digestion, biogas, enzymatic pretreatment, secondary sludge, solid-state fermentation.

1. INTRODUCTION

The activated sludge system for wastewater treatment is widely used throughout the world, due to its efficiency and robustness. The term activated sludge refers to the flocculent microbial mass formed when biodegradable wastewater is subjected to aeration. This process generally has the following system components: an aeration tank, a secondary decanter, and a system for recycling the settled flocs to the aeration tank (Metcalf & Eddy (Inc.), 1991). However, the intense production of biomass in the activated sludge system leads to the disposal of part of this biomass, called excess sludge. This sludge presents environmental risks; therefore, a correct form of treatment is necessary to reduce its environmental impacts.

Anaerobic digestion (AD) is an attractive technology for treating organic waste, generally used to stabilize organic matter in sludge and, thus, prevent or delay the release of chemical substances that can harm the environment (Romano *et al*., 2009). The AD process is divided into three steps (hydrolysis, acidogenesis, and methanogenesis). Due to the high content of solids and complex structure of the sludge, the initial hydrolysis step is a limiting step, as it takes a relatively long time (days), decreasing treatment efficiency and methane production and increasing the operational cost (Lv *et al*., 2010; Neumann *et al*., 2016).

The high cost of sludge management and the interest in alternative energy sources have amplified the attractiveness of pretreatment proposals to hydrolyze sludge, improving biogas production, reducing volatile solids, and increasing the quality of digested sludge. The existing techniques include thermal hydrolysis, physical processes dedicated to cell destruction and lysis, chemical processes, and biological processes based on the use of enzymes, as well as combinations of these pretreatments (Neumann *et al*., 2016).

Biological pretreatment using enzymes accelerates the hydrolysis process, reducing the sludge solubilization time to a few hours (Teo; Wong, 2014). More recent publications report the use of commercial enzymes for prior hydrolysis of sewage sludge, mainly lysozyme, proteases, amylases, and lipases (Roman *et al*., 2006; Yang *et al*., 2010; He *et al*., 2014; Xin *et al*., 2016, 2018; Kang *et al*., 2023). However, the large-scale application of commercial enzymes is not economically viable due to their high cost.

Biotechnological studies conducted by the UFRJ research group (Lima; Cammarota; Gutarra, 2018; Silva; Cammarota; Gutarra, 2022) have demonstrated that the Solid-state Fermentation (SSF) process could be an attractive alternative to obtain enzymes for pre-hydrolysis of sewage sludge. In this process, microorganisms develop on the surface and inside particles of solid raw materials, with little or no water not absorbed into the solid matrix. Furthermore, SSF presents little risk of contamination, requires less electricity, has lower operational costs, and may depend on the use of less complex manufacturing equipment (Pandey, 2003).

The microorganisms usually applied are filamentous fungi, capable of assimilating a wide range of substrates and synthesizing different types of enzymes. By producing enzymatic complexes containing different types of enzymes and using agro-industrial waste without pretreatment as raw material and source of substrates and nutrients, SSF can reduce costs for enzymatic pre-hydrolysis of sludge and facilitate anaerobic digestion.

2. SLUDGE GENERATED IN SEWAGE TREATMENT

Sludge is one of the by-products generated in Wastewater Treatment Plants (WWTPs) and can be in solid, semi-solid, or liquid form. Rich in organic matter and nutrients, it is generated in large volumes, has great polluting potential, and can be expensive to manage properly. WWTP sludge is mostly water, with 0.25 to 12% concentration of solids. It is conventionally called a solid phase to distinguish it from the liquid flow (sewage) being treated (Metcalf & Eddy (Inc.), 1991). Different types of sludge can be generated depending on the treatment technology applied; the more complex the flowchart of a WWTP, the greater the variability of the sludge produced. Figure 1 presents details of the treatment levels in a traditional wastewater treatment system and the different sludges generated in the plant.

To define the most appropriate treatment, it is important to know the variety of sludge that exists, considering its characteristics for adequate disposal and the volume reduction to be achieved. In the primary clarifier, primary sludge is generated, consisting of suspended solids from the sewage. Secondary or biological sludge is generated in biological treatment. Primary sludge is richer in lipids than secondary sludge, which has more nitrogen. However, large concentrations of nitrogenous and phosphorous organic material are commonly found in both primary and secondary sludge. Treatment before final disposal can be done with the primary sludge or secondary sludge separately or with both sludges together (mixed sludge) (Raposo *et al.*, 2011).

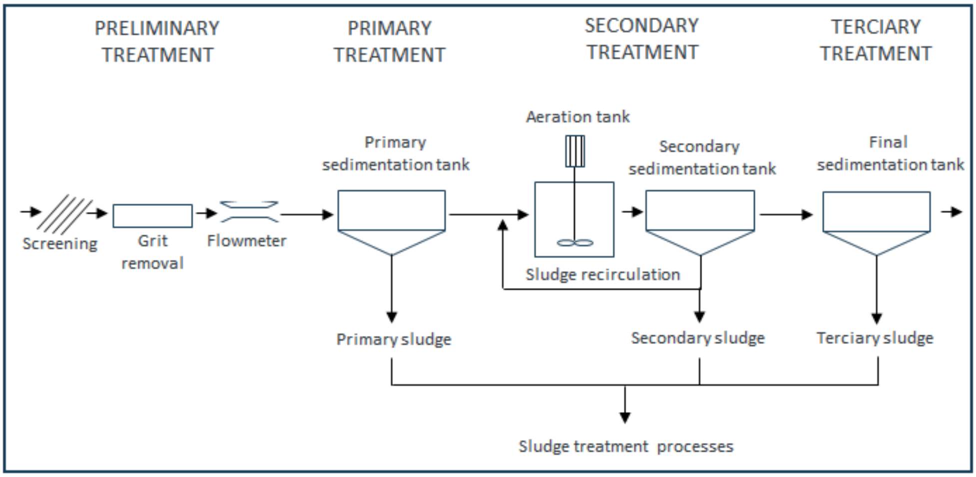


Figure 1 - Stages of a conventional wastewater treatment system and the different types of sludge generated.

Biological sludge from activated sludge systems is basically composed of microorganisms, mostly live bacteria, which grew using sewage as a substrate (Fernández; Sánchez; Font, 2005). Microbiological aggregates are held together in a three-dimensional gelatinous matrix by extracellular polymeric substances (EPS) (Flemming; Wingender, 2002), which are the main components of activated sludge flocs (Ye *et al*., 2011). These biopolymers can be formed by carbohydrates, proteins, nucleic acids, lipids, and humic substances. EPS normally have proteins and carbohydrates as their dominant components, in addition to lipopolysaccharides, glycoproteins, and lipoproteins (Shi *et al*., 2017). Several microorganisms can produce specific EPS, resulting in different exopolymers in the biological floc (Flemming; Wingender, 2002).

Sewage sludge can contribute to the proliferation of disease vectors; may contain heavy metals, persistent organic compounds, and pathogens; and has potential health and environmental risks (Fijalkowski *et al*., 2017). Thus, the final disposal of waste sludge becomes an environmental problem, and WWTPs are constantly looking for alternatives to solve the problem and for more efficient treatments.

The sludge must be removed to prevent it from accumulating in the treatment units or being released together with the final wastewater. Numerous sludge treatment alternatives are currently available. However, AD is certainly the most used, as in addition to being one of the best solutions for stabilizing and partially sanitizing the organic matter contained in sludge (around 2/3 of organic matter can be removed from the sludge), it can also produce renewable energy (through biogas formed in the process) (Khanal, 2008; Iacovidou; Ohandja; Voulvoulis, 2012).

3. ANAEROBIC DIGESTION AND BIOGAS PRODUCTION

Anaerobic digestion is a process that occurs in the absence of oxygen, in which several microorganisms convert organic matter into gases, mineral salts, and new cells. The main stages of the AD process are hydrolysis, acidogenesis, acetogenesis, methanogenesis, and sulfetogenesis (Chernicharo, 2007). The initial organic matter is degraded into simpler substances throughout these stages by different groups of microorganisms, which successively decompose the products of the previous stages (Al Seadi *et al.*, 2008). The simplified diagram in Figure 2 illustrates the metabolic routes and microbial groups involved in the AD process.

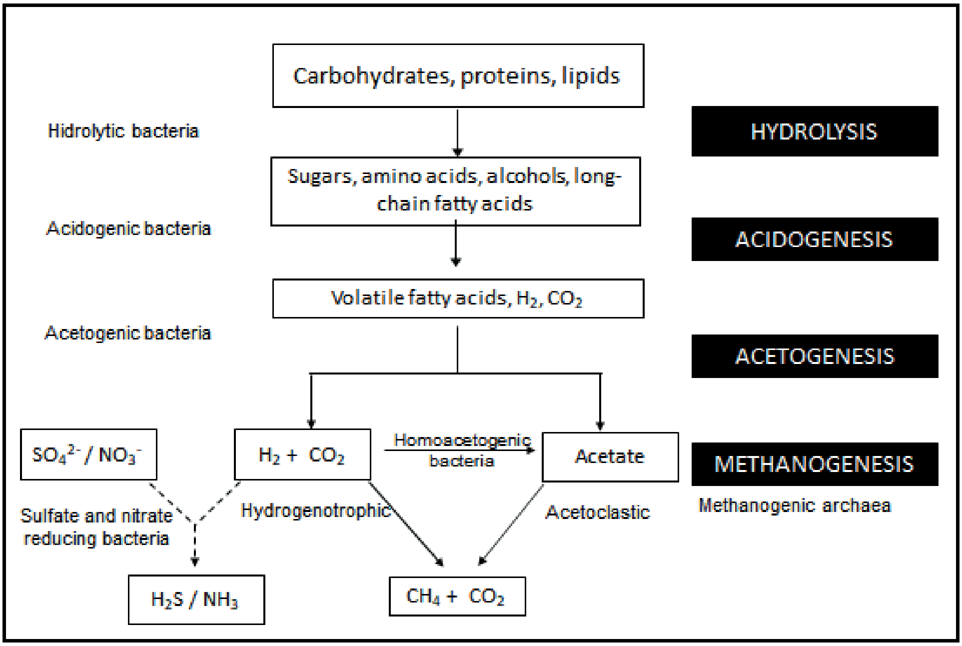


Figure 2 - Steps in the anaerobic digestion of organic matter.

Anaerobic digestion can be applied to stabilize various wastes, such as WWTP sludge, agricultural waste, and animal excrement (Chernicharo, 2007). It is an attractive technology for countries where average ambient temperatures are above 20 °C, as anaerobic microorganisms show low activity at temperatures below this, and heating the reactors is economically unfeasible (Aiyuk *et al.*, 2006).

In the 1950s and 1960s, the high availability of traditional energy sources discouraged the use of biogas in most developed countries. Countries with limited capital and energy resources used biogas in small rural regions to reduce the consumption of firewood, decrease indoor air pollution, and improve soil fertility (Vögeli *et al.* 2014). However, the environmental crisis led to the adoption in 1997 of the Kyoto Protocol, which is an international treaty to reduce the emission of greenhouse gases. Brazil adopted the Clean Development Mechanism, which is the only mechanism in the Kyoto Protocol that admits voluntary participation from developing countries (Bittencourt; Bush; Cruz, 2019). Moreover, the increase in the price of fuels has made methane generated in anaerobic digesters an interesting energy source.

In the last decade, biogas has increasingly been used as an energy source due to the incentive of the carbon credits market. Currently, Brazil has 530 biogas plants (ANEEL, 2023), which use biogas to generate thermal, electrical, and mechanical energy and produce renewable natural gas (biomethane). The main substrates currently employed are sludge from municipal WWTPs, manure, crops and crop residues, waste from the food and feed industries, source-sorted food waste, and slaughterhouse waste (Schnürer; Jarvis, 2019).

The use of biogas from WWTPs is energy efficient, in addition to meeting the requirements for cleaner production (EPA, 2011). Worldwide, WWTP biogas comes mainly from sludge digesters. At WWTP in Ribeirão Preto (São Paulo, Brazil), for example, sewage treatment is conducted in a conventional activated sludge unit, and excess sludge is sent to sludge digesters. Biogas, which was previously burned in the flare, emitting greenhouse gases, is now used to generate electrical energy consumed in the plant itself, reducing its operational cost (Probiogás, 2017).

The composition of biogas can vary depending on the material used in decomposition and the efficiency of the biodigester. The constituents normally present in biogas generated by AD of different organic wastes are represented in Table 1. Biogas is mainly composed of methane and carbon dioxide, with small amounts of other substances, including H_2S. Although H_2S is a flammable gas that contributes to the energy potential of biogas, it causes corrosion in storage tanks, metal pipes, and combustion engines. Thus, high concentrations of H_2S result in the deterioration of biogas production infrastructure.

Table 1 - Average biogas composition

Gases	**Composition (%)**
Methane (CH_4)	50 – 75
Carbon dioxide (CO_2)	25 – 45
Water vapor (H_2O)	2 (20 °C) - 7 (40 °C)
Nitrogen (N_2)	< 2
Oxygen (O_2)	< 2
Ammonia (NH_3)	< 1
Hydrogen sulfide (H_2S)	< 1
Hydrogen (H_2)	< 1

Fonte: Al Seadi *et al*. (2008).

The energy potential of biogas is established according to the amount of methane contained in the gas. Considering biogas with the standard methane content of 50%, the heating value is 21 MJ/Nm³. Biogas can be used directly or purified and stored for later use. Currently, it can be used to produce heat by direct combustion, electricity by fuel cells or micro-turbines, combined heat and power, or as vehicle fuel (Al Seadi *et al.*, 2008).

4. ENZYMATIC PRETREATMENT OF SLUDGE FOR ANAEROBIC DIGESTION

Conventional AD of sludge employs long hydraulic retention times (30 to 40 days) due to the low conversion rates of microorganisms, especially during the hydrolysis step, which is a limitation of this treatment. Applying a pretreatment to sludge to disrupt the cell wall and facilitate the release of intracellular matter, thereby increasing biodegradability, can improve anaerobic digestion. Anaerobic digestion of pretreated sludge has a shorter hydraulic retention time and higher biogas production (Pavlostathis; Gosset, 1986; Pavlostathis; Giraldo-Gomez, 1991).

Recent research shows that sludge pretreatment contributes to better development of the AD process. Different pretreatment techniques include thermal hydrolysis; physical processes for cell destruction and lysis; chemical processes with acids, alkalis, and oxidants; and biological processes using enzymes. However, these technologies are not economically viable, limiting their expansion and implementation (Neumann *et al.*, 2016).

Enzymes are molecules composed of polymers of amino acids (proteins) covalently linked by peptide bonds, with the molecular structure formed by hydrogen bonds, hydrophobic interactions, disulfide bonds, van der Waals forces, and ionic bonds. Enzymes are biocatalysts whose catalytic activity, stability, and specificity depend on their three-dimensional structure (Antranikian; Vorgias; Bertoldo, 2005; Olempska-Beer *et al.*, 2006).

In anaerobic digestion, sludge microorganisms produce and secrete hydrolytic enzymes to convert macromolecular structures into soluble matter, such as simple sugars, amino acids, glycerol, and fatty acids, facilitating transport across the cell membrane (Mshandete *et al.*, 2007).

The addition of hydrolytic enzymes favors the decomposition of insoluble organic molecules in activated sludge flocs and their conversion to simpler molecules (Wawrzynczyk *et al.*, 2008), leading to benefits such as increased methane production (Davidsson; Jansen, 2006; Dursun *et al.*, 2006) and sludge stabilization (Yang *et al.*, 2010). Figure 3 shows a generic scheme of enzymatic sludge hydrolysis followed by biogas/methane production in anaerobic digestion. Insoluble organic substances (polymers and macromolecules) from the EPS matrix, from the composition of membranes and cell walls or inside cells, are hydrolyzed to substances with lower molecular mass, soluble and readily biodegradable. These substances then serve as substrates for anaerobic microorganisms that convert them to methane in anaerobic digestion.

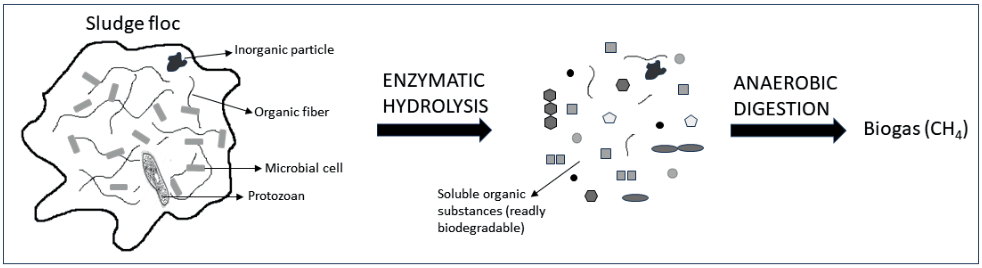


Figure 3 - Scheme of enzymatic sludge hydrolysis followed by biogas/methane production in anaerobic digestion.

Higuchi *et al*. (2005) reported that α-amylase can increase the efficiency of sludge lysis and that this enzyme may be associated with the cells or EPS of the flocs responsible for the hydrolysis of organic solids in the sludge. The use of cellulase can improve the efficiency of sludge hydrolysis. Nouha *et al*. (2018) found that *Acetobacter xylinum* bacteria synthesize cellulose for sludge flocculation. Furthermore, the sludge may contain large amounts of cellulose from other sources, mainly in municipal WWTPs and in paper and textile industries (Parmar; Singh; Ward, 2001), and hemicellulose may also be present in the sludge. Thus, the degradation of hemicellulose by hemicellulase enzymes is interesting, as it results in easily assimilable monosaccharides, such as xylose, glucose, galactose, arabinose, and mannose (Parawira, 2012).

Proteins and carbohydrates are the main components of activated sludge and its EPS, with proportions that vary with the origin of the activated sludge (Houghton; Quarmby; Stephenson, 2001; Liu; Fang, 2002). Yasunori (1994) showed that lysozyme acts in the hydrolysis of sludge by comparing the reduction in volatile suspended solids (VSS) of a concentrated sludge inoculated with bacteria that secrete lysozyme with that obtained with the same sludge without any inoculation. The VSS reduction in the inoculated sludge reached 62% after five days, while in the uninoculated sludge, it was less than 10%. The lysozyme secreted by the inoculated bacteria probably acted on the polysaccharides in the cell wall of the sludge bacteria.

Recent works have demonstrated that the application of commercial enzymes is an efficient option for the biological pretreatment of sludge, accelerating the hydrolysis step of sludge digestion. The enzymes used include amylases, cellulases, proteases, and lyzosyme (Yang *et al*., 2010; Rashed *et al*., 2010; Luo *et al*., 2012; Xin *et al*., 2016, 2018; Zhang *et al*., 2022; Kang *et al*, 2023). Different enzymes and their mixtures have varying effects on sludge hydrolysis. Therefore, selecting the appropriate enzymes is an important step to maximize the impact of pretreatment in anaerobic digestion.

Yang *et al*. (2010) evaluated the effect of different commercial protease and α-amylase mixtures on the hydrolysis of secondary sludge. The addition of exogenous enzymes increased the biological hydrolysis of the sludge, with amylase exhibiting higher hydrolysis efficiency (54.2%) than protease (39.7%). However, a greater reduction of VSS (68.4%) and solubilization of organic matter were obtained with a 1:3 protease: amylase mixture. Luo *et al*. (2012) evaluated the individual action of the α-amylase enzyme in sludge pre-hydrolysis. They obtained a 32.7% reduction in VSS and an 11-fold increase in carbohydrate solubilization compared to sludge without enzyme addition.

Rashed *et al*. (2010) studied the effect of six commercial enzyme mixtures on different combinations of primary sludge, secondary sludge, and digested sludge. The commercially available enzymes were Alcalase, Caresyme (imiglucerase), Celluclast (cellulase complex), Lipolase, Termamyl, and Viscosyme (multi-enzyme complex containing a wide range of enzymes, including arabinase, cellulase, β-glucanase, hemicellulase, and xylanase). The VSS reduction in their study depended on enzyme and sludge combinations; nevertheless, the authors demonstrated that enzymatic pretreatment can be used successfully to treat sludge mixtures produced in WWTPs.

Sludge dewaterability is essential for treatment and disposal of waste-activated sludge from WWTPs, and enzymatic biological conditioning is a promising method to increase its dewaterability. Kang *et al*. (2023) investigated the ideal conditions of pH, temperature, bioenzyme dosage, and treatment time for five biological enzymes (α-amylase, cellulase, acidic protease, neutral protease, and alkaline protease). α-Amylase and neutral protease performed well in condition optimization experiments. After biological enzymatic conditioning of the sludge, with 15.5 g/L TSS (total suspended solids) and 80.2% water content, the concentration of proteins, polysaccharides, and soluble chemical oxygen demand increased in the liquid phase. Sludge water content decreased while capillary suction time increased. The optimal conditions for α-amylase were pH 6, 45 °C, dosage of 30 mg/g TSS, and 3 h treatment time. Under these conditions, the water content reached its lowest value (68.7%). The optimal conditions for neutral protease were pH 6.5, 40 °C, dosage of 30 mg/g TSS, and 2 h treatment time, with water content of 69.8%.

Xin *et al*. (2016) studied a mixture of hydrolytic enzymes (lysozyme, α-amylase, protease, and cellulase) in sludge digestion. Soluble chemical oxygen demand, proteins, and carbohydrates in solution substantially increased to 6000–9000 mg/L, 1500–3000 mg/L, and 550–700 mg/L, respectively, after 180 min of sludge digestion with the enzyme mixture. In a later study, Xin *et al*. (2018) evaluated AD after enzymatic hydrolysis of sludge using the same mixture of enzymes and proportions. The authors proved that enzymatic catalysis improved biodegradability, obtaining 100 mL biogas/g VSS, greater yield than AD of only sludge.

The various published studies prove that enzymatic pretreatment of sludge accelerates the hydrolysis process, increasing the degree of sludge disintegration in a short operating time (Xin *et al*., 2016; Luo *et al*., 2012; Yang *et al*., 2010; Rashed *et al*., 2010), and contributes to better performance of AD (Xin *et al*., 2018).

5. FERMENTATIVE PROCESSES FOR ENZYME PRODUCTION

Fermentative processes are used to convert raw materials into products or to physically and/or chemically modify the material through the action of microorganisms. They are widely used for the production of bioproducts, such as enzymes. These processes are classified into submerged fermentation (SF) and solid-state fermentation (SSF). The difference between the two fermentations is the amount of free water in the cultivation medium. In SF, for the production of enzymes, the solids content usually does not exceed 50 to 100 g/L, while in SSF, the solids content varies from 20 to 70% of the total mass. Thus, SF uses abundant free water and a lower content of solids, while SSF occurs with a low amount (or absence) of water not absorbed into the solid material (Mitchell; Berovic; Krieger, 2002; Singhania *et al.*, 2009).

5.1. SOLID-STATE FERMENTATION

In SSF, the water content is sufficient for the microorganisms to grow. Generally, the only component necessary to add to the medium is water, with or without the addition of minerals, nitrogen, and easily assimilated carbon sources, depending on the characteristics of the raw material (Pandey, 2003).

SSF using filamentous fungi was primarily introduced to produce enzymes and other products in the textile and food industries. An example is the use of enzymes produced by *Aspergillus oryzae* in Eastern countries to manufacture soy sauce (Shoyu), miso, and sake (Machida; Yamada; Gomi, 2008). Later, SSF became an interesting process for regions with large agro-industrial production, which generates different types of residual biomass, which is a lower-cost raw material that can be used as a support medium and/or source of nutrients in the cultivation medium of different biotechnological processes (Pandey, 2003; Singhania *et al.*, 2009).

In addition to the production of enzymes, SSF is used in the production of aromas, bioactive products, biopesticides, organic acids, and fermented foods, as well as in the bioremediation and biodegradation of compounds and biological detoxification of agro-industrial waste (Pandey, 2003;).

The main parameters evaluated during fermentation processes are aeration rate, temperature, moisture and water activity, granulometry, and heat and mass transfer. These parameters are extremely important for microbial growth and, consequently, for the fermentation process (Mitchell; Berovic; Krieger, 2002). The low conductivity of the solid substrates used in SSF, combined with the low amount of water in the process, forms temperature, moisture, substrate, and product gradients. The formation of temperature gradients is one of the main problems of SSF, which is not observed in SF due to the use of a large amount of water and agitation (Te Biesebeke *et al.*, 2002). In SF, the main operational difficulty is the transfer of oxygen to microorganisms due to the low solubility of oxygen in water. In SSF, oxygen transfer is generally not limiting, as the liquid phase around the solid substrate allows oxygen transfer, which can also occur directly from the gas phase in the case of filamentous fungi (Schutyser *et al.*, 2003).

Compared to SF, SSF has advantages such as the wide use of waste as culture media, lower risk of contamination, low energy demand and operational costs, less complex equipment, and higher yields. The disadvantages are greater difficulty monitoring and controlling the process; furthermore, not all microorganisms can develop under greater water restrictions.

5.2. MICROORGANISMS IN SOLID-STATE FERMENTATION

Due to the low quantity of water, a limited number of microorganisms can perform SSF. The most commonly used microorganisms in SSF are filamentous fungi as well as some yeasts and bacteria (Pandey, 2003; Singhania *et al.*, 2009).

Filamentous fungi are eukaryotic and multicellular organisms with elongated and branched cells (hyphae), primarily reproduce by the production of spores, easily disperse through air and water, among others. Filamentous fungi have varied morphology, physiology, and biochemistry. They grow in SSF conditions because these are similar to their natural habitat. The hyphae penetrate into the agro-industrial residue (substrate/support), allowing filamentous fungi greater accessibility to nutrients and making them the most applied microorganisms in SSF (Richards *et al.*, 2006; Santos *et al.*, 2004).

Filamentous fungi are heterotrophic and can metabolize a huge variety of organic materials and convert them to a range of enzymes (lipases, amylases, cellulases, xylanases, mannanases, proteases, among others). Therefore, filamentous fungi are widely used to produce enzymes and catalyze the hydrolysis of different molecules (Corbu *et al.*, 2023).

Some species of filamentous fungi of the genus *Aspergillus* have GRAS (Generally Recognized as Safe) status by the Food and Drug Administration (FDA, USA). These microorganisms are considered safe due to their historical use in the food industry (cheese and shoyu) and the traditional beverage industry (sake), as well as in the production of enzymes (Iwashita, 2002).

Several species of Aspergillus, such as *Aspergillus niger*, *A. nidulans*, *A. oryzae*, *A. versicolor*, and *A. awamori*, can synthesize different extracellular enzymes, according to their needs, which have applications in several biotechnological areas (Cui *et al.*, 1998; Souza-Motta *et al.*, 2005).

The following are some examples of enzyme production by SSF using filamentous fungi of the genus *Aspergillus*. Vishwanatha, Appu Rao, and Singh (2010) reported the production of nearly 40,000 U/g of protease by SSF after 120 h. The authors used *A. oryzae* (MTCC 5341) and wheat bran with 4% defatted soy flour, and 2% skim milk as the substrate.

Pirota *et al*. (2013) indicated that *A. oryzae* (P6B2) produced xylanase (2,830 U/g) in the fungal cultivations carried out for 72 h using wheat bran as the solid substrate in a bioreactor at 35 °C and initial moisture of 80%. Francis *et al*. (2002) demonstrated that *A. oryzae* is also capable of producing α-amylase, using spent brewing grains as the sole carbon source; a maximum production of 6,870 U/g of dry substrate was achieved with 70% initial moisture and 30 °C after 96 h.

The effects of operating conditions to produce cellulase by *A. oryzae* were evaluated by Pirota *et al.* (2016), with wheat bran as substrate in a bioreactor with online monitoring and control of airflow and relative humidity of the incoming air. The authors found the highest production of FPase (0.4 IU/g), endoglucanase (123.6 IU/g), and β-glucosidase (18.3 IU/g) at 28 °C, using an initial moisture content of 70%, with an inlet air humidity of 80% and an airflow rate of 20 mL/min for 72 h. López *et al.* (2013) reported the variety of enzymes that *A. awamori* (IOC-3914) can secrete, obtaining a crude enzyme solution with endoamylases (22.8 U/mL), exoamylases (14.1 U/mL), proteases (1.9 U/mL), xylanases (12.3 U/mL), and cellulases (1.2 U/mL) after 96 h of SSF at 30 °C and moisture of 70% with babassu cake as the substrate.

Dias *et al.* (2018) applied the fungus *A. niger (*SCBM1) in biomass sorghum supplemented with peptone. Maximum production levels were achieved for xylanase and exoglucanase (300 and 31 U/g, respectively) after 72 h of fermentation, for *β*-glucosidase and endoglucanase (55 and 41 U/g, respectively) after 120 h, and for *β*-xylosidase (65 U/g) after 144 h.

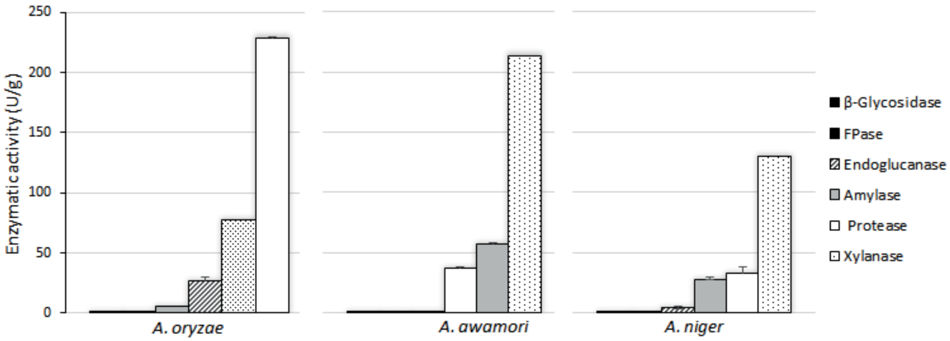
Amylolytic enzymes were produced by SSF, using the fungus *A. niger* and groundnut oil cake medium for 144 h at 37 °C. After the addition of a nitrogen source, a high yield of enzyme production (320 U/mg protein) was obtained (Suganthi *et al*., 2011).

Ahmed (2018) reported the use of SSF with *A. niger* and wheat bran as a substrate with different nitrogen sources added to produce protease. Specific activity of 3.5 U/mg protein was obtained with an initial moisture of 67% at 40 °C for 8 days.

6. ENZYMATIC HYDROLYSIS AND ANAEROBIC DIGESTION OF SLUDGE

Secondary sludge pretreatment using commercial enzymes and enzymes produced by SSF can increase the efficiency of sludge stabilization by anaerobic digestion. Silva (2020) treated different sludge samples with commercial enzymes – amylase (Termamyl – Novozyme), cellulase (Celluclast – Novozyme, containing β-glycosidase, endoglucanase, and FPase activities), protease (Alkalase – Novozyme), and hemicellulase (Sigma, xylanase) – and with enzymatic extracts obtained by SSF with filamentous fungi of the genus *Aspergillus* (*A. oryzae, A. awamori, and A. niger*).

Babassu cake (agroindustrial waste) was used as the basal medium for SSF, which was conducted at 65% initial moisture and 30 °C for 72 h. The fungi produced the enzymes of interest, with the highest production of protease and endoglucanase by *A. oryzae*. *A. awamori* produced the most amylase and xylanase. Despite not showing the highest production of any enzyme, *A. niger* had good production of amylase, xylanase, and protease (Figure 4). With the exception of endoglucanase, cellulases showed low production, which is in accordance with the low concentration of cellulose (6.94%) in the babassu cake (Castro; Castilho; Freire, 2016).



* All enzymes present values in U/g, with the exception of FPase in FPU/g.

Figure 4 - Enzymatic activities (U/g)* in the enzyme preparations obtained in SSF (72 h) with babassu cake as basal medium and the filamentous fungi *A. oryzae*, *A. awamori,* and *A. niger* (adapted from Silva, 2020).

6.1. PRE-HYDROLYSIS OF SLUDGE WITH COMMERCIAL ENZYMES

Pre-hydrolysis (rotary shaker at 100 rpm, for 5 h at 50 °C) and AD (in an oven at 35 °C until the stabilization of biogas production) were evaluated by VSS reduction and biogas/methane yield, respectively. Commercial enzymes were evaluated individually in the hydrolysis of sludge (5 g VSS/L) with enzymes (1 U/mg TSS). Only protease (16%) and lysozyme (15%) obtained a statistical reduction of VSS greater than that obtained in the Control assays (without enzyme, 4%). Hemicellulase (10%) and amylase (9%) presented statistically similar values to those of the Control (Silva, 2020).

Other authors have found higher VSS reduction values for amylase (33%, Luo *et al.*, 2012) and amylase and protease (54% and 40%, Yang *et al.*, 2010), probably due to the different concentrations of enzymes (0.36 U/g TSS amylase and 0.30 U/mg TSS amylase and protease, respectively), specificity of the commercial enzyme preparations and different compositions of the sludge used in the tests. The composition of the sludge is influenced by the characteristics of the treated wastewater, which has different organic matter content, C/N ratio, and nutrients (Mtshali; Tiruneh; Fadiran, 2014). Likewise, the chemical structure of EPS depends on the different environmental conditions in which the microbial cells grew (Nouha *et al.*, 2018).

Anaerobic digestion of sludge after hydrolysis with separate commercial enzymes led to VSS reduction and biogas yield greater than in the Control test. However, the biogas production was quite low.

6.2. SIMULTANEOUS HYDROLYSIS AND ANAEROBIC DIGESTION OF SLUDGE WITH MULTIENZYME EXTRACTS FROM SSF

In the evaluation of multienzyme extracts from SSF, a total enzyme concentration of 0.2 U/mg TSS was applied immediately before sludge incubation (22 g VSS/L) for anaerobic digestion. After 20 days at 35 °C, the sludge added of the extract containing the mixture of enzymes from *A. oryzae*, *A. awamori,* or *A. niger* showed twice as much VSS reduction as the Control (with sludge only). The biogas volume was four times greater in the mixture of sludge and enzymatic extract from the fungi *A. oryzae* and *A. niger*, compared to that obtained in the Control (Figure 5). In the mixture of sludge and *A. awamori* enzymatic extract, the biogas yield increased by approximately 1.7 times, compared to the Control (Silva, 2020).

The addition of enzymes to the sludge contributed to better hydrolysis, releasing a greater amount of organic matter that is easily assimilated by microorganisms and consequently more efficient in methane production. Among the mixtures, the one containing the enzymatic extract from *A. niger* obtained the highest concentration of methane in the biogas generated in anaerobic digestion.

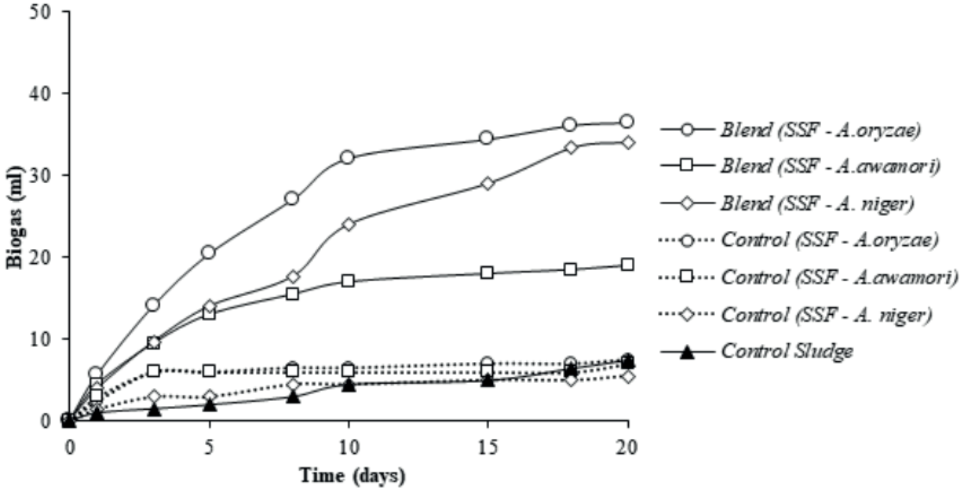


Figure 5 - Biogas production (mL at 35 °C) from secondary sludge (~22 g VSS/L) without (Sludge Control) and with enzymatic extracts from SSF with fungi (*A. oryzae, A. awamori*, and *A. niger*) at a concentration of 0.2 U/mg TSS. Controls (SSF – fungus) refer to tests with enzyme extracts and inoculum.

6.3. ANAEROBIC DIGESTION OF SLUDGE WITH MULTIENZYME EXTRACT FROM SOLID-STATE FERMENTATION AND COMMERCIAL ENZYMES

The use of enzymes produced by SSF, in addition to having a lower cost than commercial enzymes, have environmental benefits providing applicability to solid waste. Thus, Silva (2020) carried out a comparison of the enzymatic extract produced by the fungus *A. niger* and a mixture of commercial enzymes in the same proportions found in the SSF extract (total concentration of 0.2 U/mg TSS) as a way to evaluate the action of this extract and possible cost reduction.

Table 2 shows a comparison of the main results of VSS reduction, CH_4 molar concentration, and biogas/methane yields for the tests with sludge with or without enzymes. VSS reductions of 32, 23, and 16% were obtained after 12 days of AD at 35 °C of sludge with commercial enzymes blend, SSF blend, and sludge alone (Control), respectively. The biogas volume in the mixture of sludge and SSF blend, after discounting the volume of biogas produced by its enzymatic extract Control, reached 62 mL after 12 days at 35 °C. The biogas volume from the mixtures of sludge with commercial enzyme blend, also discounted from the enzymatic extract Control, reached 52.2 mL, a value close to that shown by the sludge control (53 mL). Thus, the mixture of sludge and SSF blend obtained about 1.2 times more biogas production than both the sludge Control and a mixture of sludge and commercial enzymes blend.

Table 2 - Comparison of the main results of VSS reduction, % molar methane, and biogas/methane yields after anaerobic digestion at 35 °C in tests of sludge with or without added enzymes (adapted from Silva, 2020).

Condition	AD time (days)	VSS reduction (%)	Biogas (mL)	%Molar CH_4	Biogas yield[1]	Methane yield[1]
Control (sludge)	27	17.1±2.3	56.0±2.0	33.5±2.7	73.1	24.5
	12	16.3±2.3	53.0±2.0	33.5±3.2	69.2	23.2
SSF blend (*A. niger*)	27	24.3±4.2	76.0±6.0	48.1±6.1	80.3	49.5
	12	22.8±4.2	69.7±1.5	41.7±7.7	81.8	34.1
Commercial enzymes blend	12	32.2±3.3	61.7±1.2	52.4±0.8	68.1	32.3

[1] Biogas yield and methane yield (mL biogas or CH_4/g VSS added) of the mixtures calculated by discounting the volume of biogas or methane from the enzymatic extract Control.

The action of the enzymatic SSF blend in sludge of the same batch (~ 17 g VSS/L and 0.2 U/mg TSS) and different AD times (12 and 27 days) showed similar values of VSS reduction (~ 23%). However, with a longer duration of anaerobic digestion, the methane yield increased by approximately 1.4 times. In this case, the best condition should be chosen by the WWTP depending on whether they desire a higher methane yield or shorter retention time.

CONCLUSIONS

The addition of enzymes to secondary sludge can be a viable alternative to accelerate the hydrolysis process and increase the performance of anaerobic digestion. Enzymes alone or in mixtures can have different effects on sludge hydrolysis.

Commercial enzyme mixtures are more efficient in sludge hydrolysis, but their application increases the cost of sludge treatment. However, enzyme extracts obtained by SSF are low cost, and filamentous fungi can synthesize a wide range of enzymes from varied raw materials. Therefore, this technology is an attractive alternative to promote the AD of secondary sludge.

Studies still need to be carried out to understand the mechanism of action of enzymes in sludge degradation and obtain the best conditions for applying enzymes for pretreatment of sewage sludge.

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CHAPTER 3

DEVELOPMENT AND CONSTRUCTION OF BIOREACTORS OPERATING IN CSTR OR CONTINUOUS SYSTEM FOR BIOGAS PRODUCTION

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ABSTRACT: This chapter's main objective is to present the construction and development of bioreactors capable of operating in a semi-continuous or batch system for biogas production. Low biodegradability biomass has little efficiency in the production of biogas by anaerobic digestion processes and an efficient alternative is the use of bioprocesses in continuous system. Two experiments were carried out in the same proportions but in different processes, and all control and automation parameters were tested and evaluated. For testing, mixtures of food waste, anaerobic sludge (inoculum) and raw sewage without any treatment from the sewage treatment plant, in mesophilic phase (37 °C), were used during the 60 days of experiment. The continuous system showed the greatest reduction of organic matter, expressed by the removal of 80.7% Total Volatile Solid (TVS) and the greatest volume (68.5L) and methane (CH_4) percentage (78.5%). Finally, with these and other results found, it is possible to conclude that the biodigester developed for continuous system, with the automation and control system, was satisfactory for the reduction of organic matter and biogas production. In addition, all operating system worked properly and with the use of current, low-cost technologies, the application and development on a larger scale becomes viable in the future.

KEYWORDS: anaerobic digestion, biogas, bioreactors, co-digestion, control and automation.

1. INTRODUCTION

One of the main environmental problems of today's society is the continuous increase in the production of solid organic waste and sewage and their disposal. In many countries, sustainable waste management, as well as waste prevention and reduction, have become important policy priorities, representing an important part of common efforts to reduce pollution and mitigate global climate change (Bedoic *et al.*, 2021). Intelligent management of organic waste enables energy recovery, whether carried out by the still traditional incineration or by composting and anaerobic digestion (Eriksson *et al*., 2005; Bolzonella *et al*., 2006). Therefore, an alternative for energy recovery of organic waste is the use of biogas, whether generated in landfills or in anaerobic digestion process (Li *et al*., 2017).

The anaerobic digestion process carried out in anaerobic biodigesters can play a significant role in fundamental issues for our society: waste and sewage management and treatment and production of renewable energy. The biodigester is an alternative to the Clean Development Mechanism prescribed by the United Nations and contributes to the reduction of pollutants emission into the atmosphere (ONU, 2022). In addition, it promotes local sustainable development through the treatment of organic waste generated by a particular activity, enabling not only energy generation but also the final use of waste as biofertilizer, reduces the generation of electricity from a non-renewable source and reduces water consumption of processes (Audu *et al*., 2020; Hagos *et al*., 2017; Mousa, 2022; Gómez *et al*., 2019).

The use of the biodigester enables the improvement of sanitary conditions of properties, resulting in better quality of life and health for the population and the environment. Currently, biodigesters built in Brazil and in several countries are expensive, especially in terms of implementation and operation. One of the main reasons is the lack of national technology for monitoring, control and automation systems.

Anaerobic digestion is one of the solutions to reduce these problems and also an attempt to reuse urban solid waste (USW). It is notorious that anaerobic digestion is a process by which organic waste is biologically converted through the use of a microbial consortium in the absence of oxygen (Li *et al*., 2011). In addition to stabilizing the organic load of waste, it generates products such as biogas digested and rich in methane, which can be used as soil conditioner, historically used to stabilize sludge from sewage treatment, although it is a viable application for any matter treatment (Cecchi *et al*., 1991). Besides the potential for generating renewable energy, anaerobic digestion has become increasingly studied and also more popular due to several factors, such as reduction of waste disposal in landfills and energy supply to small communities far from urban centers.

Another very evident advantage is the lower sludge generation. In anaerobic digestion, about 10% of organic waste is transformed into sludge and the remaining 90% is used as biogas. It is also important to high-light the application of anaerobic processes in both small and large scale, with low implementation cost, low area demand and good tolerance to high organic loads (Chernicharo, 1997). Therefore, biogas production and the development of technologies for biomethane generation have been encouraged by many countries as an alternative for electricity generation or cogeneration of internal engines (Budzianowski, 2015; Petterson *et al*., 2011; Jha *et al*., 2013; Venkatesh, 2013).

However, to make energy generation viable, it is necessary to use equipment built at low cost and with high technology, and simple methods of using the system aiming at large-scale reproducibility and industrial use. For this reason, the main objective of this study was to develop bioreactor with a continuous system, containing control and automation systems, in order to play a significant role in two crucial issues for our society, which are environmental protection and resource recovery. Other very important aspects are the production of national technology and the mitigation and reduction of organic waste and sewage disposal in communities, rural and industrial areas. That will be possible with the reduction of waste in the environment and the generation of new sources of energy for the generators of these wastes themselves and as an alternative for biomass anaerobic digestion with low biodegradability.

2. URBAN SOLID WASTE AND FINAL DISPOSAL

Urban Solid Waste (USW) consists of several materials with different chemical and physical compositions, among which are: biodegradable organic matter, paper, cardboard, glass, ferrous and non-ferrous metals, tree pruning and lawns and other wastes which may be inert or non-inert. The characteristics of the various types of USW vary considerably from one city to another, as well as states and countries, especially due to social, economic and cultural factors, as well as geographic and climatic factors (Patterson *et al.*, 2011). These factors are also used as indicators of development, as a tool to characterize and identify cities and communities. The per capita income of the population may be one of the factors that influence the gravimetric composition of the USW, as well as its per capita production. The search for technological alternatives for waste treatment has been one of the topics most discussed and studied in the World, mainly due to the climate changes that have occurred in recent years, due to the emission of greenhouse gases (GHG), besides the pressures exerted by the United Nations.

Based on the solid waste recycling instruments that have economic value, and within the concept of new technologies used with energetic use from the biogas generated through the anaerobic decomposition of the residues, the anaerobic digestion of solid wastes appears as an adequate alternative, of the biodegradation of organic fractions, and can reduce significant amounts of organic waste, eliminating some of the problems of disposal and treatment. Anaerobic Digestion of Organic Solid Waste also has other important advantages, which make it a cleaner development technology, such as: methane (biogas) production generating energy gains, that is, minimizing energy consumption from non-renewable sources; elimination of odors (as well controlled); reduction of CH_4 to the atmosphere; elimination of pathogens; stabilization of organic matter and production of organic fertilizer from the residue.

An example used in the treatment of residues by anerobic digestion and biogas utilization is presented in Figure 1 and has been used in industries, houses and farms around the world.

2.1. ANAEROBIC DIGESTION TECHNOLOGIES

The Continuous Stirred-Tank Reactor (CSTR) is the standard technology for the anaerobic digestion of denser substrates, with favorable characteristics for pumping and mixing. This technology is more applied in agriculture, industry and sludge treatment, being used frequently in the treatment of urban organic waste and, generally, the technology requires substrates practically free of impurities and sufficiently moist. In addition to CSTR with complete anaerobic process, there are biphasic CSTRs, in which the process occurs separately in two steps. One option is to perform the hydrolysis phase in a pre-digester and the methanogenesis phase in the main digester, allowing a better operational control for substrates with high energetic value. Another possibility is to perform a post-digestion, which provides energy gains and allows shorter retention times in the main digester.

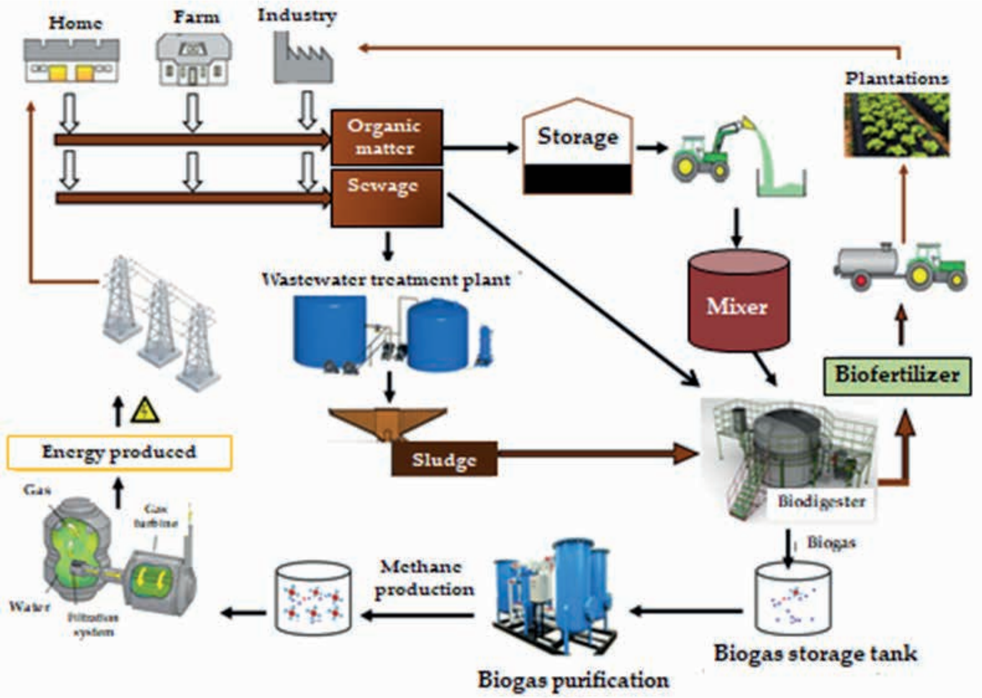


Figure 1 - Simplified scheme of waste treatment and use of biogas generated by anaerobic digestion.
Source: elaborated by the author.

However, when we work in the treatment of industrial waste with higher energy value, greater investments are necessary, due to the greater speed of the process and the high susceptibility to disturbances. The mentioned investment, when it comes to CSTR system (operating in a semi-continuous or batch system), includes expenses with automation for monitoring and control, as well as the higher quality of the material. The Bioreactor for biogas production can be developed in several ways. Figure 2 shows a complete schematic of a CSTR bioreactor with an internal heating system.

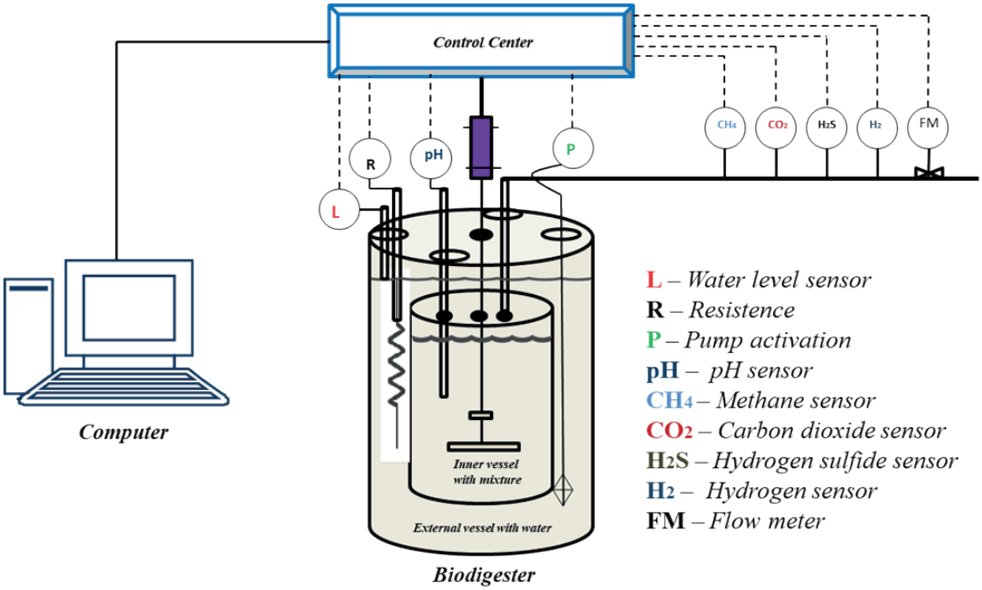


Figure 2 - Complete representation of the operation of a CSTR bioreactor used for biogas production. Source: elaborated by the author.

3. MATERIALS AND METHODS

3.1. DEVELOPMENT AND CONSTRUCTION OF BIOREACTOR

The design of this project was based on the use of materials resistant to the environment of the anaerobic digestion process and the development of systems with current technologies and simple and robust methods of use. Having that in mind, it was decided to develop jacketed vertical bioreactor, on bench scale and in a single stage, with semi-continuous or batch feeding and equipped with heating systems with an element external to the bioreactor, mechanic agitation using a long axis and with vertical entry to the bioreactor, collection and storage of biogas, and control, monitoring and automation. A glass-jacketed bioreactor was developed, with cylindrical geometry, nominal volume of 1.3 L and the following dimensions: 170.0 mm high, 100.0 mm in diameter and wall thickness of 3.0 mm. The jacket has the same volume as the bioreactor and measures 190.0 mm high, 150.0mm in diameter and 3.0 mm in wall thickness.

The first stage of this work was the development of a 3D model and technical drawing of the bioreactor (Figure 3), used for manufacturing, using Solidworks software, version

2019. It should be noted that this software was used to create 3D models and technical drawings of all parts and assemblies developed in this project.

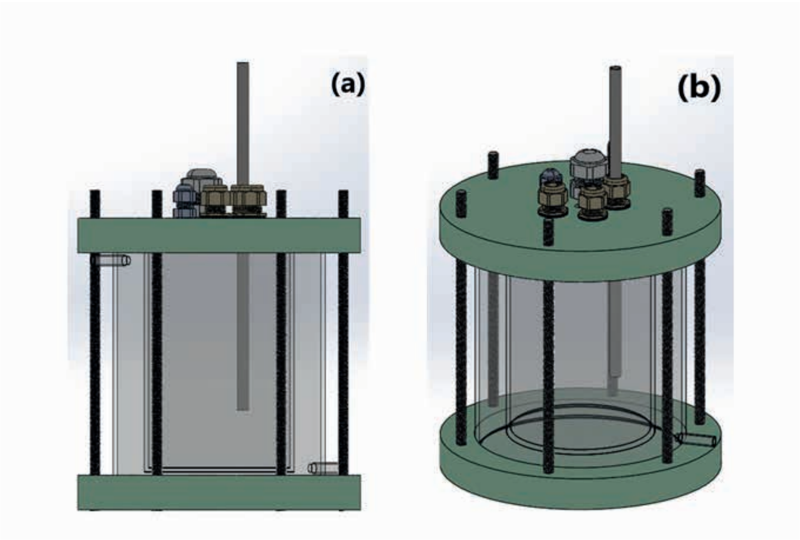


Figure 3 - 3D bioreactor model. (a) frontal view and (b) isometric view.

Source: elaborated by the author.

3.2. DEVELOPMENT AND CONSTRUCTION OF HEATING SYSTEM

The heating system was based on a heating element external to the bioreactor. Heat transfer occurs by means of heating of a thermal fluid, through an electrical resistance, transferred to the bioreactor jacket by a centrifugal pump. The design of this system consists of a container to hold the thermal fluid, an electrical resistance, a lid for the container, a thermowell for a temperature sensor and a water pump. The container to hold the thermal fluid was designed in 3D model, made of glass, having cylindrical geometry, a nominal volume of 1.7L, and the following dimensions: 150.0mm high, 136.0mm in diameter and wall thickness of 3.0mm. A polyurethane lid was also designed for the heating container, in order to prevent/reduce the thermal liquid evaporation. Four holes were drilled in this lid: one for fixing the electrical resistance, one for a thermowell, one for the thermal fluid inlet hose and the last one for the thermal fluid outlet hose.

The perforations were developed to receive three commercial cable glands, model PG9, to adjust the hoses and the thermowell, with diameters between 4–8mm and a connector, designed for resistance. This heating system was designed to use a commercial, cartridge-type resistor as a heating element with the following characteristics: 12.7mm in diameter, 152.4mm long and power between 850-1000 Watts (W); a stainless steel straight thermowell with an internal diameter of 6.0mm and a water pump fed with 12 Volts Direct Current (VDC).

3.3. DEVELOPMENT AND CONSTRUCTION OF THE AGITATION SYSTEM

At this stage, a model of agitation by mechanical means was developed using a long axis with vertical entrance to the bioreactor. This model provides a better mixture compared to magnetic stirring bars. This stirring system was projected to use an electric motor with speed control and a stirring rod. Therefore, a stainless-steel stirring rod with a straight blade propeller was developed. The passage and rotational movement of the rod in the bioreactor lid is a sensitive point in sealing the system to ambient air. Due to that, a double sealing system was used in this project, by means of a retainer with dimensions of 8.00mm x 14.00mm x 3.00mm and a sealing ring with a section diameter of 3.53mm and an internal diameter of 7.52mm.

3.4. DEVELOPMENT AND CONSTRUCTION OF CONTROL, MONITORING AND AUTOMATION SYSTEM

The control, monitoring and automation system chosen to create the biodigester was a Programmable Logic Controller (PLC) that communicates with a microcomputer through a supervisory software. This system was fully developed: hardware, firmware and supervisory software (Guimarães, 2018). The designed hardware can be divided into four main parts: microcontroller - Central Processing Unit, input modules and sensor signal conditioning, out-put and power modules and communication between microcomputer-microcontroller.

The conception of this hardware aimed to meet the following system needs: three analog inputs for temperature and pH sensors; five power actuators — for the electrical resistance manufactured by the company Dennex, model 29858, water pump manufactured Yimaker, model GDB390, digital stirring motor manufactured by Fisatom, model 713D, and 2 peristaltic pumps manufactured by Intilab, model OFA460 — and the communication system between the microcomputer-microcontroller, as shown in Figure 4. In the part of the central processing unit, the PIC16f877a microcontroller from the manufacturer Micro-chip was used. This Programmable Integrated Circuit (PIC) was designed due to the fact that its characteristics meet all the needs pre-established in this project.

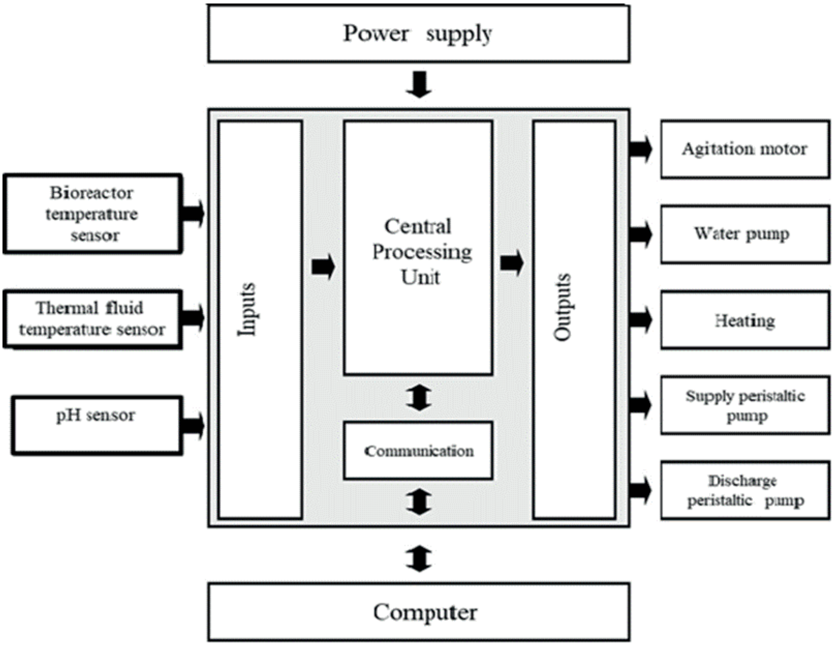


Figure 4 - Programmable Logic Controller Scheme. Source: elaborated by the author.

Source: elaborated by the author.

In the PLC inputs part, the analog signals coming from the sensors were previously conditioned in order to be in adequate conditions to be requested by the microcontroller. This conditioning was performed by means of an electronic low-pass filter in three PIC inputs (two for the bioreactor internal temperature sensors and for the heating tank and one for the pH). Two 10K Ohm NTC (Negative Temperature Coefficient) temperature sensors were used to obtain the temperature values. The NTC Thermistor is a semiconductor that de-creases its resistance value as the temperature increases and has a measurement range of -40 °C to 125 °C. The temperature sensors were calibrated using a thermal bath. The temperature of the bath was varied between 20 and 60 °C with an accuracy of ±0.1 °C. The polynomial equation obtained was saved in the supervisory software.

Monitoring of pH was performed using a shielded, diffusion-type combined electrode produced by MSTecnopon Instrumentação. This pH probe presented the following specifications: measuring range from 0 to 14, operating temperature from 0 to 60 °C, reference system: Ag/AgCl, reference electrolyte: KCl 3M, Coaxial cable and BNC type connector. The calibration of the pH sensor was performed with pH 4 and 7 standard solutions and the calibration curve obtained was automatically saved by supervisory software.

Regarding the PLC output module, the different voltages (12 VDC for the water pump and peristaltic pumps) and 220 Volts Alternating Current (VAC) for the heating element and the stirring motor) must be controlled at the output of the microcontroller, creating the need to design a drive system regardless of the load. The most viable option both economically and practically, was the load activation through a relay system. Five relays from the manufacturer ZND were used in this final system, model ZD-3FF-S-1Z-T, with five pins, operating voltage of 12 VDC which al-lows the activation of loads up to 250 VAC at 7 Amperes (A) or 14 VDC at 12 A. In the last part, the communication system that allowed the exchange of information between the microcontroller and the computer was carried out by means of an asynchronous serial communication, using an Integrated Circuit (IC) MAX232, whose function is to convert the voltage levels of TTL pattern (0 – 5 VDC) from PIC microcontroller to RS-232 pattern (±12 VDC) of the RS232 serial type communication port of the microcomputer (PC), and vice versa.

The firmware was developed in the MikroC programming and compilation environment, from the company Mikroelektronika, using the C programming language and libraries — Analog to Digital Converter (ADC), Conversions and Conversions and Universal Asynchronous Receiver/Transmitter (UART) — available in the compiler. These libraries have definitions for the analog/digital conversion and serial port functions that made programming easier. The recording of the program in the PIC microcontroller was performed using the PICkit2 tool together with the MPLAD IDE software from the manufacturer Microchip Technologies Inc.

The Firmware was programmed to perform a sequence of functions in a cyclic way, called sweep cycle or scan. The scan time, i.e., the period of time in which the PLC performs this sequence of functions repetitively while in operating mode, was defined in this work in one second. In the initialization stage, the PLC runs tests on the hardware itself to ensure that the system is working properly and loads the process variables and their libraries. Then, the microcontroller receives information from the supervisor, initial conditions of the experiment or any changes made during the process. In the processing of readings, the values read by the temperature sensors and the pH probe are obtained. In the next step, the microcontroller stores in its memory the parameters from the supervisory software and the values read by the sensors. During the program execution process, the software performs the proportional temperature control procedure and defines the time for which the heating will be on.

Therefore, the microcomputer updates its outputs (turning on, off or keeping the current state), the heating element, stirring motor, water pump and peristaltic pumps. Finally, the values read by the sensors and the current states of each actuator are sent to the supervisor, and then a new cycle begins. After assembling the hardware and programming and recording the firmware, several tests were carried out to verify the functioning of the developed PLC. The first test took place in the communication module, when a simple procedure was per-formed to send information from the computer to the PLC and a return message from the PLC to the computer and vice versa. This test could prove the efficiency of the communication system that was programmed in the software, as well as the physical connections made by the serial connection cable.

Then, PLC inputs tests were performed analyzing the measurements made by the sensors. To carry out these tests, a program was developed, which performed the readings of the sensors connected to the PLC every second, and reported: the values of the last reading, the lowest and highest measured values, their average, the number of readings and the historic. It then became possible to analyze the operation of the analog inputs and to test the sensors in controlled temperature and pH environments. Regarding the output module, the actuators activation tests were carried out simultaneously with the supervisory software functioning tests. Finally, a metallic box was developed, with dimensions of 300mm x 165mm x 350mm, called control unit, to accommodate the PLC, the power supplies, water pump and peristaltic valves used in the system for entrance and removal of material from the bioreactor.

3.5. DEVELOPMENT OF SUPERVISORY SOFTWARE

The supervisory software for control, monitoring and automation was developed by means of a Microsoft Visual Studio 2012 software using the object-oriented programming and the Visual Basic.NET (VB.NET) programming language. The requirements, defined in its initial conception, were temperature and pH online monitoring, automated control of water pump activation, stirring and temperature motor, alarm system for the main critical parameters, storage of collected data in a database, analysis and visualization of parameters monitored in loco and remotely.

3.6. CONSTRUCTION AND DEVELOPMENT OF A BIOGAS COLLECTION AND STORAGE SYSTEM

The continuous feeding process requires the development of an antireflux collection and storage system for biogas due to the different pressures formed in the system during input/output of material and formation of biogas. The system design for this project consists of a gas washer bottle without commercial porous plate, a low-pressure retention valve and a storage device for the generated biogas. In this system, replacing the washer bottle, a gas/liquid trap was developed using a reagent bottle, with 250mL in volume, and two quick coupling type connectors in order to protect the retention valve and the biogas storage device. 5L Sigma Aldrich tedlar bags, also known as gas collection bags, were used for gas storage. These bags are built from very thin tedlar film, characterized as a non-reactive material, are extremely low in permeability and flexible over a wide temperature range. The biogas generated in the biodigester was directed to the gas collection bag through a polyurethane hose.

3.7. CHARACTERIZATION OF SAMPLES TO TEST OPERABILITY OF THE BIODIGESTER DEVELOPED AND BIOGAS PRODUCTION

In order to evaluate the operational performance of the biodigester developed and the efficiency of biogas production, two experiments were carried out, the first with a batch bioprocess and the other in a continuous system of food residue co-digestion, an-aerobic sludge (inoculum) and raw sewage. The raw sewage sample was obtained before any type of treatment of the sewage treatment plant. The characterization was performed considering moisture, pH, Total Volatile Solid (TVS) and Total Kjeldahl Nitrogen (TKN). The anaerobic sludge used as inoculum in the experiments was collected from the Upflow Anaerobic Sludge Blanket (UASB) reactor in operation at a local industry, and the same characterizations were carried out for the raw sewage. After the characterization, the sludge was refrigerated (4 °C) until the moment of use. All analyzes were determined according to American Public Health Association (APHA, 2005).

The collection of food residues was carried out after lunch in the restaurant of the Federal University of Rio de Janeiro, where leftovers removed from the dishes and utensils were sorted to separate the organic fraction, and homogenized by quartering, following Brazilian Association of Technical Standard (ABNT, 2004). Then, the homogenized material was ground with distilled water in appropriate proportions, with part of the crushed material (called food waste) refrigerated (4 °C) until the moment of use, and part frozen (-20 ºC). The two experiments were carried out in the same proportion for 60 days, with the addition of anaerobic sludge (inoculum) in the proportion of 20%, to evaluate the seeding effect. In the batch system, there was only one addition of the mixtures (waste, raw sewage and sludge) at the beginning of the experiment, whereas in the continuous system it was fed in the same proportions of the mixtures until 1L of the biodigester volume was completed, every 10 days during the experiment. The selected moisture was also used as basis for mixing the residues in the biodigester experiments. The mixtures had their pH corrected to values between 7 and 8 using 1 M sodium bicar-bonate solution ($NaHCO_3$). In these experiments, analyzes of Total Solids (volatile and fixed), moisture and pH were performed in triplicate before and after the anaerobic digestion process.

3.8. CHARACTERIZATION OF BIOGAS PRODUCED

Characterization of the biogas produced was carried out for the CO_2, CH_4 and H_2S compounds and performed in a gas chromatograph (GC). The calibration curve of the chromatograph was constructed from 6 points of known concentrations. All samples were made in duplicate, with error less than 5%. The samples were analyzed in duplicate and CO_2, CH_4 and H_2S standards, by White Martins were used to calculate the concentrations. The chromatographic conditions for CO_2 and CH_4 are described as follows: Equipment: Agilent Technologies, model 7820A, with thermal conductivity detector (TCD); Column

Type: HP-PLOT Q (30 m x 0.53 mm x 40 µm); Input with Flow splitter 2:1; Heater: T = 200 °C; P = 8 psi; Column: Flow = 7 mL/min; P = 8 psi; P = constant; Oven: T = 35 °C; Time = 6.0 minutes; Detector Temperature = 160 °C; Reference Flow = 26 mL/min; Auxiliary Flow = 5 mL/min and Carrier Gas = He and the chromatographic conditions for H_2S are describe as follows: Equipment: Varian CP-4900 Micro GC was used with TCD detector; Columm Temperature: 50 °C; Injection Time = 20 ms; Time = 100 s and Carrier Gas = He.

4. RESULTS

4.1. CONSTRUCTION OF BIOREACTOR

The bioreactor is the central part of the biogas production process. Figure 5 shows the glass jacketed bioreactor with a volume of 1.3 L and the following dimensions: 170 mm high, 100 mm in diameter and wall thickness 3 mm. The jacket had the same volume as the bioreactor and dimensions of 190 mm in height, 150 mm in diameter and wall thick-ness of 3 mm. To keep the environment hermetically closed, a polyurethane cover and a base for fixing were designed, connected by threaded bars, with butterfly nuts, which keep the bioreactor hermetically closed, in addition to 5 mouths with nylon connectors that al-lowed to fix the thermowell, a commercial pH probe, the biogas removal hose and the hose for material inlet/outlet.

Figure 5 - Complete jacketed bioreactor developed.

Source: elaborated by the author.

4.2. CONSTRUCTION OF BIODIGESTER WITH HEATING AND AGITATION SYSTEMS

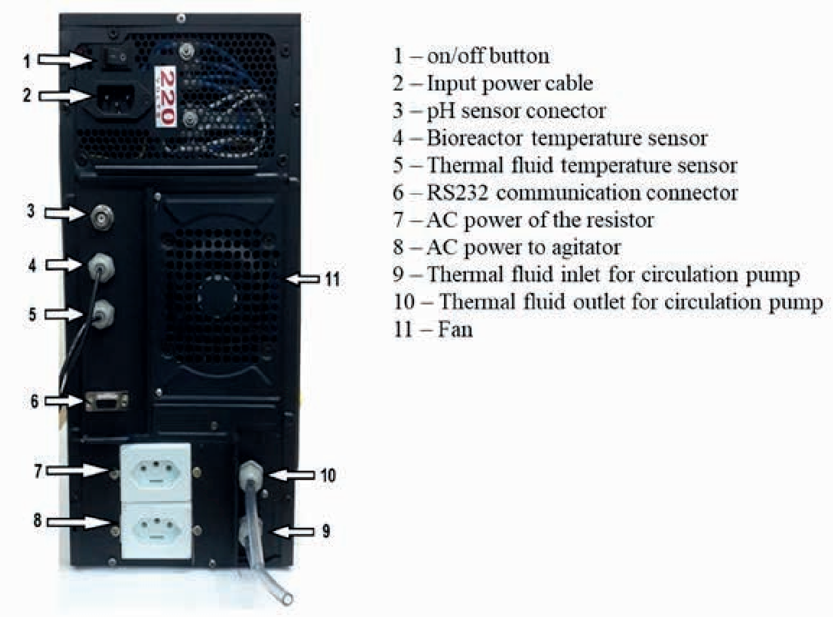
The purpose of supplying heat to a biodigester is to keep the temperature inside the bioreactor constant. The cartridge-type resistance used at 1000 W power and the water pump were acquired to be used in the heating system. A mechanic agitation model was developed using a long axis with vertical entrance to the bioreactor and that rotates the agitators slowly and in brief and previously defined time intervals. A digital, bivolt mechanical stirrer with two drive shafts was used to perform the rotation of the stirring rod. Figure 6 shows the heating and agitation system of the biodigester developed.

Figure 6 - Biodigester with heating and stirring system.

Source: elaborated by the author.

4.3. CONSTRUCTION OF CONTROL UNIT AND SUPERVISORY SOFTWARE DEVELOPMENT

The Programmable Logic Controller is a digital electronic equipment, consisting of hardware and embedded software (firmware), which performs automation, control and monitoring functions. After assembling the hardware and programming and recording the firmware, the PLC, the power supplies, the water pump and the peristaltic valves, used in the system for input/output of material from the bioreactor, were placed in a metal box designed to this project, as shown in Figure 7 and 8. The supervisory software developed is a software for supervision and control of processes in real time and for data acquisition, aimed to perform all steps in simple and intuitive interfaces.



1 – on/off button
2 – Input power cable
3 – pH sensor conector
4 – Bioreactor temperature sensor
5 – Thermal fluid temperature sensor
6 – RS232 communication connector
7 – AC power of the resistor
8 – AC power to agitator
9 – Thermal fluid inlet for circulation pump
10 – Thermal fluid outlet for circulation pump
11 – Fan

Figure 7 - Rear view of control unit.

Source: elaborated by the author.

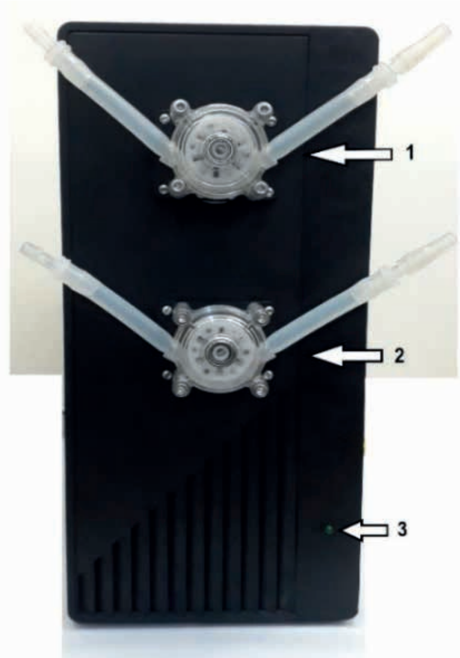


Figure 8 - Front view of the control unit.

Source: elaborated by the author.

4.4. BIODIGESTER COMPLETE OPERATING SYSTEM

A scheme of test equipment, developed and used in this project, is represented in Figure 9, consisting of the jacketed vertical anaerobic biodigester, in bench and batch scale and in a single stage, which can be used in semi-continuous or batch system and is equipped with heating systems, mechanical agitation, collection and storage of biogas, and control, monitoring and automation.

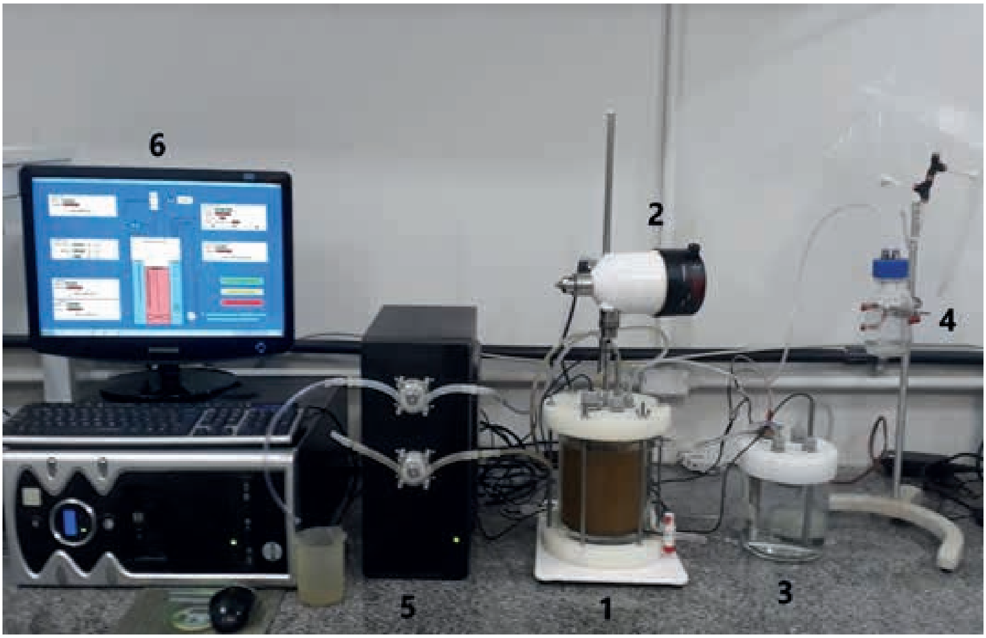


Figure 9 - Operability and efficiency experiments in built biodigesters. (1) Bioreactor, (2) Stirring system, (3) Heating system, (4) Biogas collection and storage system, (5) control and automation unit and (6) Supervisory software.

Source: elaborated by the author.

4.5. OPERATIONAL TEST OF THE BIODIGESTER DEVELOPED AND BUILT FOR BIOGAS PRODUCTION

4.5.1. Characterization of waste

During the efficiency stage between biogas production with biodigester in continuous system and the operation in batch system, three collections of secondary sludge, food waste and raw sewage were carried out. The other characterizations are presented in Table 1.

Table 1 - Description of residues used in mixtures.

Parameters	Food waste (Average ±SD)	Raw sewage (Average ±SD)	Sludge (Average ±SD)
Moisture %	82.6±8.2	91.5±2.1	98.6±4.1
pH	5.1±0.2	5.7±0.6	8.1±0.1
TVS (mg/g)	98.7±25.1	1.4±0.2	34.4±2.4
TKN (mg/L)	15.6±1.1	29.6±5.4	24.4±4.2

The residues had an acid pH, below 7, indicating that their final mixture will have acid pH, and that the addition of an alkalizing agent was necessary in order to adjust the pH at the beginning of the experiments. Initially, the pH adjustment was performed with $NaHCO_3$, which could make the anaerobic treatment difficult, as it would cause an in-crease in the concentration of sodium at inhibitory levels.

The high TVS value in food waste indicates the possibility of increase in biogas production, especially methane, when mixed with anaerobic sludge. It can be observed a TFS concentration higher than TVS for the raw sewage, result that may be due to the fact that the raw sewage collection is done before entering the primary decanter, i.e., there is still a lot of solid to be removed.

4.5.2. Efficiency of co-digestion in different types of processes

At this stage, the objective was to test the biodigester and the efficiency of co-digestion for biogas production. Two experiments were carried out. Experiment 1 was performed in batch system and experiment 2 in continuous system, both for 60 days. In both of them, a mixture of food waste, raw sewage without treatment and anaerobic sludge (inoculum) were used in the same proportions. Experiment 2 was fed every 10 days until the 60th day and in the feeding, 80% of the volume was removed and the same amount was added with food waste and raw sewage and experiment 1 was only fed at the beginning.

The efficiency of the anaerobic co-digestion bioprocess showed, for experiment 1, low removal of volatile solids (VS), compared to experiment 2, but with constant removal from the beginning. In experiment 1, there was removal of total and volatile solids of 52.5% TS and 60.4% TVS, and experiment 2 showed high removal of organic matter, expressed by the removal of 68.5% TS and 80.7% TVS. The average production rate and the total biogas volume produced in experiment 1 were respectively 0.4 L/day and 18.5 L, and in experiment 2, respectively, 1.5 L/day and 68.5 L. Srisowmeya *et al.* (2020) evaluated that for processes carried out with USW and at mesophilic temperatures, it was possible to find volatile solids removals in the ranges of 71.6% with 24 days of experiment and in cases where there was recirculation, the removal can be optimized, reaching 80% in 12 days of experiment. The efficiency of methane production associated with pH variation in biogas production is shown in Figure 10. H_2S behavior was similar for the two biodigesters.

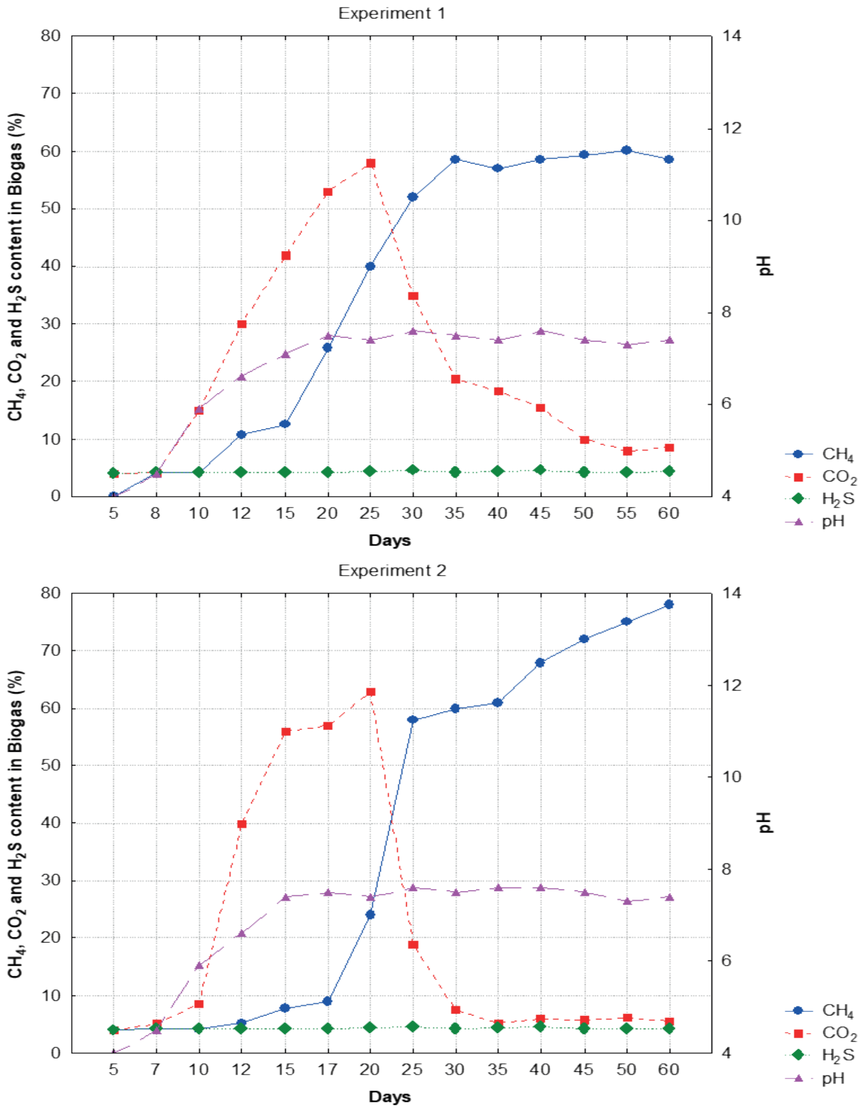


Figure 10 - Biogas production profile obtained during the 60 days of experiments. Experiment 1: Bioprocess operating in batch system and Experiment 2: Bioprocess operating in continuous system.

Source: elaborated by the author.

5. DISCUSSION

During the experiments carried out with the developed biodigester, some adjustments were necessary, such as the PLC communication test that demonstrated the information dispatch and receipt was working within the programmed time of one second. On the other hand, the test experiments of PLC input showed that the input module was working, however the readings were oscillating, especially the pH sensor. In general, these variations occur due to electronic noise in the system and for this reason electronic filters were previously installed in each of the inputs.

The solution for this problem was the implementation of a digital average moving filter, for a set of five samples, to the embedded software. This type of filter is obtained by calculating the average of a set of values, always adding a new value to the set while discarding the oldest one at each reading. After the application of this filter the sensors showed, in 25 readings, a variation of +/- 0.4 °C; temperature and pH +/- 0.06. It can be concluded that the PLC analog input module and the sensors worked well and presented a stable reading signal. The developed software supervised and controlled the processes in real time, including data acquisition. In the developed window, the operator can determine all parameters of control and monitoring and the biodigester automation, before and during the experiment, and provide the operator with interaction and visualization of the equipment.

Regarding the biodigesters, it was observed that, during the 60 days of the experiment, the materials used in the bioreactors construction showed good results and were suitable for the anaerobic digestion process. The sealing system was efficient and maintained the environment hermetically closed, which was evidenced by the absence of odors in the place with low H_2S concentration, efficiency of the organic matter removal process and biogas production. Throughout the test experiment, the heating and temperature control systems were efficient, considering that they did not present any faults; the volume of thermal fluid was adequate for heating the medium in fermentation; and the resistance was able to reach and maintain the temperature at the value established by the control system. The temperature in most of the experiments was maintained at 37±0.3 °C. In addition, the agitation automation systems worked as expected and did not present failures in the test experiment. The motor and stirring rod were able to maintain mixing and homogenization of the medium.

After carrying out the experiments in batch and continuous systems, it could be observed that the continuous system showed better efficiency in the removal of organic matter, biogas volume and CH_4 percentage. H_2S Behavior was similar for the two experiments. The behavior of the gases (CH_4, CO_2 and H_2S) was similar during the experiments, i.e., initially there was a high production of CO_2 (acetogenesis phase) and over time the concentration was decreasing and increasing methane concentration with basic pH. In experiment 1 it was necessary to adequate the pH during the first 20 days and in experiment 2 in the initial 15 days. The necessary pH control had addition of using 1 M sodium bicarbonate solution ($NaHCO_3$).

CONCLUSIONS

It was possible to evaluate the influence of both food waste and raw sewage co-digestion without treatment in the biogas production for different processes of anaerobic digestion, with the semi-continuous process being the most efficient in the removal of organic matter and production of biogas. This greater efficiency, compared to the batch process, can be attributed to the addition of residue, raw sewage and sludge mixtures throughout the experiment, as it may have increased the amount of organic matter and microorganisms in the medium, facilitating biodegradation and, consequently, greater biogas production.

The lower efficiency of the experiment in the batch system may be as-sociated with the composition of substances present in the raw sewage of low biodegradability. The main results obtained in this work allowed us to evaluate/conclude that the biodigester developed, in addition to the operation flexibility, is clean and presents easy maintenance.

The agitation system developed for the biodigester provided the mixture of the medium according to its design, and the heating system was effective in the mesophilic biodigestion process. The control, monitoring and automation system developed for the anaerobic biodigestion process proved to be efficient and presented the main functionalities and architecture of commercial PLCs. In addition, the supervisory software was efficient in all aspects defined in its conception: display of monitoring data and process parameters; storage of monitored data, system and experiments configuration; display of historical monitoring data in different formats; visual alarm system and e-mail of critical parameters to the process; and remote equipment monitoring and control.

Regarding the biodigester developed, it can be used for semi-continuous and batch bioprocesses, allowing the flexibility of operation for different types of substrates. The biodigester physical system was adequate and allowed us a clear visualization of the fermentation medium, in addition to checking whether the agitation system is being effective or not, and to ensuring the low production of H_2S in biogas, due to the complete sealing of the system which prevents oxygen into the medium.

Finally, with these and other results found, we can conclude that the biodigester developed with the automation and control system was satisfactory for the reduction of organic matter and biogas production. All operating parameters worked properly and with the use of current, low-cost technologies, the application and development on a larger scale becomes viable in the future.

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CHAPTER 4

THERMODYNAMICALLY AND ENVIRONMENTALLY EFFICIENT OFFSHORE GAS-TO-WIRE FROM CO_2-RICH NATURAL GAS WITH CARBON CAPTURE

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ABSTRACT: Increase in power generation from natural gas is predicted for the next decades, due to expansion of proved reserves and energy demand. In the Brazilian Pre-Salt offshore basin, oil reserves have a high gas-oil ratio with CO_2-rich associated gas. To bring such a gas to market demands the use of high-depth long-distance subsea pipelines making Gas-to-Pipe expensive. Gas-to-Wire instead of Gas-to-Pipe is a more suitable solution since it is easier to transport electricity than gas through long subsea distances. This work investigates the implementation of environment-friendly and thermodynamically efficient Gas-to-Wire for CO_2-rich NG (CO_2≈*44%mol*) from high-depth offshore oil-&-gas fields. The process comprises natural gas combined-cycles, exhaust-gas recycle to reduce volume and increase CO_2 content of flue-gas, CO_2 post-combustion capture with aqueous-monoethanolamine for flue-gas decarbonation, and CO_2 dehydration with triethylene-glycol for exportation as enhanced oil recovery agent. The overall process exports *534.4 MW* of low-emission net power. Second Law analysis reveals that the overall thermodynamic efficiency is *33.35%*. Lost-work analysis showed that the greatest sink of power destruction lies in the gas-combined-cycle sub-system (*80.7%* lost-work), followed by the post-combustion capture plant (*14.0%* lost-work).

KEYWORDS: exhaust-gas recycle, gas-to-wire, natural gas combined-cycle, post-combustion carbon capture, second law analysis, thermodynamic analysis.

Nomenclature

$\dot{EE}$	*Electricity (MW)*
Fi	*Flowrate of i^{th} feed-stream (kmol/s)*
$\bar{H}$	*Molar enthalpy (MJ/kmol)*
Nf	*Number of feed-streams (inputs)*
Np	*Number of product-streams (outputs)*
P	*Pressure (bar)*
Pi	*Flowrate of i^{th} product-stream (kmol/s)*
$\dot{Q}$, $\bar{S}$	*Heat duty (MW), Molar entropy (MJ/K.kmol)*
T, W	*Temperature (K), Power (MW)*
Greeks	
η	*Thermodynamic efficiency (%)*
Superscripts	
CW, Eq, LPS	*Cooling-water, Equivalent, Low-pressure steam*

1. INTRODUCTION

Despite the growing renewable energy utilization, fossil fuels still dominate the global energy matrix. Large growth in power generation from natural gas is anticipated for the incoming decades, due to expanding natural gas (NG) reserves and because NG is the cleanest fossil fuel (Neseli *et al*., 2015).

According to Arinelli *et al.* (2017), in the Brazilian Pre-Salt offshore basin, deep-water oil reserves have a high gas-oil ratio with CO_2-rich associated gas ($CO_2 \approx 44\%mol$). To bring such a NG to market demands high-depth long-distance subsea pipelines entailing high investment despite the low-quality gas. In this scenario, Gas-to-Wire (GTW), instead of Gas-to-Pipe, is competitive since it is easier to transport electricity than gas through long subsea distances. In this context, floating Gas-to-Wire plants located nearby the offshore gas field convert the produced gas directly into electricity via NG combined-cycles (NGCC) for higher efficiency and the electricity is exported through High-Voltage Direct-Current (HVDC) cables for lower power losses (Watanabe *et al*., 2006). Considering the climate-change conjuncture, Gas-to-Wire must include carbon capture and storage (CCS) to decrease the carbon-footprint of power generation (Zhou *et al*., 2018). For GTW over offshore deep-water oil-&-gas fields, CCS must comprehend: (i) exhaust-gas recycle (EGR) to increase flue-gas CO_2 content and to decrease flue-gas volume both lowering CCS costs; (ii) post-combustion carbon capture from CO_2-rich flue-gas via benchmark absorption in aqueous-monoethanolamine (aqueous-MEA); i.e., the PCC-MEA plant; (iii) CO_2 compression; (iv) high-pressure CO_2 dehydration in a CO_2 Dehydration Unit (CDU) for low water content (*≈200 ppm-mol*) avoiding CO_2 hydrates; and (v) dense CO_2 injection in the oil-&-gas field for enhanced oil recovery (EOR) accomplishing two objectives: CO_2 storage while improving oil production (Roussanaly *et al.*, 2019). Offshore GTW for CO_2-rich NG with EGR, CCS and CDU is written here as GTW-EGR-CCS-CDU.

There is a clear literature gap regarding GTW-EGR-CCS-CDU and its Thermodynamic Analysis (Second Law Analysis), thanks to the following cumulative process extreme particularities: CO_2-rich NG fuel-gas, EGR and CDU as process intensifiers. To fill this gap, the present work investigates the implementation and thermodynamic performance of GTW-EGR-CCS-CDU firing CO_2-rich NG from offshore deep-water oil-&-gas fields, simultaneously identifying the power destruction sinks and quantifying Lost-Work of the overall system and its sub-systems in order to pinpoint process components that should be upgraded for better thermodynamic efficiency.

2. METHODS

Offshore GTW-EGR-CCS-CDU firing CO_2-rich NG and exporting power and CO_2-to-EOR was designed and simulated in Aspen-HYSYS for technical and thermodynamic evaluations. The necessary theoretical frameworks follow.

2.1. PROCESS SUB-SYSTEMS

Figure 1 displays a block-diagram defining GTW-EGR-CCS-CDU sub-systems, while Table 1 depicts simulation and design assumptions. The skeleton of the medium-capacity (≈ *600MW*) offshore GTW-EGR-CCS-CDU comprises: (i) NGCC Plant; (ii) Direct-Contact Column (DCC) for flue-gas cooling; (iii) low-pressure PCC-MEA for CO_2 capture; (iv) 1st CO_2 Compression Unit (CU-1); (v) CO_2 dehydration via high-pressure absorption with triethylene-glycol (TEG) for water removal from the CO_2-to-EOR stream (CDU-TEG); (vi) Stripping-Gas Unit (SGU) that adjusts the stripping-gas to the CDU-TEG reboiler; (vii) CO_2 pumping plant (CU-2) that dispatches CO_2-to-EOR; and (viii) EGR structure.

Table 1 - Simulation assumptions.

	Item	***Assumption***
A1	*Thermodynamic Models*	*Gas-Streams: Peng-Robinson Equation-of-State; Rankine-Cycle: ASME Steam-Table; PCC-MEA: HYSYS Acid-Gas Package; CDU-TEG: HYSYS Glycol-Package*
A2	*Raw CO_2-Rich NG*	*6.5MMSm³/d; T=40°C; P=25bar; CH_4=49.82%mol, CO_2=43.84%mol, C_2H_6=2.99%mol, C_3H_8=1.99%mol, iC_4H_{10}=0.3%mol, C_4H_{10}=0.2%mol, iC_5H_{12}=0.2%mol, C_5H_{12}=0.1%mol, C_6H_{14}=0.1%mol, C_7H_{16}=0.05%mol, C_8H_{18}=0.03%mol, C_9H_{20}=0.01%mol, $C_{10}H_{22}$=0.01%mol, H_2O=0.36%mol*
A3	*Air*	*T=25°C; P=1.013bar; N_2=77.14%mol; O_2=20.51%mol; H_2O=2.35%mol*
A4	*Gas-Turbine*	*Aero-Derivative GE LM2500+G4; Efficiency^{LHV}=36.5%; P^{Inlet}=23bar; Air-Ratio=6.2mol/mol; $T^{Flue\text{-}Gas}$=549°C.*
A5	*Steam-Turbine*	*HPS: $P^{Inlet=}$24bar; $P^{Outlet=}$0.12bar; T^{Inlet}=524°C; Outlet-Quality=98.1%.*
A6	HRSG	$\Delta P^{Flue\text{-}Gas}$=0.025bar; ΔP^{Steam}=0.05bar; $\Delta T^{Approach}$=25°C.
A7	LPS	P^{LPS}= 3bar, T^{LPS}=133.5°C.
A8	DCC	$\text{Stages}^{Theoretical}$=10; P^{Top}=1.053 bar; $T^{Top\text{-}Flue\text{-}Gas}$=40ºC.
A9	PCC-MEA	Absorber: $\text{Stages}^{Theoretical}$=40; P^{Top}=1.013bar; $T^{Inlet\text{-}Top=}$40°C; Capture=90%; Stripper: $\text{Stages}^{Theoretical}$=10; P^{Top}=1.013bar; T^{Top}=40°C; $T^{Reboiler}$=103°C; Lean-MEA: H_2O=63.3%w/w, MEA=31.6%w/w, CO_2=5.1%w/w; Capture-Ratio: CR»14$\text{kg}^{Solvent}/\text{kg}^{CO2}$**;** Stripping Heat-Ratio: HR»225kJ/mol^{CO2}
A10	CDU-TEG	Absorber: $\text{Stages}^{Theoretical}$=15; P=50bar; T^{Inlet}=35°C; Solvent: TEG=98.5%w/w; Stripper: $\text{Stages}^{Theoretical}$=10; P^{Top}=1.013 bar; T^{Top}=40°C; $T^{Reboiler}$=128°C;
A11	Compressors	Stage Compression-Ratio=2.85; Intercoolers: $T^{Gas\text{-}Outlet}$=35°C; $\Delta T^{Approach}$=5°C; ΔP=0.5bar.
A12	CO_2-to-EOR	T=35°C; P=300bar; Purity: CO_2≥99.9%mol
A13	Cooling-Water	CW: T^{Inlet}=30°C; T^{Outlet}=45°C; P^{Inlet}=4bar; P^{Outlet}=3.5bar.
A14	Exchangers	$\Delta T^{Approach}$=10°C (gas-gas, liq-liq); $\Delta T^{Approach}$=5ºC (gas-liq); ΔP=0.5bar.
A15	Adiabatic Efficiencies	η^{Pumps}=$h^{Compressors}$=$\eta^{Steam\text{-}Turbine}$=75%; Gas-Turbines:$h^{Air\text{-}Compressor}$=87%, $\eta^{Expander}$=85.4%.
A16	Steam Production	Priority: $LPS^{PCC\text{-}MEA}$+$LPS^{CDU\text{-}TEG}$; Surplus: $HPS^{Rankine\text{-}Cycle}$

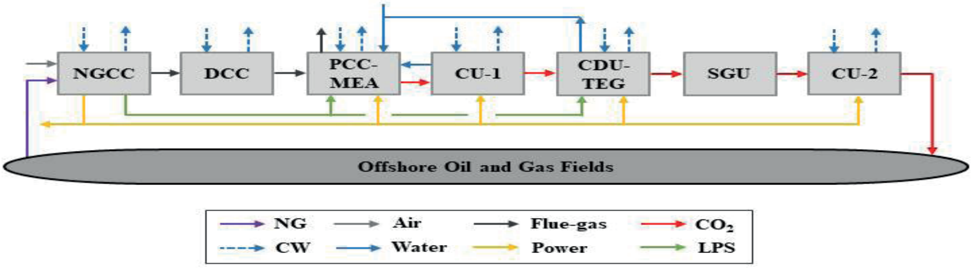

Figure 1 - Process sub-systems (NGCC=NG-Combined-Cycle, DCC=Direct-Contact-Column, PCC-MEA=Post-Combustion Capture with Aqueous-MEA, CU=CO_2-Compression-Unit, CDU-TEG=CO_2-Dehydration-TEG-Unit, SGU=Stripping-Gas-Unit, EGR=Exhaust-Gas-Recycle).

2.1.1. NGCC Plant

NGCC Plant comprehends five parallel NGCC elements for *≈600MW* total electricity generation. Each NGCC element (Figure 2) has four gas-turbines connected to one Heat-Recovery Steam-Generator (HRSG) which heats the steam-cycle of the NGCC element (Rankine-Cycle). Aero-derivative gas-turbines (Table 1) are suitable for offshore rigs due to high power-to-weight ratio and low footprint (GE, 2019). Gas-turbines burn raw CO_2-rich NG ($CO_2 \approx 44\%$mol) without any conditioning. The resulting flue-gas feeds the HRSG at $T=549°C$ (GE, 2021) generating high-pressure superheated steam (HPS) ($T=524°C$, $P=24bar$) and low-pressure steam (LPS) ($T=133.5°C$, $P=3bar$). HPS expands in the steam-turbine to $P=0.12bar$ and is cooled down in the sub-atmospheric condenser with cooling-water (CW) returning as condensate to HRSG at $T=45°C$. LPS heats PCC-MEA and CDU-TEG reboilers, consequently the steam-cycle power is limited by LPS demand.

Gas-turbine model in HYSYS consists of: (i) adiabatic single-stage air compressor; (ii) combustion-chamber modeled as adiabatic conversion reactor; and (iii) adiabatic expander. This model was calibrated to factory settings by adjusting adiabatic efficiencies of its air compressor and expander. Air is supplied at stoichiometric proportion for complete NG combustion. To limit combustion temperature to factory constraints, stoichiometric air is mixed with Exhaust-Gas Recycle (EGR). Recycled flue-gas is withdrawn after the DCC cooler and before the PCC-MEA and its flowrate was adjusted to match recommended flue-gas temperature at the expander outlet ($T=549°C$).

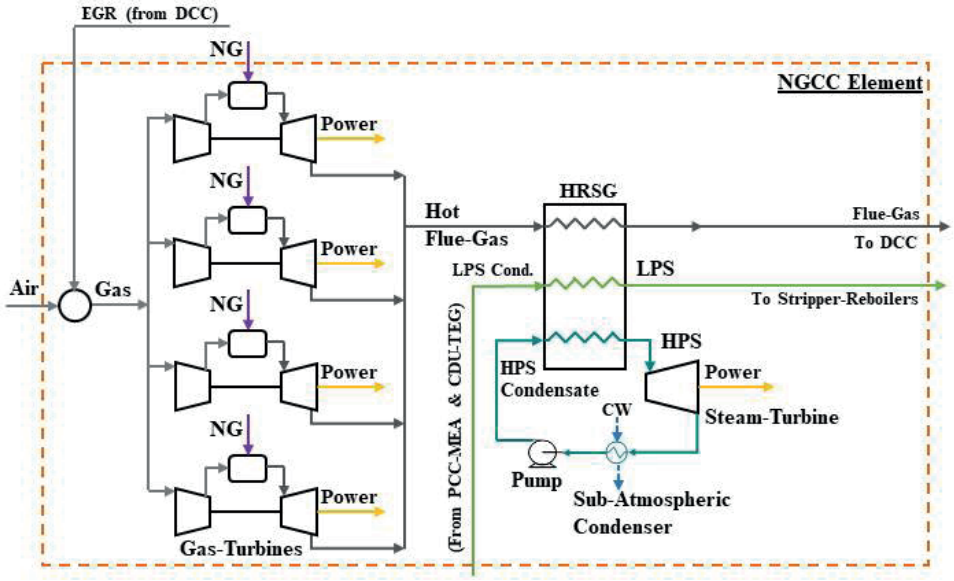

Figure 2 - NGCC Element (EGR=Exhaust-Gas-Recycle, HRSG=Heat-Recovery Steam-Generator, LPS=Low-Pressure-Steam, HPS=High-Pressure-Steam, CW=Cooling-Water, Direct-Contact-Column, PCC-MEA=Aqueous-MEA-Post-Combustion-Capture, CDU-TEG=CO_2-Dehydration-TEG-Unit).

2.1.2. Direct-Contact Column and Post-Combustion Capture with Aqueous-MEA

Flue-gas that leaves HRSG from the five NGCC elements is cooled down to 40°C and is water-saturated through direct-contact with CW (*T=30°C*) in the Direct-Contact Column (DCC). The cooled flue-gas is divided: around 50% returns as EGR to the gas-turbine air feed to abate flame temperature; and the rest is sent to PCC-MEA for decarbonation with aqueous-MEA ($MEA \approx 30\%w/w$). Flue-gas is split into four smaller feeds (Figure 3) to improve capture-efficiency (Oh *et al.*, 2016). LPS ($P=3bar$, $T=133.5°C$) heats the reboiler ($T=103°C$) of the atmospheric PCC-MEA stripper. The stripper condenser operates in total reflux (i.e., 100% condensate reflux) and releases water-saturated CO_2 ($P=1atm$) through its vent. In order to keep CO_2 imprisoned in the CO_2-loop between PCC-MEA and CDU-TEG, all condensed carbonated waters ($T=35^oC$) from CU-1 knock-out vessels and from the TEG stripper condenser ($T=40^oC$) are recycled to tray#1 of the PCC-MEA stripper, while Wet-CO_2 from TEG stripper condenser vent ($T=40^oC$) is recycled to tray#10. These recycles reduce make-up water and condenser duty, and avoid CO_2 emissions from CU-1 and CDU-TEG. A pump recirculates Lean-MEA to PCC-MEA absorber after receiving make-up water. PCC-MEA is designed to capture 90% of CO_2 in the flue-gas under two key ratios that define solvent recirculation and stripper duty: the Capture-Ratio ($CR \approx 14kg^{Solvent}/kg^{CO2}$) as the ratio of Lean-MEA to captured CO_2 and the stripper Heat-Ratio ($HR \approx 225kJ/mol^{CO2}$). DCC and PCC-MEA sub-systems are shown in Figure 3.

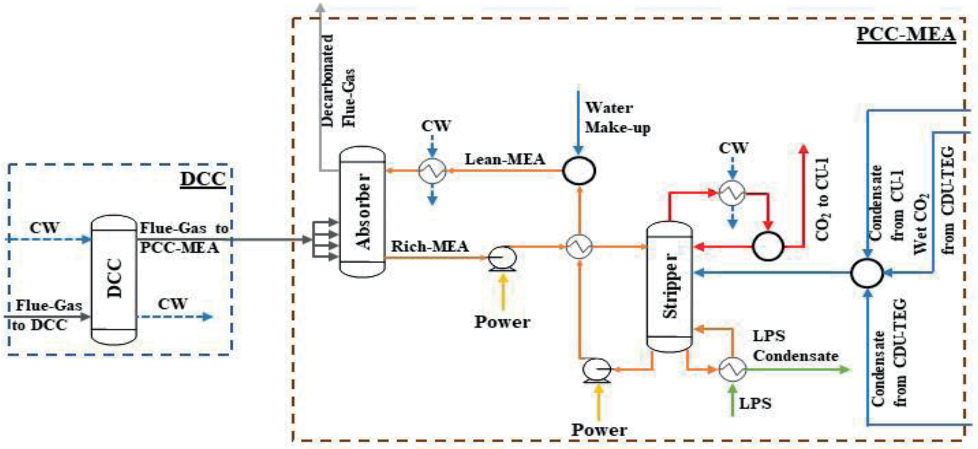

Figure 3 - Direct-Contact Column (DCC) and Aqueous-MEA-Post-Combustion-Capture (PCC-MEA) (LPS=Low-Pressure-Steam, CW=Cooling-Water, CDU-TEG=CO_2-Dehydration-TEG-Unit, CU=CO_2-Compression-Unit).

2.1.3. CO_2 Compression Units, CO_2 Dehydration Unit and Stripping-Gas Unit

CU-1 (Figure 4) is a 4-staged intercooled compression train (*stage-compression-ratio=2.85*) to raise the CO_2 pressure to *50 bar* for CO_2 dehydration. The CO_2-to-CDU-TEG stream (≈ 2700 *ppm-mol* H_2O) and TEG solvent (*98.5%w/w TEG*) feed the 15-staged TEG-absorber of CDU-TEG producing Dry-CO_2 to SGU (≈ 200*ppm-mol* H_2O) at the top and rich-TEG ($H_2O \approx 60\%mol$) at the bottom. TEG is regenerated in the 10-staged TEG-stripper, which produces Lean-TEG as bottoms ($T=128°C$), and vapor Wet-CO_2 and carbonated liquid water top distillates in the partial condenser. Water and Wet-CO_2 distillates are recycled to PCC-MEA. SGU is a small unit that adjusts the stripping-gas (*1%* of Dry-CO_2) in order to keep TEG-stripper reboiler temperature below *140°C*. The remaining Dry-CO_2 is forwarded to CU-2, to achieve EOR pipeline pressure (*P=300bar*).

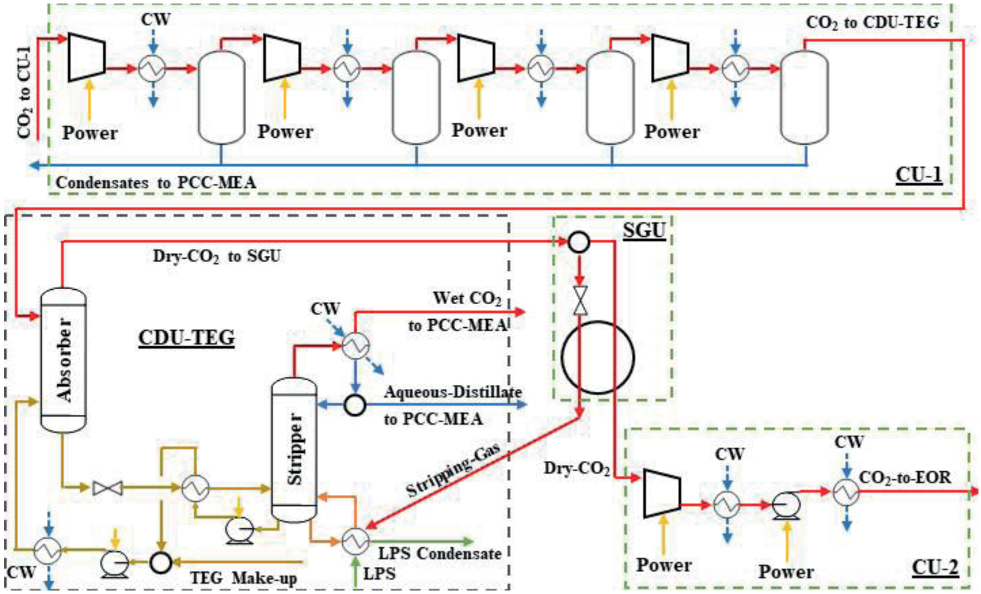

Figure 4 - Compression Units (CU1/CU2), CO_2-Dehydration-TEG-Unit (CDU-TEG) and Stripping-Gas-Unit (SGU) (CW=Cooling-Water, LPS=Low-Pressure-Steam, PCC-MEA=Aqueous-MEA-Post-Combustion-Capture, EOR=Enhanced Oil Recovery).

2.2. THERMODYNAMIC ANALYSIS OF PROCESSES

Thermodynamic analysis is effective to reveal resource degradation through processes. Steady-state Offshore GTW-EGR-CCS-CDU and its sub-systems are assessed via the Second Law analysis of processes. For 2nd Law analysis, systems and their sub-systems are previously classified as either power-consuming or power-producing systems. Figure 5 displays a steady-state open-system for thermodynamic analysis with several feed/product streams (green/blue arrows, respectively) interacting with an infinite isothermal heat reservoir R_0 at temperature T_0. The overall system and its sub-systems can be power-producing ($\dot{W}>0$) or power-consuming ($\dot{W}<0$), but can only have thermal interactions with R_0 either absorbing ($\dot{Q}>0$) or rejecting ($\dot{Q}<0$) heat. $F_n, \bar{H}_{F_n}, \bar{S}_{F_n}$ respectively represent molar flowrate (*kmol/s*), enthalpy (*MJ/kmol*) and entropy (*MJ/kmol.K*) of the *n*th feed-stream (*n=1..Nf*), while $P_n, \bar{H}_{P_n}, \bar{S}_{P_n}$ are analogous for the *n*th product-stream (*n=1..Np*).

2.2.1. Maximum Power

Eq. (1) and Eq. (2) represent the First Law of Thermodynamics applied to the steady-state Open-System (Figure 5). The System Maximum Power (Maximum Work) $\dot{W}^{MAX}$ is calculated via the 2nd Law at reversible conditions using Eq. (3), Eq. (4), Eq. (5) and Eq. (6), where Eq. (4) represents the Universe entropy balance at reversible conditions and $\dot{S}^{UNIV^{REV}}$ is the Universe entropy-creation rate at reversible conditions. Eq. (5) results from Eq. (2), under reversibility, and Eq. (6) derives from Eq. (4). Thus, $\dot{W}^{MAX}$ is given by Eq. (7)

or Eq. (8). For Power-Consuming Systems (e.g., PCC-MEA, CU-1, CU-2 and CDU-TEG) Eq. (8) gives negative $\dot{W}^{MAX}$, while for Power-Producing systems (e.g., NGCC Plant, DCC and SGU) Eq. (8) gives positive $\dot{W}^{MAX}$.

$$\sum_{i=1}^{Nf} F_i \bar{H}_{F_i} + \dot{Q} - \dot{W} = \sum_{i=1}^{Np} P_i \bar{H}_{P_i} \tag{1}$$

$$\dot{W} = -\left(\sum_{i=1}^{Np} P_i \bar{H}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{H}_{F_i} \right) + \dot{Q} \tag{2}$$

$$\dot{W} = \dot{W}^{MAX} \; , \; \dot{Q} = \dot{Q}^{REV} \tag{3}$$

$$\sum_{i=1}^{Np} P_i \bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{S}_{F_i} - \frac{\dot{Q}^{REV}}{T_0} = \dot{S}^{UNIV^{REV}} = 0 \tag{4}$$

$$\dot{W}^{MAX} = -\left(\sum_{i=1}^{Np} P_i \bar{H}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{H}_{F_i} \right) + \dot{Q}^{REV} \tag{5}$$

$$\dot{Q}^{REV} = T_0 \left(\sum_{i=1}^{Np} P_i \bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{S}_{F_i} \right) \tag{6}$$

$$\dot{W}^{MAX} = -\left(\sum_{i=1}^{Np} P_i \bar{H}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{H}_{F_i} \right) + T_0 \left(\sum_{i=1}^{Np} P_i \bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i \bar{S}_{F_i} \right) \tag{7}$$

$$\dot{W}^{MAX} = -\left(\sum_{i=1}^{Np} P_i (\bar{H}_{P_i} - T_0 \bar{S}_{P_i}) - \sum_{i=1}^{Nf} F_i (\bar{H}_{F_i} - T_0 \bar{S}_{F_i}) \right) \tag{8}$$

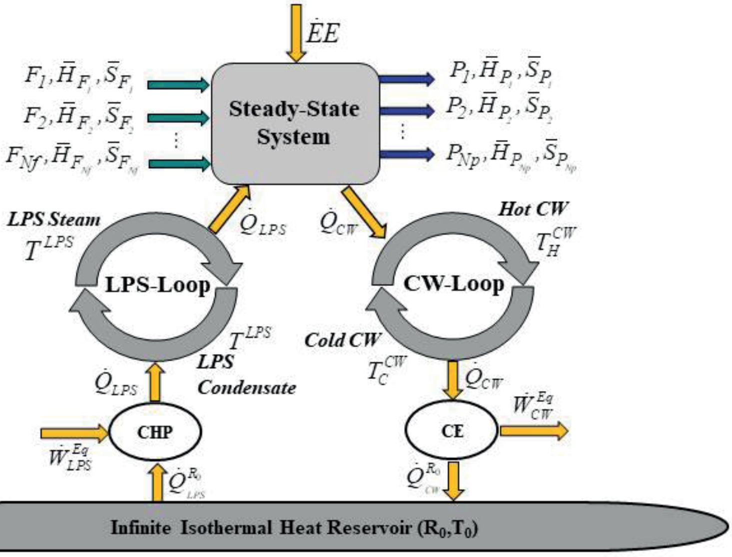

Figure 5 - Equivalent power for power-consuming System (blue-arrows=product-streams, green-arrows=feed-streams): imports electricity ($\dot{E}E$), exports equivalent power via CW-Loop ($\dot{W}_{CW}^{Eq}$) and imports equivalent power via LPS-Loop ($\dot{W}_{LPS}^{Eq}$) (CW=Cooling-Water, LPS=Low-Pressure-Steam, CHP=Carnot-Heat-Pump, CE=Carnot-Engine).

2.2.2. Equivalent Power

Equivalent power $\dot{W}^{Eq}$ is always-positive for "regular" systems, but can be negative for "lawless" systems like a theoretically power-producing system (i.e., spontaneous system) that consumes power (e.g., CW-Tower). $\dot{W}^{Eq}$ is the thermodynamic power equivalence of electricity consumption (production) and utility consumption (production). For instance, LPS consumption (production) is equivalent to $\dot{W}^{Eq}$ consumption (production), while CW consumption is always equivalent to $\dot{W}^{Eq}$ production. Offshore GTW-EGR-CCS-CDU uses three kinds of utilities: (i) CW with flowrate J^{CW} (*kmol/s*), isobaric heat capacity $\bar{C}_P^{CW}$ (*MJ/kmol.K*) and hot/cold temperatures T_H^{CW} (*K*), T_C^{CW} (*K*); (ii) LPS with flowrate J^{LPS} (*kmol/s*), vaporization-enthalpy $\Delta\bar{H}_{LPS}^{VAP}$(*MJ/kmol*) and temperature T^{LPS}(*K*)*;* and (iii) Electricity $\dot{E}E$ (*MW*)*.* $\bar{C}_P^{CW}$ and $\Delta\bar{H}_{LPS}^{VAP}$ are assumed constant considering CW and LPS narrow temperature ranges.

Equivalent Power is related to electricity consumption/production ($\dot{E}E$) and equivalent power effects associated to thermal utilities consumption/production (Carminati *et al.*, 2020). Heat-Power equivalences are settled through reversible heat-engines with maximum heat-work conversion yield; namely, the Carnot Engine (CE) and the Carnot Heat-Pump (CHP) (Milão *et al.*, 2021). CE absorbs heat from a hot source, exports power and rejects heat to a colder source, while CHP imports power, absorbs heat from a cold source and rejects heat to a hotter one. Figure 5 shows a Power-Consuming System with the following utility effects: absorbs $\dot{E}E$, rejects heat $\dot{Q}_{CW}$ to CW-Loop (exports power $\dot{W}_{CW}^{Eq}$) and absorbs heat $\dot{Q}_{LPS}$ from LPS-Loop (imports power $\dot{W}_{LPS}^{Eq}$). In Figure 5, CW-Loop and LPS-Loop are external to the System, R_0 is always a cold heat reservoir (cold source), and $\dot{W}_{CW}^{Eq}$, $\dot{Q}_{CW}$, $\dot{W}_{LPS}^{Eq}$, $\dot{Q}_{LPS}$ are always positive. It is easy to construct an analogous version of Figure 5 for a Power-Producing System (i.e., electricity and LPS are exported and CW is imported).

The steady-state Power-Consuming System (Figure 5) rejects heat $\dot{Q}_{CW}$ to cold-CW producing hot-CW, which is restored to cold-CW via a CW-Loop using CE that exports power $\dot{W}_{CW}^{Eq}$ and rejects heat $\dot{Q}_{CW}^{R_0}$ to R_0. Analogously, the Power-Consuming System absorbs heat $\dot{Q}_{LPS}$ from LPS becoming LPS-Condensate, which is restored to LPS via a LPS-Loop using CHP that imports power $\dot{W}_{LPS}^{Eq}$ and absorbs heat $\dot{Q}_{LPS}^{R_0}$ from R_0. $\dot{W}_{CW}^{Eq}$ is given by Eq. (10) using Eq. (9a), Eq. (9b) and CE entropy conservation in Eq. (9c). Accordingly, is given by Eq. (12) using Eq. (11a), Eq. (11b) and CHP entropy conservation in Eq. (11c). Eq. (12) also works for $\dot{W}_{LPS}^{Eq}$ in Power-Producing Systems, but LPS-Loop rotates counter-clockwise, CHP is replaced by CE, and all effects are reversed.

$$\dot{W}_{CW}^{Eq} = \dot{Q}_{CW} - \dot{Q}_{CW}^{R_0} \tag{9a}$$

$$\dot{Q}_{CW} = J^{CW}\bar{C}_P^{CW}(T_H^{CW} - T_C^{CW}) \tag{9b}$$

$$\frac{\dot{Q}^{R_0}_{CW}}{T_0} + J^{CW}\bar{C}^{CW}_{P}\, ln\left(\frac{T^{CW}_{C}}{T^{CW}_{H}}\right) = 0 \tag{9c}$$

$$\dot{W}^{Eq}_{CW} = J^{CW}\bar{C}^{CW}_{P}\left(T^{CW}_{H} - T^{CW}_{C} - T_0.ln\left(\frac{T^{CW}_{H}}{T^{CW}_{C}}\right)\right) \tag{10}$$

$$\dot{W}^{Eq}_{LPS} = \dot{Q}_{LPS} - \dot{Q}^{R_0}_{LPS} \tag{11a}$$

$$\dot{Q}_{LPS} = J^{LPS}\Delta\bar{H}^{VAP}_{LPS} \tag{11b}$$

$$-\frac{\dot{Q}^{R_0}_{LPS}}{T_0} + J^{LPS}\frac{\Delta\bar{H}^{VAP}_{LPS}}{T^{LPS}} = 0 \tag{11c}$$

$$\dot{W}^{Eq}_{LPS} = J^{LPS}\Delta\bar{H}^{VAP}_{LPS}\left(1 - \frac{T_0}{T^{LPS}}\right) \tag{12}$$

Eq. (13a) calculates the Equivalent Power *consumed* by a Power-Consuming System that consumes $\dot{EE}$, CW and LPS. Analogously, Eq. (13b) gives the Equivalent Power *produced* by a Power-Producing System that exports $\dot{EE}$ and LPS (counter-clockwise LPS-Loop in Figure 5) and consumes CW. Substituting Eqs. (10) and (12) into Eqs. (13a) and (13b), Eq. (14a) and Eq. (14b) are respectively created, giving the Equivalent Power consumed by a Power-Consuming System and the Equivalent Power produced by a Power-Producing System.

$$\dot{W}^{Eq} = \dot{EE} + \dot{W}^{Eq}_{LPS} - \dot{W}^{Eq}_{CW} \qquad \{\textit{Power-Consuming System} \tag{13a}$$

$$\dot{W}^{Eq} = \dot{EE} + \dot{W}^{Eq}_{LPS} + \dot{W}^{Eq}_{CW} \qquad \{\textit{Power-Producing System} \tag{13b}$$

$$\dot{W}^{Eq} = \dot{EE} + J^{LPS}\Delta\bar{H}^{VAP}_{LPS}\left(1 - \frac{T_0}{T^{LPS}}\right) - J^{CW}\bar{C}p^{CW}\left(T^{CW}_{H} - T^{CW}_{C} - T_0.ln\left(\frac{T^{CW}_{H}}{T^{CW}_{C}}\right)\right) \tag{14a}$$

$$\dot{W}^{Eq} = \dot{EE} + J^{LPS}\Delta\bar{H}^{VAP}_{LPS}\left(1 - \frac{T_0}{T^{LPS}}\right) + J^{CW}\bar{C}p^{CW}\left(T^{CW}_{H} - T^{CW}_{C} - T_0.ln\left(\frac{T^{CW}_{H}}{T^{CW}_{C}}\right)\right) \tag{14b}$$

2.2.3. Thermodynamic Efficiency

Second Law Analysis obtains the Thermodynamic Efficiency and the Lost-Work (Lost-Power) of the System in order to calculate resource degradation. With $\dot{W}^{MAX}$ (Eq. (8)) and $\dot{W}^{Eq}$ (Eqs. (14a) and (14b)) the thermodynamic efficiencies of Power-Consuming Systems and of Power-Producing Systems are calculated by Eq. (15a) and Eq. (15b), respectively.

$$\eta\% = 100.(-\dot{W}^{MAX})/\dot{W}^{Eq} \qquad \{\textit{Power-Consuming System} \tag{15a}$$

$$\eta\% = 100.\dot{W}^{Eq}/\dot{W}^{MAX} \qquad \{\textit{Power-Producing System} \tag{15b}$$

2.2.4. Lost-Work

Eq. (16a) and Eq. (16b) are naturally intuitive Lost-Work (Lost-Power) formulas for Power-Consuming Systems and Power-Producing Systems, respectively.

$$\dot{W}^{LOST} = \dot{W}^{Eq} - (-)\dot{W}^{MAX} \qquad \{\textit{Power-Consuming System} \tag{16a}$$

$$\dot{W}^{LOST} = \dot{W}^{MAX} - \dot{W}^{Eq} \qquad \{\textit{Power-Producing System} \tag{16b}$$

An alternative way to calculate Lost-Work can be derived from the 2nd Law formula Eq. (17a) that accounts for all Universe changes caused by System transitions, where $\dot{S}^{UNIV}$ is the entropy-creation rate of the Universe due to the System operation. Hence, Eq. (17b) and Eq. (17c) are Lost-Work formulas generated by Eq. (17a) for Power-Consuming Systems and for Power-Producing Systems, respectively, where $\dot{S}^{R_0}$ was replaced by Eq. (18a) and Eq. (18b), respectively for Power-Consuming Systems (Figure 5) and Power-Producing Systems.

$$\dot{W}^{LOST} = T_0\dot{S}^{UNIV} = T_0\left(\dot{S}^{R_0} + \sum_{i=1}^{Np} P_i\bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i\bar{S}_{F_i}\right) \tag{17a}$$

$$\dot{W}^{LOST} = -J^{LPS}\Delta\bar{H}^{VAP}_{LPS}\left(\frac{T_0}{T^{LPS}}\right) + J^{CW}\bar{C}p^{CW}T_0.ln\left(\frac{T_H^{CW}}{T_C^{CW}}\right) + T_0\left(\sum_{i=1}^{Np} P_i\bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i\bar{S}_{F_i}\right) \tag{17b}$$

$$\dot{W}^{LOST} = J^{LPS}\Delta\bar{H}^{VAP}_{LPS}\left(\frac{T_0}{T^{LPS}}\right) + J^{CW}\bar{C}p^{CW}T_0.ln\left(\frac{T_H^{CW}}{T_C^{CW}}\right) + T_0\left(\sum_{i=1}^{Np} P_i\bar{S}_{P_i} - \sum_{i=1}^{Nf} F_i\bar{S}_{F_i}\right) \tag{17c}$$

$$\dot{S}^{R_0} = \frac{\dot{Q}^{R_0}_{CW}}{T_0} - \frac{\dot{Q}^{R_0}_{LPS}}{T_0} = J^{CW}\bar{C}_P^{CW}ln\left(\frac{T_H^{CW}}{T_C^{CW}}\right) - J^{LPS}\frac{\Delta\bar{H}^{VAP}_{LPS}}{T^{LPS}} \tag{18a}$$

$$\dot{S}^{R_0} = \frac{\dot{Q}^{R_0}_{CW}}{T_0} + \frac{\dot{Q}^{R_0}_{LPS}}{T_0} = J^{CW}\bar{C}_P^{CW}ln\left(\frac{T_H^{CW}}{T_C^{CW}}\right) + J^{LPS}\frac{\Delta\bar{H}^{VAP}_{LPS}}{T^{LPS}} \tag{18b}$$

3. RESULTS AND DISCUSSION

Results from technical and thermodynamic analyses of the Offshore GTW-EGR-CSS-CDU follow and are discussed.

3.1. TECHNICAL PERFORMANCE

Table 2 summarizes the technical performance of Offshore GTW-EGR-CCS-CDU.

Table 2 - Technical results.

GTW-EGR-CCS-CDU	
Gross Power (MW)	599.3
Power Demand (MW)	64.9
Net Power (MW)	534.4
CO_2 Flue-Gas (t/h) (PCC-MEA Feed)	557.2
CO_2 Emissions (t/h) (Atmosphere)	59.6
PCC-MEA Results	
$CO_2^{Captured}$ (t^{CO2}/h)	497.6
Capture-Ratio ($kg^{Solvent}/kg^{CO2}$)	13.7
Heat-Ratio (kJ/mol^{CO2})	225
Lean-Solvent (t/h)	6,814
Absorber: T^{Top}(°C) / T^{Bottom}(°C)	62.2/61.9
Flue-Gas Inlet (%molCO_2)	17.3
Decarbonated Flue-Gas (%molCO_2)	1.8
Stripper: T^{Feed}(°C)/T^{Top}(°C)/T^{Bottom}(°C)	83/40/103
Reboiler Duty (MW)	722
CO_2 to CU-1 (%molCO_2)	92.7
CDU-TEG Results	
Capture-Ratio (kg^{TEG}/kg^{H2O})	3.7
Lean-Solvent (t/h)	2.1
CO_2 Inlet (ppm-mol H_2O)	2690.2
CO_2 Outlet (ppm-mol H_2O)	192.8
Absorber: T^{Top}(°C)/T^{Bottom}(°C)	36.4/35.3
Stripper: T^{Feed}(°C)/T^{Top}(°C)/T^{Bottom}(°C)	62/40/128
Reboiler Duty (MW)	0.6

Utilities Demand	**LPS (t/h)**	**CW (t/h)**	**Power (MW)**
NGCC Plant	-	6,109	0.15
DCC	-	-	0.36
PCC-MEA	1,230	36,249	0.35
CU-1	-	3,894	50.9
CDU-TEG	1.1	22.4	0.00355
SGU	-	-	-
CU-2	-	2,324	13.17
Total	**1,231**	**48,598**	**64.9**

The NGCC Plant (with five parallel NGCC elements) of Offshore GTW-EGR-CCS-CDU generates *599.3MW* of gross power (*≈92.4%* from gas-turbines) allowing *534.4MW* of net exported power. Each gas-turbine fires *≈4.76 kg/s* of fuel-gas producing *≈30MW* at *36.5%* LHV-efficiency. Thanks to the EGR, each NGCC element produces *370.6 kg/s* flue-gas at *16.5%*mol CO_2. HRSG cools down the gas-turbine flue-gas from *549°C* to *140°C*, the minimum temperature to maximize HPS generation allowing sufficient LPS for PCC-MEA and CDU-TEG.

PCC-MEA stripper requires *722.2MW* of LPS and discharges *144.2kg/s* of water-saturated CO_2 top product. CU-1 pressurizes the CO_2 stream up to *50bar* and feeds CDU-TEG. CDU-TEG removes *≈93%* of water from CDU-TEG feed and produces *503.8 t/h* of Dry-CO_2 (*≈193ppm-mol* H_2O). SGU sends *5.3 t/h* of low-pressure Dry-CO_2 to the TEG stripper reboiler to keep its temperature below *140°C*. TEG stripper reboiler demands 0*.6MW* of LPS. CU-2 exports *498.8 t/h* of Dry-CO_2 (*P=300bar, T=35°C*) to EOR. The power demand of Offshore GTW-EGR-CCS-CDU corresponds to *10.8%* of its gross power. The greatest electricity consumers are CU-1 and CU-2 compressor trains, while the greatest LPS and CW consumer is PCC-MEA. CDU-TEG requires a small LPS flowrate because the flowrate of captured water from the CO_2 stream is a tiny one.

3.2. THERMODYNAMIC ANALYSIS

Thermodynamic analysis and Lost-Work analysis were performed for Offshore GTW-EGR-CCS-CDU overall-system and its sub-systems, namely: (i) NGCC Plant; (ii) DCC; (iii) PCC-MEA; (iv) CU-1; (v) CDU-TEG; (vi) SGU and (vii) CU-2. There is no sub-system left; i.e., the GTW-EGR-CCS-CDU is correctly partitioned among the above sub-systems, which entail that the respective sums of $\dot{W}^{MAX}$, $\dot{W}^{Eq}$ and $\dot{W}^{LOST}$ over sub-systems would give the same value of the overall-system which are calculated independently of the sub-systems. Confrontation of overall-system values with the respective sum over sub-systems configures a consistency check of the thermodynamic analysis. In practice, there is always some divergence between overall-system and the sums over sub-systems, such that divergences below *1%* can be used to attest consistency of thermodynamic analysis.

3.2.1. Maximum Power, Equivalent Power and Thermodynamic Efficiency Results

Table 3 depicts thermodynamic efficiencies and other results of Second Law analysis of Offshore GTW-EGR-CCS-CDU and its sub-systems. Sub-systems PCC-MEA, CU-1, CDU-TEG and CU-2 are Power-Consuming Systems ($\dot{W}^{MAX} < 0$), thus Eq. (13a), Eq. (14a), Eq. (15a), Eq. (16a), Eq. (17b) and Eq. (18a) were used for $\dot{W}^{Eq}, \eta\%$, $\dot{W}^{LOST}$. On the other hand, the overall-system, NGCC Plant, DCC and SGU are Power-Producing Systems ($\dot{W}^{MAX} > 0$) and require Eq. (13b), Eq. (14b), Eq. (15b), Eq. (16b), Eq. (17c) and Eq. (18b) for $\dot{W}^{Eq}$, $\eta\%$, $\dot{W}^{LOST}$. The thermodynamic efficiency of overall Offshore GTW-EGR-CCS-CDU reaches 33.35% (Table 3).

The NGCC Plant is evidently a Power-Producing System due to its spontaneous transformations within the NGCC elements totaling a positive $\dot{W}^{MAX} = 1678.12MW$. The $\dot{W}^{Eq}$produced by each NGCC element is calculated as follows: $\dot{EE}$ produced as gas-turbines+steam-turbine power minus the Rankine-Cycle pump power (Figure 2), added to $\dot{W}^{Eq}_{CW}$ generated by Rankine-Cycle condenser, added to $\dot{W}^{Eq}_{LPS}$ from HRSG LPS exportation. The thermodynamic efficiency of NGCC Plant reached *48.62%*.

In DCC, CW should not be counted as utility ($\dot{W}^{Eq}_{CW} = 0$), since CW is a process stream suffering evaporation loss through DCC. Additionally, LPS was not consumed ($\dot{W}^{Eq}_{LPS} = 0$). Thus, only $\dot{EE}$ from the pump contributes (negatively) to $\dot{W}^{Eq}$. DCC $\dot{W}^{Eq}$ is negative because it is a Power-Producing System performing spontaneous changes ($\dot{W}^{MAX} > 0$), but no power was produced at all and electricity was consumed.

Table 3 - Second Law Analysis and Lost-Work Validation.

Second Law Analysis

Sub-System	$\dot{W}^{MAX}$ ***(MW)***	$\dot{W}^{Eq}_{LPS}$ ***(MW)***	$\dot{W}^{Eq}_{CW}$ ***(MW)***	$\dot{EE}$ ***(MW)***	$\dot{W}^{Eq}$ ***(MW)***	***η%***
NGCC Plant	*1678.12*	*212.37*	*4.40*	*599.18*	*815.96*	*48.62%*
DCC	*26.31*	-	-	*-0.36*	*-0.36*	*-1.37%*
PCC-MEA	*-31.29*	*212.19*	*31.41*	*0.35*	*181.14*	*17.27%*
CU-1	*-28.41*	-	*2.81*	*50.90*	*48.09*	*59.09%*
CDU-TEG	*-0.00014*	*0.18*	*0.07*	*0.00355*	*0.12*	*0.12%*
SGU	*0.48*	-	-	-	-	*0.00%*
CU-2	*-4.88*	-	*1.68*	*13.17*	*11.49*	*42.49%*
Overall System	***1602.33***	**-**	**-**	***534.40***	***534.40***	***33.35%***

Lost-Work and Lost-Work Validation

Sub-System	$\dot{W}^{LOST}$ ***(MW)****[*]*	$\dot{W}^{LOST}$ ***(MW)****[#]*	$\Delta\dot{W}^{LOST}$ ***(%)***
NGCC Plant	*862.16*	*860.66*	*0.17*
DCC	*26.67*	*26.50*	*0.64*
PCC-MEA	*149.85*	*149.03*	*0.55*
CU-1	*19.67*	*19.74*	*-0.36*
CDU-TEG	*0.1193*	*0.1189*	*0.34*
SGU	*0.480*	*0.478*	*0.42*
CU-2	*6.61*	*6.59*	*0.30*
Sum-Crosscheck	***1065.56***	***1063.12***	***0.23***
Overall-System	***1067.93***	***1061.74***	***0.58***

[*] *via Eqs. (16a)-(16b);* [#] *via Eqs. (17b)-(17c).*

As any separation process, PCC-MEA is a Power-Consuming System since $\dot{W}^{MAX}$ is negative due to CO_2 separation from flue-gas (*-31.29 MW*); i.e., PCC-MEA requires power consumption to work. PCC-MEA $\dot{W}^{Eq}$ consumption is calculated as follows: $\dot{E}E$ consumed in solvent recirculation and water make-up pumps is added to $\dot{W}^{Eq}_{LPS}$ consumed in PCC-MEA stripper reboiler, minus $\dot{W}^{Eq}_{CW}$ exported as Hot-CW from PCC-MEA stripper condenser and from lean-MEA cooler. PCC-MEA thermodynamic efficiency is *17.27%*.

CDU-TEG, another separation process, is too a Power-Consuming System ($\dot{W}^{MAX}$ *= -0.00014MW*). The small $\dot{W}^{MAX}$ derives from the small flowrate of water removed for CO_2 dehydration (from *≈2700 ppm-mol* H_2O to *≈200ppm-mol* H_2O). CDU-TEG has $\dot{W}^{Eq}$ *=0.12MW* calculated as follows: (i) $\dot{E}E$ consumed in TEG recirculation pumps is added to $\dot{W}^{Eq}_{LPS}$ consumed through LPS consumption in stripper reboiler, minus $\dot{W}^{Eq}_{CW}$ exported through Hot-CW from stripper condenser and from lean-TEG cooler. CDU-TEG thermodynamic efficiency is *0.12%*.

SGU is another sub-system driven by spontaneities; i.e., it is a Power-Producing System ($\dot{W}^{MAX}$*=0.48MW*). But its thermodynamic efficiency is *0%* because $\dot{E}E$, $\dot{W}^{Eq}_{LPS}$ and $\dot{W}^{Eq}_{CW}$ are all zero.

CU-1 and CU-2 perform non-spontaneous (compression) changes and are evidently Power-Consuming Systems ($\dot{W}^{MAX}$*=-28.41MW* and $\dot{W}^{MAX}$*=-4.88MW*). The respective $\dot{W}^{Eq}$ is calculated as follows: $\dot{E}E$ consumed in compressors and pump is subtracted from $\dot{W}^{Eq}_{CW}$ exported with Hot-CW from intercoolers. There is no LPS consumption ($\dot{W}^{Eq}_{LPS} = 0$). CU-1 and CU-2 thermodynamic efficiencies are *59.09%* and *42.49%*, respectively.

3.2.2. Lost-Work Results

Lost-Work reveals the power potential destroyed in GTW-EGR-CCS-CDU and its sub-systems due to irreversibility (spontaneity). Table 3 presents Lost-Work results and also proves the consistency of the present thermodynamic analysis by comparing Lost-Work values obtained via two thermodynamically independent ways: (i) via $\dot{W}^{MAX}$ and $\dot{W}^{Eq}$ in Eq. (16a) and Eq. (16b); and (ii) via $T_0 \cdot \dot{S}^{UNIV}$ in Eq. (17b) and Eq. (17c) for Power-Consuming and Power-Producing Systems, respectively. Table 3 also demonstrates consistency crosscheck in the sum of Lost-Works over sub-systems which, theoretically, should equals the overall-system Lost-Work (divergences are smaller than *1%*).

Figure 6 displays Sankey diagrams for $\dot{W}^{MAX}$, $\dot{W}^{Eq}$ and $\dot{W}^{LOST}$ flows for overall-system and its sub-systems. In Figure 6, $\dot{W}^{LOST}$ is the sum over sub-systems of Lost-Works ("pink" flows), while $\Delta\dot{W}^{LOST}$ is the difference to overall-system Lost-Work (Table 3). For *1602.3.2MW* of power availability ($\dot{W}^{MAX}$) in Offshore GTW-EGR-CCS-CDU *66.65%* is lost due to irreversibility. NGCC Plant has the greatest $\Delta\dot{W}^{LOST}$ (*832.2MW, 80.7%*) due to highly spontaneous combustion reactions, followed by PCC-MEA (*149.9MW, 14.0%*), DCC (26.7*MW, 2.5%*), CU-1 (*19.7MW, 1.8%*), CU-2 (*6.6MW, 0.6%*), SGU (*0.48MW, 0.04%*), and CDU-TEG (*0.1MW, 0.01%*).

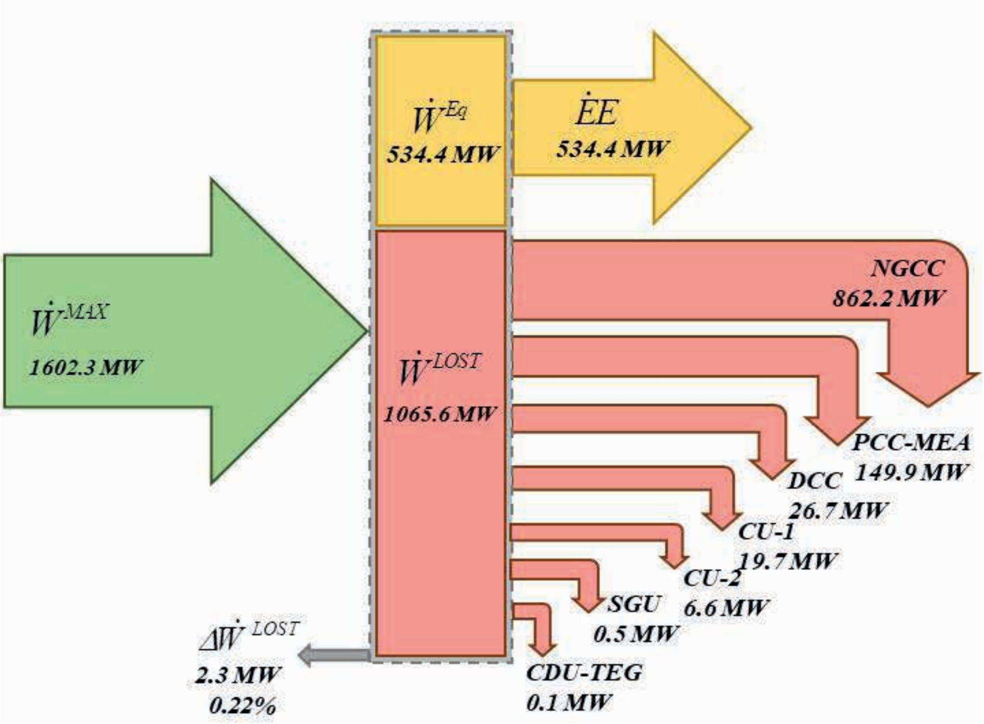

Figure 6 - Lost-Work Sankey diagram ($\dot{EE}$=Electricity, $\dot{W}^{MAX}$=Maximum-Power, $\dot{W}^{LOST}$=Lost-Work, $\dot{W}^{Eq}$ = Equivalent Power, NGCC=NG-Combined-Cycle, DCC=Direct-Contact-Column, PCC-MEA=Aqueous-MEA-Post-Combustion-Capture, CU=CO_2-Compression-Unit, CDU-TEG=CO_2-Dehydration-TEG-Unit, SGU=Stripping-Gas-Unit).

CONCLUSIONS

This work performed Technical and Thermodynamic Analyses of a conceptual Offshore GTW-EGR-CCS-CDU process firing *≈6.5MMSm³/d* of CO_2-rich NG (*CO_2≈44%mol*), exporting low-emission electricity and dense CO_2 as EOR-Fluid for economic and environmental benefits. Offshore GTW-EGR-CCS-CDU exports *534.4MW* of net power capturing *≈90%* of the flue-gas CO_2. CU-1 compresses the CO_2 stream up to *50bar* in order to perform CO_2 dehydration in CDU-TEG. Offshore GTW-EGR-CCS-CDU is an intensified process, whose factors of intensification comprehend the Exhaust-Gas Recycle (EGR) and the high-pressure CO_2 dehydration in CDU-TEG which removes *≈93%* of water from the CO_2-to-EOR stream delivering a safe CO_2-to-EOR stream with *»200ppm-mol* H_2O. By its turn, EGR is important whenever post-combustion capture is being used because it dismisses air excess (typically *»100%*) for gas-turbine flame temperature abatement, consequently reducing by *»50%* the flue-gas volumetric flow and raising its CO_2 content from typical *»8%mol* (no EGR) to *»17%mol* (with EGR). These two consequences of EGR drastically reduce investment and manufacture cost of the PCC-MEA plant due to reductions of column diameter and height improving low-emission GTW profitability.

The 2nd Law analysis of Offshore GTW-EGR-CCS-CDU overall-system unveils a *33.35%* thermodynamic efficiency with *66.65%* of Lost-Work, whose greatest Lost-Work sink lies in the NGCC Plant sub-system (*80.7%* share), due to the highly spontaneous gas-turbine firing process. The second Lost-Work sink lies in PCC-MEA sub-system (*14.0%* share*)*. Thus, the NGCC Plant and PCC-MEA are the main units of GTW-EGR-CCS-CDU that deserve upgrading in order to bring most benefits to GTW-EGR-CCS-CDU. The consistency of the thermodynamic analysis was established through Lost-Work sum-crosschecks and lateral checks using the alternative 2nd Law formula $T_0 \cdot \dot{S}^{UNIV}$ for the Lost-Work (Table 3).

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CHAPTER 5

BIOENERGY WITH CARBON CAPTURE AND STORAGE VIA LANDFILL GAS OXY-COMBUSTION

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ABSTRACT: Landfill gas collection and utilization is necessary to reduce emission of greenhouse gases and promote transition into a renewable energy matrix. Power generation (landfill-gas-to-wire) is a common choice for availing this resource, as it avoids purification and transportation issues, with direct benefits of electricity supply to local community. Since urban wastes are typically rich in biomass, the generated CO_2 is partially biogenic, so a plausible implementation of carbon capture and storage would configure a way to promote carbon dioxide removal from atmosphere, from a carbon life-cycle viewpoint. In this work, economic evaluation of a zero-emission landfill-gas-to-wire process is addressed, where CO_2 capture occurs by adoption of an oxyfuel combined cycle, which performance is compared against a conventional CO_2-emitting combined cycle charged by carbon taxation. The analysis is supported by simulation in Aspen Hysys, assuming that the process has a fixed large-scale feed along 20 years of operation, as base destination for collected landfill gas. Operating conditions for different gas turbine pressure-ratios are defined for the maximization of net present value of both conventional and oxyfuel process concepts. The greatest net present value of oxyfuel and conventional processes is attained at combustion pressure of ≈20 and ≈8 bar, respectively. This indicates that compression demands and plant investment considerably lower gas turbine optimal pressure-ratio for landfill-gas processing. At best conditions, the efficiency penalty is 9.2%LHV and the proportion of CO_2 capture flow to net power export is 0.875 kg/kWh. Higher net present value of proposed zero-emission oxyfuel power generation over conventional combined cycle occurs if the CO_2 tax is above 95 USD/t.

KEYWORDS: CO_2 capture, combined cycle, oxyfuel, power generation, techno-economic analysis.

ABBREVIATIONS

ASU Air Separation Unit; BECCS Bioenergy with Carbon Capture and Sequestration; CCUS Carbon Capture, Utilization, and/or Storage; CONV Conventional; GOX Gaseous Oxygen; GT Gas-Turbine; HRSG Heat-Recovery-Steam-Generation; LGTW Landfill-Gas-To-Wire; LHV Lower Heating Value; RIOC-CC Regenerative Intercooled Oxy-Combustion Combined-Cycle; SCOC-CC Semi-Closed Oxy-Combustion Combined-Cycle; ST Steam-Turbine; TVR-2REB Top Vapor Recompression Distillation with Two Reboilers; USD US Dollar.

Nomenclature

c_p	*Specific heat capacity at constant pressure (kJ.kg^{-1}.K^{-1})*
c_v	*Specific heat capacity at constant volume (kJ.kg^{-1}.K^{-1})*
CEPCI	*Chemical engineering plant cost index (dimensionless)*
F	*Molar flow (kgmol.h^{-1})*
NPV	*Net present value (USD)*
P	*Pressure (bar)*
T	*Temperature (°C)*
W	*Mechanical power (kW)*
Y_k	*Mol-fraction of specie k (dimensionless)*
Greeks	
γ	*Gas isentropic exponent (dimensionless)*
η	*Adiabatic efficiency (%)*
Subscripts	
comb	*Combustor outlet*

1. INTRODUCTION

Major efforts in all economy sectors are necessary to reduce greenhouse gas emissions and meet the targets of the Paris Agreement. This requires large-scale employment of renewable resources and minimum fossil-based power generation, preferably associated to CO_2 capture, for a desired drastic cut on current CO_2 emissions (IPCC, 2013). To assist meeting these targets, carbon dioxide removal (CDR) from atmosphere will be important for mitigation of climate change (Fuss *et al.*, 2014). This can be done either by CO_2 biological fixation or direct air capture. The latter is significantly more expensive to invest and operate, so CDR will seriously depend on deploying bioenergy with carbon capture and storage (BECCS) (IPCC, 2014), which can offset emissions that are more expensive to mitigate (Haszeldine *et al.*, 2018). In this context, the use of biomass wastes avoids is a way to avoid social and ecological issues related to energy-oriented crops (Pour *et al.*, 2018), thus offering a sustainable alternative for fossil fuels displacement (Mukherjee *et al.*, 2020) featured by significant socio-economic benefits (Creutzig *et al.*, 2015).

1.1. LANDFILL GAS

Municipal solid waste can be viewed as a potential resource for the economy. In this regard, an ideal waste management approach would be to promote waste valorization, with only the inevitable residues being sent to landfills, or to cost-effective biochemical (e.g., anaerobic digestion, composting) or thermochemical conversion (e.g., gasification, incineration) (Garibay-Rodriguez *et al.*, 2018). The least expensive method is landfilling (Kalyani; Pandey, 2014), but the option lead to significant socio-environmental impacts – beyond the loss of valorization opportunity – if naturally-generated landfill gas is emitted to atmosphere and not recovered. In open dumps, for example, final disposal of solid waste occurs without any environmental care, thus severely impacting air, water, and soil, while bringing explosion risks (Intharathirat *et al.*, 2016) and threatening the health of local population (Kalyani; Pandey, 2014). In this case, hazardous species in landfill gas and leachate contamination could be causes of health disorder (Mataloni *et al.*, 2016). To avoid these impacts planned sanitary landfills are necessary, with suitable management of landfill gas and leachate.

Landfill gas generation is influenced by waste profile and various features of the landfill (e.g., age, size, collection system) (Aguilar-Virgen *et al.*, 2014). It normally consists in a gas comprising mostly CH_4+CO_2, which can be availed as a fuel. For example, at approximately steady conditions (after some years of operation), a typical US landfill gas has the following dry-basis composition: 50-55%vCH_4, 45-50%vCO_2, and 2-5%v other species (e.g., volatile organic compounds, N_2, H_2S, siloxanes). According to EPA (2017), this production is nearly stable for ≈20 years. Possible uses include upgrading to biomethane, heating and/or electricity generation, evaporation of leachate, and conversion to other substances (e.g., hydrogen, methanol, bio-plastic) (Chidambarampadmavathy *et al.*, 2017). The mitigation of landfill gas direct emission is of great importance for combating climate change (Broun; Sattler, 2016), as the global warming potential of 1 kg CH_4 is 28 times higher than that of 1 kg CO_2 for 100 years, and 84 times higher for 20 years (IPCC, 2014). Moreover, less greenhouse gases are emitted if landfill gas is utilized to replace fossil fuels (Broun; Sattler, 2016). Therefore, net environmental performances strongly depend on efficient collection and utilization of landfill gas (Wanichpongpan; Gheewala, 2007). The collected gas not availed for useful purpose has to be flared to ensure elimination of CH_4, volatile organic compounds, toxic and odorant components (Fei *et al.*, 2019).

Landfill gas recovery and utilization is beneficial for governments and helps improving energy efficiency and energy security, with reduced dependence on remote suppliers of natural gas and electricity (Hetland *et al.*, 2016). Power plants using landfill gas can entail significant economic growth, create jobs and revenues, increase income tax collection, and benefit the environment directly by mitigation of greenhouse gases emission and indirectly due to fossil fuels avoidance (EPA, 2016). The electricity price is not expected to increase, as the break-even value is usually not high. For example, less than 0.04 USD/kWh was required in a study based on 2005 year, without government subsidies (Jaramillo; Matthews, 2005).

Power generation from landfill gas usually adopts internal combustion engines due to small feed capacities of 50-960 standard ft³/min (0.1-3.0 MW_e). Gas turbine (GT) is generally suitable for over 3 MW output, when supply is high and stable enough, above 1050 standard ft³/min at ≈50%v CH_4. Lower operation and maintenance costs, compact size, greater resistance to corrosion, complete and cleaner combustion are advantages over internal combustion engines (EPA, 2011). Furthermore, steam turbine (ST) is sometimes also prescribed in large projects, offering advantages of dismissing gas compression, greater resilience to gas contaminants, and greater operational flexibility (Rajaram *et al.*, 2011).

Many works on landfill gas conversion to electricity are reported in the literature but very few focus on technical aspects of the power cycle. Purmessur and Surrop (2019) modeled gas production in a specific landfill and assessed potential for power generation, which was simply estimated using literature data on net efficiencies. Also focusing on modeling landfill gas generation and further regarding collection efficiency, Broun and Sattler (2016) compared conventional and bioreactor landfill in terms of greenhouse gas emissions and electricity potential, but similarly considered literature data for efficiency of internal combustion engines. In contrast, this work presents full techno-economic analysis of a landfill gas-driven power cycle.

1.2. BIOENERGY WITH CARBON CAPTURE AND STORAGE

Besides fossil-based carbon capture, utilization and/or storage (CCUS), geological storage of biogenic CO_2 is way to promote effective mitigation of global warming (IPCC, 2014). BECCS deployment results in negative life-cycle emission of CO_2, because biomass growth occurs with CO_2 biofixation by photosynthesis, which indirectly introduces solar energy to life-cycle production chains. Contrarily to soil carbon sequestration and afforestation, BECCS is not subjected to terrestrial carbon stocks, contributing to mitigation of global warming with permanent CO_2 sequestration (Pour *et al.*, 2018), leading to continuous carbon dioxide removal from atmosphere (Milão *et al.*, 2019). Moreover, BECCS also improves diversity and flexibility of the energy portfolio of a country (Pour *et al.*, 2018), increasing renewable share of electricity mix, and enhancing regional energy security (Hetland *et al.*, 2016). However, large-scale deployment is likely to require strong policy support, even in countries with accumulated knowledge on CCUS and bioenergy production (Pour *et al.*, 2018), wherein carbon taxation may be regarded as important instrument (Meltzer, 2014).

Widespread implementation of BECCS depends on certain technical, economic and social issues. Bioenergy also has its environmental impacts (Gibson *et al*., 2017), especially if it depends on biomass cultivation and harvesting (Withey *et al*., 2019). In addition, further sustainability challenges are site availability for CO_2 geological sequestration and the possibility of competition for land and resources (Fuss *et al*., 2014), which could create a driver for deforestation and displacement of local communities, impacting biodiversity, tenure arrangements (Creutzig *et al*., 2015), and net CO_2 balance (Johnson, 2009). In some cases, project feasibility is also challenged by biomass transportation and production costs (Brigagão *et al*., 2019a). Nonetheless, such difficulties are alleviated if: (i) BECCS is part of a waste management system; and (ii) a CO_2 utilization pathway is adopted. The problem with the case (ii) is the large gap between potential market for CO_2 use as feedstock and scale requirements for climate stabilization (Mikulcic *et al*., 2019). Hence, an ideal mix of CO_2 storage and utilization routes should fit the objectives of CO_2 abatement. Currently, there is no other large-scale option yet to monetize captured CO_2 (for ≈1 million t/y) other than limited and early solution of enhanced oil recovery (Bui *et al*., 2018). Therefore, in this work, only geological storage is adopted.

1.3. OXY-COMBUSTION

Among the CO_2 capture routes for power generation, oxy-combustion is the only way for attaining zero-emission power (Foy; Yantovski, 2006). The alternative offers greater environmental performance, possibly with good profitability potential and higher overall efficiency. Combustion with nearly pure gaseous oxygen (GOX) implies in the production of flue gases constituted mainly by CO_2+H_2O, so that CO_2 is easily recovered after water condensation, being ready to be compressed for dispatch, unless finishing purification is needed depending on specificities of transport, storage and utilization (Pipitone; Bolland, 2009). The economic performance is highly dependent on air separation unit (ASU) capital investment and operating cost (Brigagão *et al*., 2019b), where cryogenic fractionation is currently the only economical route for large-scale GOX supply to oxy-combustion (Higginbotham *et al*., 2011). The most efficient cryogenic ASU ever developed for GOX production was presented by Brigagão *et al*. (2019b), with basis on cryogenic top vapor recompression distillation with two reboilers (TVR-2REB) to produce GOX at nearly atmospheric pressure, requiring only 139 kWh/t O_2 for 95%mol O_2. This nominal purity is conceived as a standard for oxyfuel power generation, because it avoids high power demand for Ar/O_2 fractionation, which occurs above 97%mol (Brigagão *et al*., 2019b).

A further challenge for large-scale implementation of this capture route is the requirement of utilizing special equipment for operation in oxyfuel mode, which may be not fully developed yet, as in the case of oxy-combustion GTs (Stanger *et al*., 2015). Nevertheless, several oxy-fired power-cycles have been proposed in the literature, among which the semi-closed oxy-combustion combined cycle (SCOC-CC), which is inspired in conventional air-blown natural gas combined cycle (Bolland; Saether, 1992). CO_2-based power-cycles sometimes comprises intercooled compression to supercritical conditions (e.g. Allam-cycle) and a bottoming steam-cycle is not always included (Stanger *et al.*, 2015). Water-injection is another design approach, where combustion temperature is abated by flue gas condensate, dismissing large gas-recycle compression in exchange to less expensive water pumping. The concept presents higher technology readiness level (Stanger *et al.*, 2015), given the report of a successful demonstration (Anderson *et al.*, 2008), but the overall efficiency is substantially lower than that of gas-recycle configurations (Chakroun; Ghoniem, 2015a). Processes combining both gas-recycle and water-injection techniques are also found in the literature (e.g. S-Graz cycle), eventually leading to greater net efficiency, at the expense of much higher design complexity (Kvamsdal *et al.*, 2007).

The GT pressure ratio is a key aspect in the design of an oxyfuel combined cycle (Dahlquist *et al.*, 2013). The optimum value highly depends on combustion temperature (T_{comb}) and steam-cycle operating conditions (Stanger *et al.*, 2015). Oxyfuel GTs have higher optimum pressure ratios than conventional air-blown GTs, if the same T_{comb} and steam-cycle conditions are considered (Mletzko; Kather, 2014). For example, in spite of usual combustion pressure of ≈20 bar in conventional machines (Dahlquist; Genrup, 2016), GTs for SCOC-CC are often conceived with 40-60 bar (Mletzko; Kather, 2014). The major reason is the lower isentropic exponent ($\gamma = c_p/c_v$) of the CO_2-rich working-fluid (Dahlquist *et al.*, 2013), which undergoes a lower temperature change on adiabatic compression and expansion (IPCC, 2005). The reduced temperature of CO_2-rich fluid adiabatic compression compared to air favors the increase of combustion pressure for higher power outputs. Nevertheless, higher combustion pressure implies in larger and more complex turbomachinery, which has to be weighed against net efficiency improvements (Dahlquist *et al.*, 2013). The behavior of the working-fluid is also influenced by greater density and lower sound speed of CO_2 in comparison with N_2-rich fluid of conventional GTs, leading to modifications in GT annular flow area (Stanger *et al.*, 2015).

Most works addressing definition of oxyfuel GT pressure-ratio only accounts the overall power efficiency, with temperature raise of gas compression being what usually limits the increase of combustion pressure (P_{comb}). However, the decision on a suitable pressure for construction of a real equipment has to account design challenges in turbomachinery and heat recovery steam generation (HRSG). In the case of SCOC-CC, the net efficiency curve plotted as a function of combustion pressure is flat around the optimum (Yang *et al.*, 2012), making the economically best condition to be slightly below the theoretical optimum for maximum efficiency (Dahlquist *et al.*, 2013). For instance, Dahlquist et al. (2013) found a theoretically optimum pressure ratio of ≈45 for the maximum net efficiency of SCOC-CC with T_{comb}≈1340°C, but indicated ≈34 as a better practical choice for equipment design. Another issue discussed in a later work (Dahlquist; Genrup, 2016) highlighted that pressure-ratios beyond 30 are common only in aero-derivative machinery – where GT compressor design seeks to favor aerodynamics and shaft-power output, at the expense of higher complexity – while industrial/heavy-duty GTs adopt a simpler design solution to minimize capital investment. In this sense, determination of the best GT pressure-ratio is addressed in this work through the perspective of economic performance, by accounting equipment sizes and their effect over the net present value (NPV), besides the fact that – on the contrary to NG-fired GTs – the fuel demands compression as it is received at atmospheric pressure, thus influencing the solution of best operating conditions.

1.4. THE PRESENT WORK

In analogy to conventional Gas-To-Wire solution applied to avail natural gas (Interlenghi *et al*., 2019), the idea of utilizing landfill gas for power generation is hereinafter referred to as landfill-gas-to-wire (LGTW). In this sense, an oxyfuel LGTW-BECCS solution for landfill gas use to power generation is evaluated in this work through technical and economic perspectives, aiming atmospheric CO_2 removal and CH_4 emission avoidance, in a scenario of carbon taxation. Few works in the literature have presented rigorous evaluation of oxyfuel processes using CO_2-rich feed gas, and the incidence of a carbon tax charging process emissions is not usually considered in LGTW studies, despite its important role for global warming mitigation (PEREIRA et al., 2016). A relevant study was presented by Chakroun and Ghoniem (2015a), where combined cycles based on sour gas oxy-combustion were analyzed, but the work does not fully apply to LGTW context, as CO_2 and H_2S contents in feed gas substantially diverges from what would be expected in landfill gas streams (EPA, 2017; Ko *et al*., 2015).

This work focuses on demonstrating economic performance of an oxyfuel LGTW-BECCS process, evaluated with economically optimum GT combustion pressure against a conventional air-blown combined cycle without CO_2 capture (LGTW-CONV). Besides being environmentally superior, the proposed LGTW-BECCS concept is proved as potentially more profitable than LGTW-CONV depending on CO_2 taxation charge.

2. METHODS

Assumptions adopted in this work are presented as following: Sec. 2.1 covers description of processes and simulation inputs, and Sec. 2.2 deals with equipment sizing and economic evaluation. The comparison of the concepts LGTW-BECCS – zero-emission oxyfuel combined cycle – and LGTW-CONV – CO_2-emitting air-blown combined cycle – is made after a pre-screening of process alternatives, where the economically-optimal version of each concept is explored to determine the respective base process. The comparison of the concepts does not cover feed gas upstream aspects, such as solid-waste transportation and handling, landfill operation, gas collection, and gas pre-purification, as they would perform the same regardless of the concept choice.

2.1. PROCESS SIMULATION

Figure 1 depicts a general diagram of the two concepts being compared (LGTW-CONV and LGTW-BECCS). The process alternatives were technically evaluated in Aspen HYSYS v8.8 utilizing the assumptions shown in Table 1.

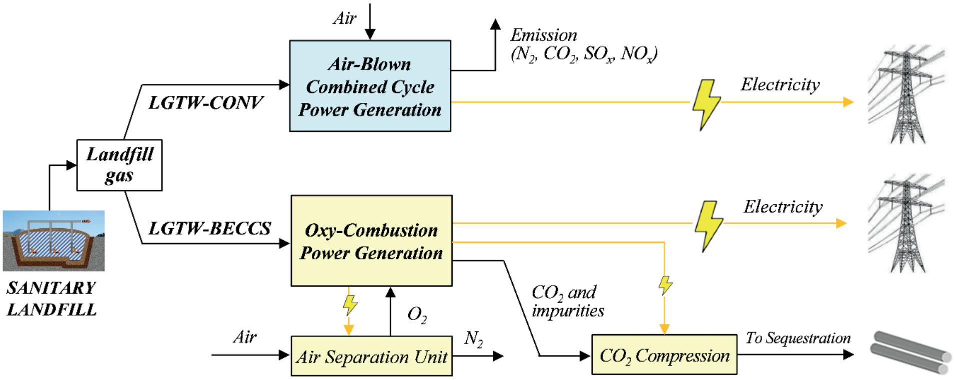

Figure 1 - Overview of considered landfill-gas-to-wire routes

All processes are combined cycles fed by ≈1.08 MMSm³/d of landfill gas. The considered composition ({P2}, Table 1) is in accordance with expected ranges reported by EPA (2017). The considered H_2S content (≈100 ppmv) was chosen with basis on Ko *et al.* (2015). Large facility for electricity generation is considered to favor combined cycle adoption and take advantage of economy of scale (Wanichpongpan; Gheewala, 2007), as feasibility of oxy-combustion requires cost-effective cryogenic ASUs. Assuming a hypothetical large landfill capable of producing more than 1.08 MMSm³/d of gas along 20 years, the fixed flow rate supplying the power plant would serve as bulk destination for the collected gas. The remaining portion is supposed to be directed to other uses (e.g. heating), which are not addressed in present analysis.

Table 1 - Assumptions of process simulation

Item	Assumption
{P1}	Thermodynamic modeling: Peng-Robinson Equation-of-State, with ASME-Table for water-steam
{P2}	Landfill gas (%mol): P=1 atm, T=40°C, F=1869 kmol/h (1.08 MMSm³/d), 46.37%CH_4, 44.51%CO_2, 1.85%N_2, 0.01%H_2S, 7.26%H_2O (water-saturated)
{P3}	GOX (%mol): P=1 atm, T=15°C, 1832 kmol/h (1.41*10⁶ kg/d), 95%O_2, 2.39%Ar, 2.61%N_2
{P4}	Specific power consumption of air separation unit: 139 kWh/t O_2 (BRIGAGÃO et al., 2019b)
{P4}	Combined cycle configuration (gas turbines : steam turbines): 1:1
{P5}	Adiabatic efficiency of expanders: η=90%
{P6}	Adiabatic efficiency of axial compressors: η=85%
{P7}	Adiabatic efficiency of centrifugal compressors: η=80%
{P8}	Adiabatic efficiency of pumps: η=75%
{P9}	Gas turbine (GT) expander inlet temperature: T=1300°C
{P10}	Steam turbine (ST) inlet conditions: 560°C@70 bar (single-pressure)
{P11}	Vacuum condenser: inlet pressure 0.10 bar, ΔP=1 kPa, T^{OUTLET}=43.8°C
{P12}	Heat recovery steam generator (HRSG): $\Delta T^{APPROACH3}$ 20°C, ΔP^{GAS}=3 kPa, ΔP^{H2O}=50 kPa
{P13}	Direct contact column: theoretical-stages=3, Recycled-water 35°C, P^{TOP}=1 atm, ΔP=2 kPa
{P14}	Intercoolers: T^{GAS}=40°C, ΔP=3%$P \leq$ 50 kPa; Cooling-water: T^{SUPPLY}=30°C, T^{RETURN}=40°C
{P15}	CO_2 liquefaction: P=150 bar, T=40°C
{P16}	CO_2 exportation: P=250 bar

Landfill gas is supplied at atmospheric pressure and has to be compressed to feed the GT. A multistage intercooled compressor (maximum 150°C) is utilized for safety, as the gas may react at high temperatures (e.g., O_2 may be present in small content due to air intrusion). The hot flue gas leaving the GT is sent to HRSG, which operates with steam-cycle operated at fixed temperature and pressure conditions. Single-pressure Rankine is adopted to minimize process complexity and capital investment. Also, relatively high flue gas temperatures are known to reduce the need for multiple steam pressure levels (Dahlquist *et al.*, 2013).

2.1.1. Conventional Combined Cycle

Figure 2 depicts the process flowsheet of LGTW-CONV with values at economically optimal conditions for maximum NPV. Additional compression stages for landfill gas are included if GT P_{comb} exceeds 9 bar (not shown in Figure 2).

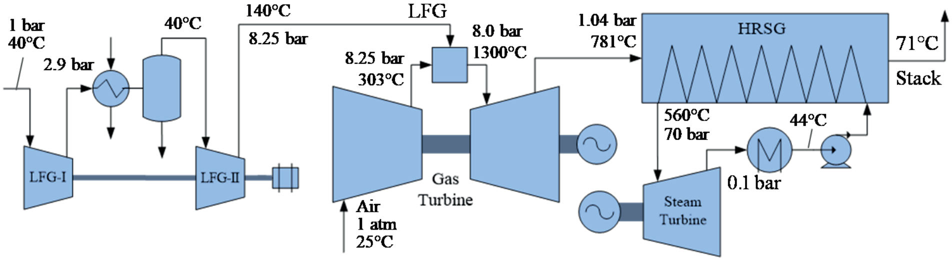

Figure 2 - LGTW-CONV base-process flowsheet

2.1.2. Oxy-Combustion Combined Cycles

Two oxyfuel configurations are compared to define the base-process of LGTW-BECCS: (a) semi-closed oxy-combustion combined cycle (SCOC-CC) (Bolland; Saether, 1992), involving adiabatic compression of gas-recycle (Figure 3); and (b) regenerative intercooled oxy-combustion combined cycle (RIOC-CC), where gas-recycle is subjected to intercooled multistage compression (Figure 4). RIOC-CC comparison with SCOC-CC aims to verify whether reduced power input to CO_2 compression improves NPV. RIOC-CC appears as modified version of the E-Matiant cycle without GT reheat (Mathieu *et al.*, 2000), into which a bottoming Rankine cycle is incorporated. Both oxyfuel processes have the following characteristics in common: (i) GOX at atmospheric pressure is supplied in stoichiometric proportion by a highly efficient standalone ASU (Brigagão *et al.* 2019b); (ii) intercooled compression (with maximum 150°C) of GOX is also considered for the best process safety and the lowest capital investment – thus contributing to process sustainability – as it avoids working with high-temperature pressurized GOX; (iii) the exhaust gas leaving HRSG is cooled by recycled condensate in a direct contact cooler (DCC) (Dahlquist *et al.*, 2013); (iv) combustion temperature abatement is promoted by recycling part of the cooled exhaust gas leaving the top of the DCC (Chakroun; Ghoniem, 2015a); (v) the unrecycled exhaust gas that leaves the DCC top (captured CO_2) is sent to compression for dispatch as a dense supercritical fluid at 250 bar.

Figure 3 presents the flowsheet of SCOC-CC, where annotations refer to economically optimal conditions for maximum NPV. The number of compression stages required for landfill gas and GOX depends on GT pressure ratio, thus entailing minor changes in the flowsheet. The recycled gas is sent to an adiabatic axial compressor installed in the front-end of the oxyfuel GT, which replaces the air compressor of a conventional GT.

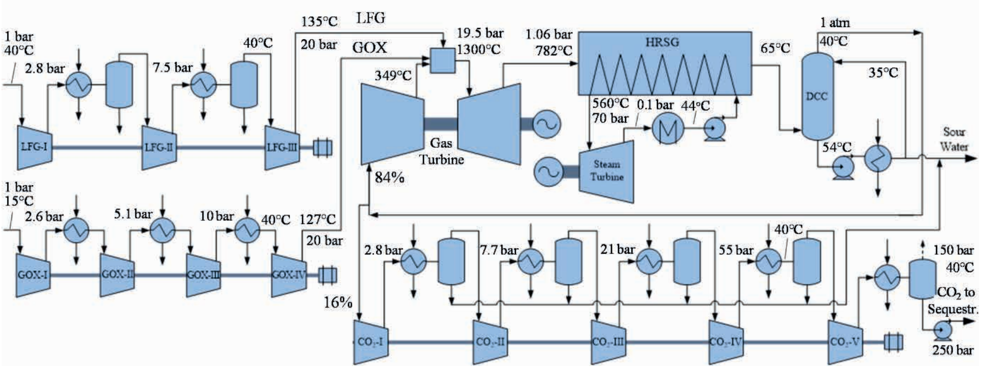

Figure 3 - Semi-closed oxy-combustion combined-cycle (SCOC-CC) at economically optimal conditions (LGTW-BECCS base-process)

Figure 4 presents RIOC-CC flowsheet with operating conditions at economically optimal values for maximum NPV. The process adopts regenerative Brayton cycle and the recycled gas is subjected to intercooled compression (as in E-Matiant cycle). Therefore, the shaft of its GT runs without driving any adiabatic axial compressor. Before entering the combustion chamber, the compressed gas recycle is heated within HRSG by GT exhausts up to a temperature 35°C below GT outlet. Even though this implies in higher recirculation flowrate, this is accomplished to ensure high-temperature injection in the combustion chamber for better overall efficiency.

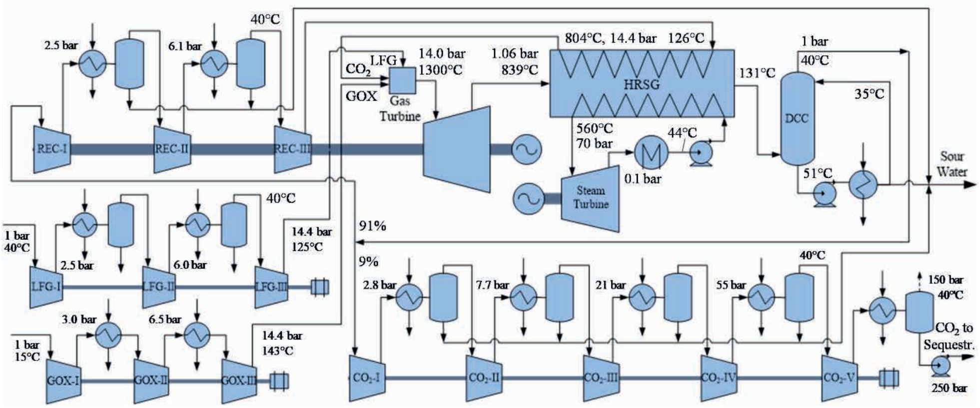

Figure 4 - Regenerative intercooled oxy-combustion combined-cycle (RIOC-CC) at economically optimal conditions

2.2. ECONOMIC EVALUATION

The economic performance of LGTW alternatives is analyzed using the assessment framework of Turton et al. (2012). Fixed capital investment estimates are updated using the chemical engineering plant cost index (CEPCI) for 2018-average. Since commercial oxyfuel GTs are not yet commercially available, the same procedure for GT capital investment estimation is adopted in LGTW-CONV and LGTW-BECCS processes, which is addressed by adding expander, compressor, and generator contributions, estimated separately via Turton et al. (2012). The equipment sizes are obtained through the methods of Campbell (1984), with basis on process simulation data.

Table 2 reveals the premises of economic analysis. Since zero-emission LGTW-BECCS can outperform CO_2-emitting LGTW-CONV in profitability potential if carbon taxation applies, the required tax level that makes the NPV of LGTW-CONV lower than that of LGTW-BECCS is estimated (for 20 years of operation). Emissions not directly related with power generation are not included in the analysis (i.e., those from other landfill gas uses, fugitive emissions, flare gas, and upstream activities).

Table 2 - Assumptions of financial analysis

Item	Assumption
{F1}	Electricity price: 108.7 USD/MWh (USA Price June/2018).
{F2}	CO_2 taxation in base-scenario: 0 USD/kg
{F3}	Utilities cost: cooling-water=0.016 USD/t
{F4}	ASU investment: extrapolated with 0.5 exponent from 141 MMUSD for GOX 52 kg/s (CLAUSEN et al)
{F5}	Fixed capital investment of equipment: extrapolated with six-tenth rule if exceeds Turton et al. ranges
{F6}	Fixed capital investment update*: *CEPCI*=603.1 (2018-average)
{F7}	Investment distribution: 20%/30%/50% (3 years of construction)
{F8}	Annual operation time: 8000 h/y
{F9}	Annual depreciation: 10% of total fixed capital investment
{F10}	Income tax rate: 34%
{F11}	Project horizon: 20 years of operation
{F12}	Annual interest rate: i=10%

*CEPCI≡Chemical engineering plant cost index

3. RESULTS AND DISCUSSION

Section 3.1 deals with definition of LGTW-CONV base process operating conditions by evaluation of P_{comb} variants ({P2}, Table 1). Similarly, Section 3.2 covers definition of LGTW-BECCS base process by techno-economic comparison of SCOC-CC and RIOC-CC variants. In Section 3.3, LGTW-CONV and LGTW-BECCS best performances are discussed, and the effect of CO_2 taxation is investigated.

3.1. LGTW-CONV VARIANTS

Five variants are evaluated, each one with its P_{comb}. Table 3 presents details on contribution of machines to net power generation, where a trade-off between ST and GT power is evinced for different GT outlet temperatures, as expected. GT pressure-ratio increase to ≈20 enhances power generation, but just a minor benefit is obtained by P_{comb} increase from 16 to 20 bar, due to power consumption to landfill gas compression. The emission factor of each variant, also presented in Table 3, ranges 711-753 g/kWh due to different net power outputs. A way to decrease the emission factor is to adopt a more efficient Rankine cycle – e.g., with reheat and multiple pressure levels – which could suit efficient operation with increased GT pressure-ratio and reduced outlet temperature, leading to higher power exportation. However, the increased complexity would also increase plant investment, possibly offsetting the advantage on NPV, so this aspect is not investigated in present work.

Table 3 - Performance of LGTW-CONV variants: power contribution of process machinery and CO_2 emission factor.

LGTW-CONV Alternative	**#1**	**#2***	**#3**	**#3**	**#4**	**Unit**
Combustion Pressure	**6.0**	**8.0**	**12.0**	**16.0**	**19.5**	**bar**
Fuel Gas Compressor	-3.35	-3.93	-4.56	-5.11	-5.49	MW
Gas Turbine	55.27	62.11	70.30	75.33	78.47	MW
Steam Turbine	48.12	45.30	-39.63	35.66	32.94	MW
Rankine-Cycle Pump	-0.38	-0.35	-0.31	-0.28	-0.26	MW
Overall Output	**99.67**	**103.13**	**105.06**	**105.59**	**105.66**	**MW**
CO_2 Emission Factor	**0.753**	**0.728**	**0.715**	**0.711**	**0.711**	**kg/kWh**

* LGTW-CONV Base-Process

While combined cycle power plants fed by natural gas usually adopts P_{comb}*≈20 bar* (Dahlquist; Genrup, 2016), a lower optimal pressure should be expected for LGTW systems given the need to compress the fuel. Table 4 confirms it in the comparison of LGTW-CONV variants regarding many techno-economic metrics, including the NPV for 20 years of operation (as a function of the various selected P_{comb}, without CO_2 tax). Figure 5 further portrays curves for net efficiency and NPV-20years, showing that despite maximum efficiency is attained in variant #5 (P_{comb}≈20 bar), the highest profitability potential is obtained in variant #2 (P_{comb}≈8 bar), indicating it as best LGTW-CONV base-process for comparison against LGTW-BECCS.

Table 4 - Summary of techno-economic sensitivity analysis for LGTW-CONV

Process alternative	P_{comb} (bar)	#Stages landfill gas	Net Power (MW)	Net Efficiency (%LHV)	*FCI*** (MMUSD)	*NPV* (MMUSD)
1	6.0	2	99.67	51.58	79.1	248.6
2*	8.0	2	103.1	53.37	84.6	254.0
3	12.0	3	105.1	54.36	91.4	252.0
4	16.0	3	105.6	54.64	96.0	248.5
5	19.5	3	105.7	54.67	99.4	244.3

* LGTW-CONV Base-Process; **FCI ≡ Fixed capital investment

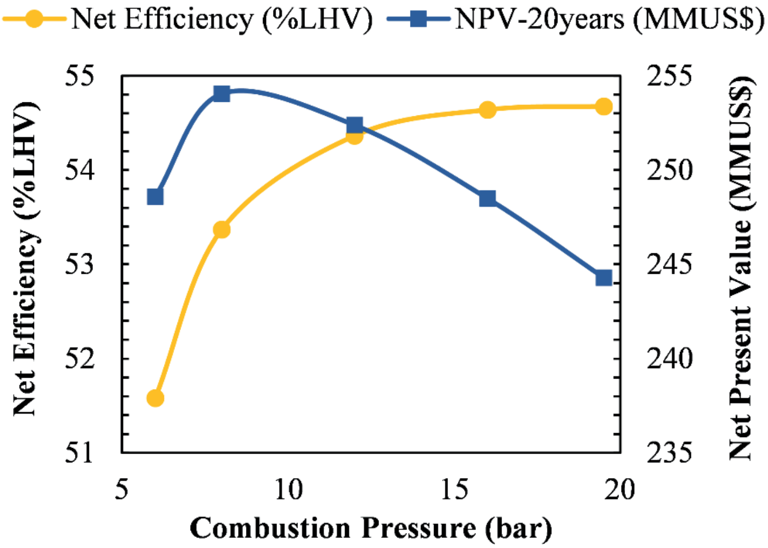

Figure 5 - Influence of GT combustion pressure on LGTW-CONV overall efficiency and NPV for 20 years of operation

3.2. LGTW-BECCS OXYFUEL VARIANTS

Ten oxyfuel variants are evaluated through energy and economic perspectives, five of which using SCOC-CC configuration for different P_{comb} (variants #1-5), while the remaining adopts RIOC-CC (variants #6-10). All LGTW-BECCS variants capture the totality of generated CO_2, presenting 74.7 t/h of CO_2 sequestration, thus leading to zero-emission power generation. Table 5 unveils the contribution of each process machine to the net power output of each variant.

Table 5 - Performance of LGTW-BECCS variants: power contribution of process machinery

LGTW-BECCS Alternative	**#1**	**#2**	**#3†**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**	**Unit**
Combustion Pressure	**8.0**	**14.0**	**19.5**	**29.5**	**39.5**	**14.0**	**19.5**	**29.5**	**39.5**	**59.5**	**bar**
Process Configuration	**SCOC-CC**					**RIOC-CC**					
Air Separation Unit	-7.74	-7.74	-7.74	-7.74	-7.74	-7.74	-7.74	-7.74	-7.74	-7.74	MW
Oxygen Compressor	-3.84	-4.97	-5.54	-6.37	-6.97	-4.97	-5.54	-6.37	-6.97	-7.66	MW
Fuel Gas Compressor	-3.93	-4.86	-5.49	-6.12	-6.64	-4.86	-5.49	-6.11	-6.64	-7.38	MW
Gas Turbine	52.39	63.59	69.62	76.46	80.92	102.0	103.8	106.8	108.1	109.5	MW
Steam Turbine	50.59	46.51	44.28	40.81	37.89	13.43	12.16	10.56	9.41	7.86	MW
CO_2 Compressor & Pump	-9.42	-9.42	-9.42	-9.42	-9.42	-9.41	-9.41	-9.41	-9.41	-9.41	MW
Auxiliary Equipment	-0.43	-0.40	-0.38	-0.36	-0.34	-0.16	-0.15	-0.13	-0.12	-0.11	MW
Overall Output	**77.63**	**82.71**	**85.33**	**87.26**	**87.71**	**88.25**	**87.60**	**87.57**	**86.69**	**85.04**	**MW**

† LGTW-BECCS Base-Process.

The comparison of variants #3 and #7 in Table 5 shows that electricity contribution of GT for the same design P_{comb}≈20 bar is lower in SCOC-CC (69.62 MW) than in RIOC-CC (103.8 MW), mainly as a consequence of reduced recycle of exhaust gas and higher specific compression power demand, which are 306 and 264 kJ/kg recycle-gas, respectively. Differences in working-fluid circulation leads compressor demand to 35.52 and 52.32 MW, and gas-expander power to 105.14 and 156.08 MW, respectively.

In both configurations, the power output ratio of GT and ST (W_{GT}/W_{ST}) substantially diverges from that of a conventional combined-cycle. SCOC-CC working-fluid has high CO_2 content, which implies in relatively low isentropic exponent ($\gamma=c_p/c_v$), thus requiring an increase in GT pressure-ratio to ≈40 (variant#5) to obtain a typical power ratio of about 2:1 (Table 5). RIOC-CC involves much smaller ST of ≈10 times lower power output comparatively to its GT, because the available heat in hot flue gas is transferred in HRSG mostly to the recycle-gas instead of to the steam-cycle. Therefore, RIOC-CC power generation is concentrated within the regenerative Brayton cycle, which leaves small heat duty available to drive the Rankine cycle. The relatively low availability of superheated steam – and consequently low power generation capacity – allows to conceive one or two STs as compressor drivers (e.g., for compression of CO_2 and landfill gas, which in variant#6 could reduce plant investment by 4 MMUSD).

Table 5 unveils P_{comb} entailing opposite influence over the performance of SCOC-CC and RIOC-CC at considered operating ranges. RIOC-CC presented the highest overall efficiency (variant#6: 45.67%LHV), where reduced P_{comb} favored net power (88.25 MW), since it leaves more heat available to preheat recycle gas (hot flue gas leaves GT at 839°C). Further reduction on GT P_{comb} should be limited by higher losses in heat exchange and reduced power in gas expansion. In contrast, the overall efficiency of SCOC-CC is favored when P_{comb} increases up to ≈40 bar, with minor benefits seen within 30-40 bar. A higher P_{comb} is not recommended and may imply in efficiency loss, mostly because the recycle gas becomes too hot for further adiabatic compression, drastically increasing subtraction of GT shaft-power.

3.2.1. Comparative Discussion with Literature Data

Indication of simulation results similarities is worthy even when slightly different design conditions are applied (most notably the assumed T_{comb}). In this regard, similar behavior of SCOC-CC overall efficiency response to P_{comb} was evinced by Dahlquist *et al*. (2013) for T_{comb}=1340°C, which shows a curve that also flattens out at around 40 bar. Yang et al. (2012) evaluated the influence of even higher pressure-ratio levels and also found flat efficiency curves, indicating ≈60 as the theoretical-optimum for T_{comb}=1418°C. Since small benefit is evinced from pressure-ratio increase within 40-60, a more realistic design would more likely consider P_{comb}≈40 bar in view of equipment investment and other practical issues in the design of large machines. Table 5 then indicates that, from a net efficiency perspective, the suitable P_{comb} for a plausible LGTW-BECCS using SCOC-CC configuration should be within 30-40 bar. In fact, the GT pressure-ratio for SCOC-CC is typically conceived at 30-40 when T_{comb} is between 1300-1400°C, which is slightly below the condition of maximum output estimated from process simulation (Stanger *et al*., 2015). Small efficiency increase is not likely to motivate development of much larger machines of higher P_{comb}. This aspect was discussed by Dahlquist *et al*. (2013), which pointed out that designing a GT with a pressure-ratio above 40 is defying even for an air-blown machine, then becoming more challenging in case of CO_2-rich working-fluid (e.g., due to lower sound speed). Hence, P_{comb}≈32 bar was regarded as more adequate for the application with T_{comb}=1340°C, accounting for GT outlet temperature at 620°C.

3.2.2. Optimal Pressure-Ratio

Determination of the most suitable pressure-ratio is here addressed with basis on NPV criteria for 20 years of operation. Although SCOC-CC is usually conceived with P_{comb}>30 bar – due to adoption of maximum net efficiency criteria – the economic perspective of present application to LGTW-BECCS reveals that P_{comb}≈20 bar is more adequate, mainly as a consequence of high impact of capital investment on NPV. In this sense, a comparison of LGTW-BECCS variants #1-10 is shown in Table 6, which presents assumed P_{comb} and corresponding number of compression stages for GOX and landfill gas, with the respective power output, net efficiency, fixed capital investment, and NPV of the overall process.

Table 6 - Summary of techno-economic sensitivity analysis for LGTW-BECCS

Process alternative	CC. Config.	P^{Comb} (bar)	#Stages recycle	#Stages landfill gas	#Stages GOX	Net Power (MW)	Net Efficiency (%LHV)	*FCI*** (MMUSD)	*NPV* (MMUSD)
1	SCOC	8.0	1	2	3	77.63	40.18	193.1	7.81
2		14.0	1	3	3	82.71	42.81	203.6	12.39
3†		19.5	1	3	4	85.33	44.16	210.2	13.08
4		29.5	1	4	4	87.26	45.16	217.4	10.35
5		39.5	1	4	4	87.71	45.39	221.6	6.36
6	RIOC	14.0	3	3	3	88.25	45.67	237.3	-12.68
7		19.5	3	3	4	87.60	45.33	237.7	-16.24
8		29.5	4	4	4	87.57	45.31	247.1	-29.40
9		39.5	4	4	4	86.69	44.86	247.0	-32.37
10		59.5	4	4	4	85.04	44.01	248.5	-40.60

† LGTW-BECCS Base-Process; **FCI ≡ Fixed capital investment

Despite the slightly lower overall efficiency, SCOC-CC has much greater NPV than RIOC-CC. The latter is also evinced as economically unfeasible even after 20 years of operation, as a consequence of relatively high capital investment, indicating that RIOC-CC inefficiently exploits the economic potential of landfill gas-fired power generation. Therefore, only SCOC-CC is considered for application to LGTW-BECCS from this point on.

Figure 6 portrays the influence of P_{comb} over the net efficiency and NPV of SCOC-CC. The curve of net efficiency flattens out close to the maximum in a similar behavior to the results of Bolland and Saether (1992), Yang et al. (2012), and Dahlquist *et al.* (2013). Despite maximum efficiency is attained at P_{comb}≈40 bar (variant#5), the NPV curve shows that the economically-optimal condition is attained at P_{comb}≈20 bar, which defines variant#3 as LGTW-BECCS base-process for subsequent comparison with LGTW-CONV.

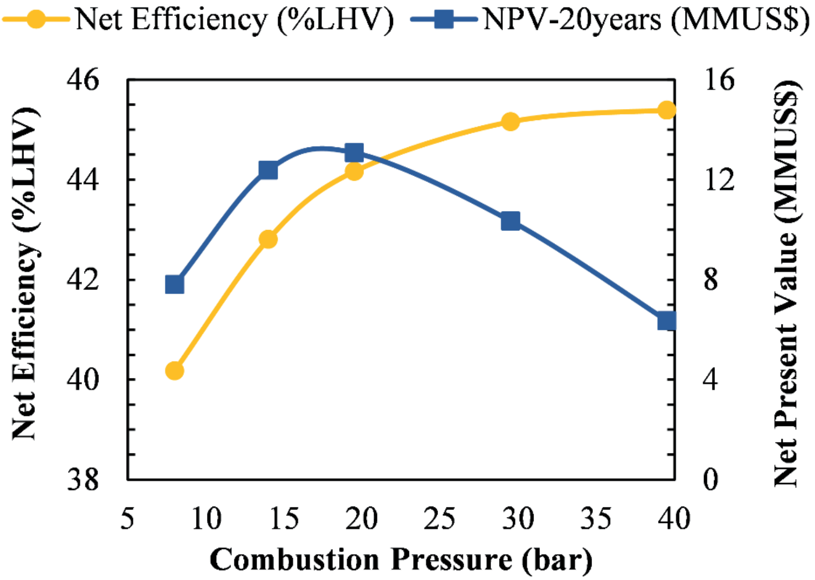

Figure 6 - Influence of GT combustion pressure on LGTW-BECCS overall efficiency and NPV for 20 years of operation

In relation to other possible oxyfuel processes, few other configurations seem suitable for LGTW-BECCS, making SCOC-CC a good choice. For example, Graz-cycles are efficient but involves complex configurations, an aspect that is likely to challenge process competitiveness. The Allam-cycle is efficient and has a simpler configuration, which reminds the E-Matiant process without a bottoming steam-cycle, but the capital investment is too high, because it is based on supercritical CO_2 cycle operated at very high pressures, with gas-expander inlet at P_{comb}≈300 bar and outlet at P≈30 bar (ALLAM et al., 2014). In contrast, water-injections processes worth investigation in a future work, as they may present a cost-effective performance due to reduced plant investment, despite of the relatively low efficiency (Chakroun; Ghoniem, 2015a), given the relatively low feed-gas capacity of typical LGTW plants.

3.3. COMPARISON OF LGTW CONCEPTS

Figures 7a-f portray sensitivity analysis profiles of NPV ÷ NPV_{max} as a function of P_{comb} – for the purpose of evaluating the influence of different parameters and confirming the obtained the optimum P_{comb} – for the concepts LGTW-CONV (Figures 7a-c) and LGTW-BECCS (Figures 7d-f). The profiles are calculated for various scenarios of annual interest rate (Figures 7a and 7d), annual operating hours (Figures 7b and 7e), and electricity price (Figures 7c and 7f). All profiles evince small influence of the selected parameters over the optimum P_{comb}. With base-processes for LGTW-CONV (variant #2) and LGTW-BECCS /

SCOC-CC (variant #3) defined accordingly to their respective P_{comb} for greatest long-term NPV, the concepts are compared in greater details in this section in technical and economic grounds.

3.3.1. Process Conditions

Table 7 presents operating conditions of main streams for LGTW-CONV and LGTW-BECCS plants, which results are complemented by process data in Figures 2 and 3, respectively. Stack emissions at LGTW-CONV reaches 75.05 t/h CO_2 with further 0.0111 t/h SO_2, while LGTW-BECCS entails no atmospheric emissions and produces 0.510 kmol/s of CO_2-rich supercritical fluid for sequestration (92.45%CO_2, 4.48%N_2, 2.38%Ar, 0.36%O_2, 0.33%H_2O, mol-basis). Significant amount of nitrogen and argon are carried to the fluid mainly due to presence of these species in GOX (95%O_2) and landfill gas ({P2}, {P3}, Table 1). A higher CO_2 content would reduce the power demand for CO_2 compression, and this can be accomplished by using GOX at a greater purity (up to 98%mol for the best overall efficiency) in exchange to slightly higher separation power in the ASU (Brigagão *et al*., 2019b). Nevertheless, further purification unit would be necessary in case the CO_2 stream has to follow strict purity specifications.

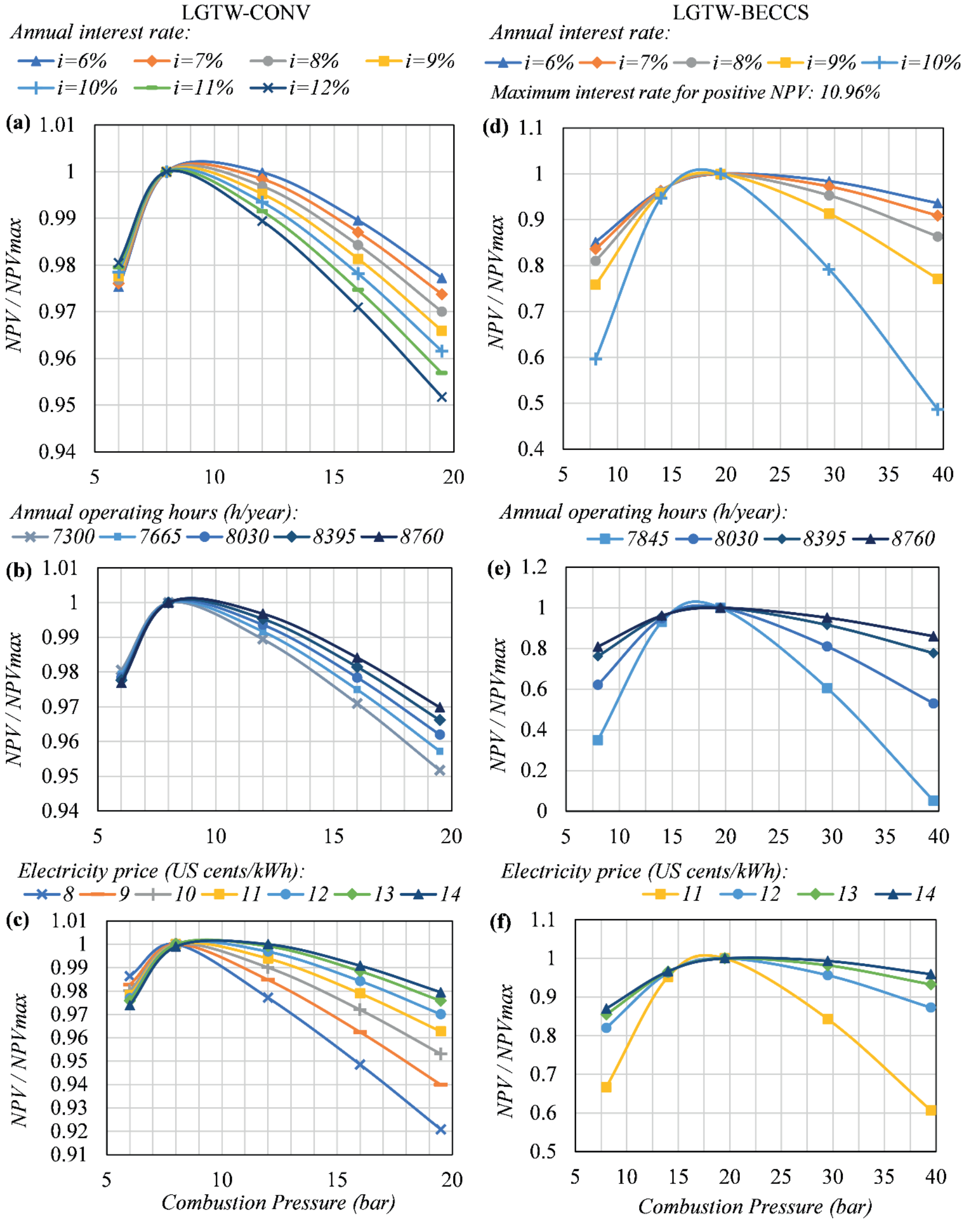

Figure 7 - Influence of Annual Interest Rate, Annual Operating Hours and Electricity Price over NPV ÷ NPV_{max} dependence upon GT combustion pressure (P_{comb}) for LGTW-CONV (a-c) and LGTW-BECCS (d-f)

Table 7 - Operating conditions and molar composition of main process streams

	LGTW-CONV					**LGTW-BECCS**						
Stream	Air Intake	Comb. Outlet	GT Outlet	Stack Gas	ST Inlet	GOX Feed	Comb. Outlet	GT Outlet	DCC Top	ST Inlet	Sour Water	CO_2 to Sequest.
P (bar)	1.013	8.00	1.043	1.013	70.0	1.013	19.5	1.060	1.013	70.0	1.50	250
T (°C)	25.0	1300	781	70.9	560	15.0	1300	782	40.0	560	35.4	61.2
F (kmol/h)	17254	19034	19034	19034	7482	1832	13699	13699	12089	7312	1747	1836
Y_k (molfrac)												
CO_2 :	0.0004	0.0896	0.0896	0.0896	-	-	0.7589	0.7589	0.8599	-	0.0004	0.9245
H_2O :	0.0189	0.1106	0.1106	0.1106	1.000	-	0.1817	0.1817	0.0729	1.000	0.9996	0.0033
O_2 :	0.2055	0.0953	0.0953	0.0953	-	0.9500	0.0029	0.0029	0.0033	-	0.0000	0.0036
Ar :	0.0091	0.0083	0.0083	0.0083	-	0.0239	0.0196	0.0196	0.0222	-	0.0000	0.0238
N_2 :	0.7660	0.6982	0.6982	0.6982	-	0.0261	0.0368	0.0368	0.0417	-	0.0000	0.0448

Operating conditions of LGTW-BECCS base-process (variant #3) – shown in Figure 3 – reveal an exhaust-gas recirculation ratio of 84%, which may be regarded as relatively low in relation to typical ≈90% of similar power-cycles (Stanger *et al.*, 2015). This is mainly a consequence of high CO_2 content in the fuel ({P2}, Table 1), which considerably reduces the required recycle ratio, because the temperature of landfill gas sent to GT is much lower than that of recycle gas. Even at greater P_{comb}≈40 bar (LGTW-BECCS variant #5), gas recirculation increases to only 85%, despite the higher recycle-gas temperature (442°C versus 349°C of base-process).

Regarding the flue gas temperature in oxyfuel GT outlet, other studies on SCOC-CC indicated that it is usually close to that of conventional air-blown GT at optimal pressure-ratio for combined cycle (Stanger *et al.*, 2015). The results shown in Table 7 also evinces this fact, as GTs have similar outlet temperatures in LGTW-BECCS and LGTW-CONV. A relatively high temperature of ≈782°C is achieved due to adoption of low P_{comb}, which is also a consequence of assumptions on steam-cycle (Table 1), since more complex Rankine cycles usually favor reduced GT outlet temperatures as a result of more efficient heat exchange, leading to higher optimum pressure-ratio. As discussed by Dahlquist *et al.* (2013), the advantage of using multiple steam pressure levels is lowered when GT outlet temperature is increased. More available heat beyond the boiler pinch-point allows greater steam generation, and the increased water flowrate also helps recovering more heat below the pinch-point. Then, depending on the steam-cycle configuration, the exhaust gas after HRSG may vary within 65-130°C (Dahlquist *et al.*, 2013). This explains relatively low temperature of this stream in both processes, as seen in Figures 2-3. The more efficient heat recovery shown in the oxyfuel process (65°C in HRSG outlet) is explained by deeper fall of flue gas specific heat capacity (c_p) along the HRSG – from 1.32 to 0.98 kJ/kgK in oxyfuel LGTW-BECCS, in contrast with 1.25-1.07 kJ/kgK shown in LGTW-CONV – which implies in less available heat to be recovered in the economizer, lowering heat transfer delta temperature in the end section of HRSG.

Tables 3 and 5 indicates ≈3.4%LHV (6.49 MW) higher gross power output of GT+ST in LGTW-BECCS, and also the consumption of 4.87%LHV in CO_2 compression and pumping, with further 4.00%LHV and 2.87%LHV for GOX production and compression, respectively. LGTW-BECCS overall efficiency is 44.16%LHV (TVR-2REB ASU demand included), thus power generation is reduced by 9.20%LHV (17.78 MW) from LGTW-CONV base-process. The efficiency penalty is consistent with the generally expected penalty of 8-11%LHV from previous works on oxyfuel GT cycles (Stanger *et al.*, 2015), but this result notably assumes a highly efficient ASU demanding 139 kWh/t O_2 (Brigagão *et al.*, 2019b). As conventional ASUs of double-column design typically require 200 kWh/t O_2 (Darde *et al.*, 2009), if such plants were considered for LGTW-BECCS in spite of TVR-2REB, power generation would be ≈3.7 MW lower, reducing power plant net efficiency by further 1.9%LHV.

3.3.2. Environmental Aspects

LGTW-CONV offers limited potential for mitigation of greenhouse gas emissions, essentially due to conversion of CH_4, reducing from 425.90 t/h of CO_2-equivalent (100-years horizon) to 75.05 t/h of CO_2 emissions (stack). Another problem is atmospheric release of SO_2 (e.g., contributing to acid rain formation), which may be up to 30 times higher than estimated 0.0111 t/h, as H_2S content in landfill gas can be as high as 3000 ppmv depending on solid-waste profile. In contrast, oxyfuel LGTW-BECCS allows removal of up to 37.36 t/h of CO_2 from atmosphere through carbon life-cycle (i.e., CDR, negative emission), if 50% of carbon source within landfilled waste derives from biomass (POUR et al., 2018). Nevertheless, production of SO_2-containing sour water is a practical issue, related to flue gas condensate from DCC and CO_2 compression, due to high SO_2 absorption by water (e.g., solubility at 25°C/1 atm is ≈94 g/L). The condensate can be neutralized by addition of CaO/$Ca(OH)_2$ (e.g., at DCC sump) to precipitate $CaSO_3$, which can be sent to landfill as inorganic waste or to finishing purification for sale (Chakroun; Ghoniem, 2015b).

3.3.3. Economic Analysis

Figure 8 depicts fixed capital investment comparison between LGTW-BECCS (including ASU) and LGTW-CONV with detailed contribution of process components. It evinces high investment on cryogenic ASU (1410 t/d GOX), which together with GOX compressor involves more investment than total LGTW-CONV facility. Since LGTW-BECCS also involves CO_2 compression for dispatch and requires more power to send landfill gas to GT due to increased P_{comb}, the fixed capital investment of this alternative (≈210.2 MMUSD) is unsurprisingly substantially higher, being almost 2.5 times higher than that of LGTW-CONV (≈84.6 MMUSD).

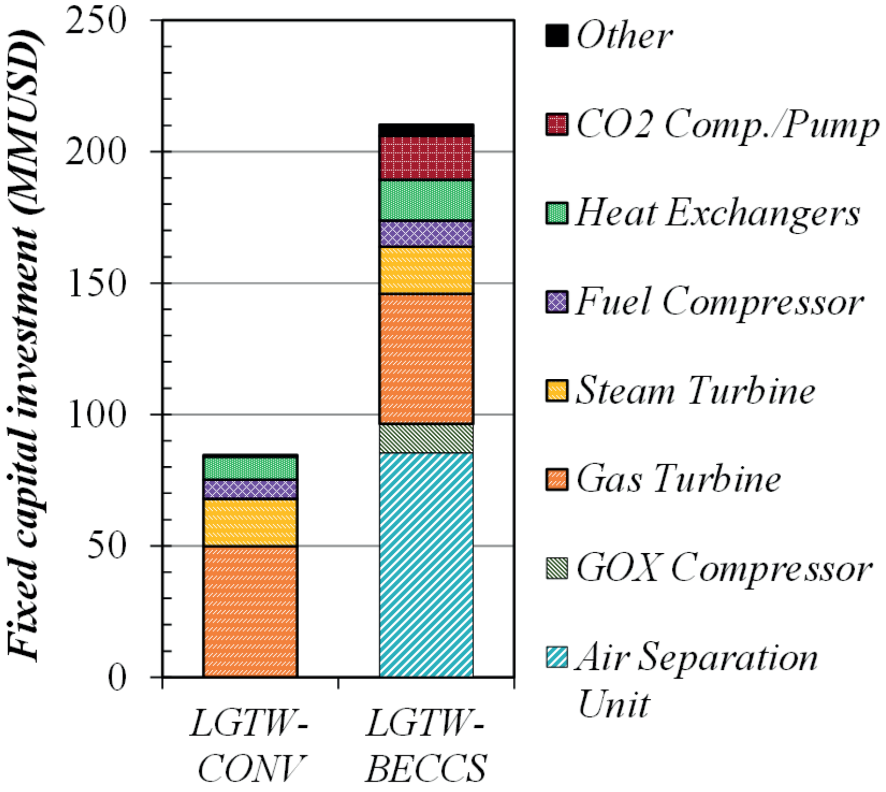

Figure 8 - Fixed capital investment of LGTW-CONV and LGTW-BECCS Base-Processes

Figure 8 further evinces both LGTW-CONV and LGTW-BECCS with similar capital investments on GT (≈50 MMUSD for ≈65 MW) and ST (≈18 MMUSD for ≈45 MW). Such results are reasonable comparatively to typical GT and ST costs collected by Jaramillo and Matthews (2005). By using CEPCI-update and log-extrapolation from their data for GT (1-40 MW) and ST (0.5-15 MW), it is possible to estimate corresponding investments to GT and ST actual capacities: ≈56 MMUSD (869 USD/kW) and ≈19 MMUSD (288 USD/kW), respectively. The small discrepancy confirms ±20% usual accuracy of Turton et al. (2012) methods and indicates suitability of utilized methods for application to main power plant equipment.

Economic performance details of selected processes LGTW-CONV and LGTW-BECCS with TVR-2REB ASU are presented in Table 8 for several carbon taxation scenarios, where positive NPVs are revealed for both concepts. LGTW-CONV has much greater NPV if no CO_2 tax is applied: 254 against 13 MMUSD, an outcome of lower capital investment and greater annual profit (51 against 30 MMUSD/y), as CO_2 capture is not involved. LGTW-BECCS produces 17% less electricity, and proportionally lower is its total revenue

(74 MMUSD/y). The manufacturing cost of LGTW-BECCS is higher mostly due to indirect contribution of greater capital investment on the plant (e.g., incurring in maintenance, insurance, fixed costs linked to plant complexity), and in a small extent due to higher cost with utilities (linked to greater use of cooling water in intercoolers).

Table 8 - Economic performance of base-processes under different CO_2 taxes

Power Plant	LGTW-CONV					LGTW-BECCS	Unit
CO_2 taxation	0	25	50	75	100	(any)	USD/t_{CO2}
Fixed capital investment	84.62	84.62	84.62	84.62	84.62	210.21	MMUSD
Total revenue	89.68	89.68	89.68	89.68	89.68	74.21	MMUSD/y
Raw material costs	0.00	0.00	0.00	0.00	0.00	0.00	MMUSD/y
Utilities costs	1.15	1.15	1.15	1.15	1.15	1.60	MMUSD/y
Manufacturing costs	17.08	32.03	46.98	61.93	76.88	40.25	MMUSD/y
Gross annual profit	72.60	57.65	42.70	27.75	12.80	33.96	MMUSD/y
Annual profit (net)	50.79	40.92	31.06	21.19	11.32	29.56	MMUSD/y
Net Present Value	254.0	190.9	127.8	64.70	1.58	13.08	MMUSD

The results shown in Table 8 are reasonable because increased operational expenses and capital investment usually follows CO_2 capture solutions, thus such economic disadvantage against CO_2-emitting conventional processes have to be compensated by CO_2 mitigation policies (e.g., carbon tax over emissions) or CO_2 monetization whenever viable (e.g., enhanced oil recovery), otherwise implementation of CO_2 capture would continue to be seen with little commercial interest. Therefore, it is possible to have an oxyfuel LGTW-BECCS outperforming the profitability of a CO_2-emitting LGTW-CONV. In this regard, comparison of NPV performances along project years under different carbon taxation scenarios (0, 25, 50, 75, or 100 USD/t) is provided in Figure 9, where several curves apply to LGTW-CONV, while LGTW-BECCS alternative is expressed as a single curve as it entails zero-emission power generation. The initial 3 years expresses the phase of plant construction with distributed capital outlay (20/30/50%), where LGTW-BECCS evinces the lowest NPV due to its higher capital investment. Table 8 presents the corresponding values of manufacturing cost, annual profit, and NPV (at 20 years of operation) for each scenario. The reduction of annual profits in LGTW-CONV caused by payment of CO_2 taxes allows the zero-emission solution LGTW-BECCS to progressively surpass its economic performance throughout the years of analysis. By the 17th year from start-up, the proposed oxyfuel LGTW-BECCS starts to outperform LGTW-CONV if carbon taxes are above 95.45 USD/t CO_2.

Figure 9 shows that 3 years of operation are enough to occur the discounted payback of LGTW-CONV without CO_2 taxation charge. Since the adoption of a combined cycle allows the production of more power than a Rankine cycle alone based on steam turbines, it is reasonable to find a faster payback than that of the Puente Hills project, where a large-scale project based on steam turbines had payback within only 5 years of operation (Rajaram *et al.*, 2011). Under CO_2 taxation, LGTW-CONV project payback is delayed, especially if CO_2 taxes are above 75 USD/t (Figure 9), where reduced annual profits (Table 8) would require a medium-term (5-10 years) or long-term (>10 years) horizon of operation for a positive NPV. At 75 USD/t, LGTW-BECCS already outperforms LGTW-CONV in terms of annual profit, but the much higher capital investment (Figure 7) hinders the attainment of a greater NPV.

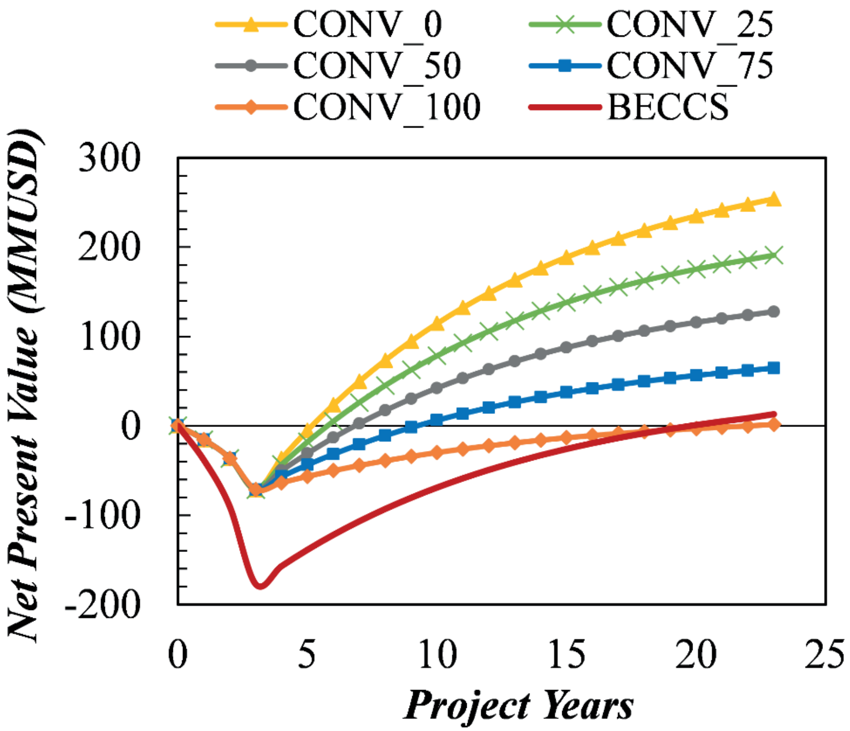

Figure 9 - Net present value profile of LGTW-BECCS coupled to TVR-2REB ASU and LGTW-CONV under different CO_2 taxation scenarios (USD/t)

By last, Figure 10 portrays sensitivity analysis of delta NPV between LGTW-BECCS and LGTW-CONV, as a function of CO_2 tax and electricity price, with indication of the most profitable LGTW concept for each region of the graph, defined by zero contour line. Figure 10 reveals break-even CO_2 tax within ≈85-102 USD/t for greater NPV of zero-emission LGTW-BECCS, if it is subjected to electricity price variations of ≈25% around base-price (0.1087 USD/kWh). Although such taxation level is relatively high for current practice, it is already seen in some European countries and is plausible to be widely employed in the future, due to intensification of climate change mitigation policies.

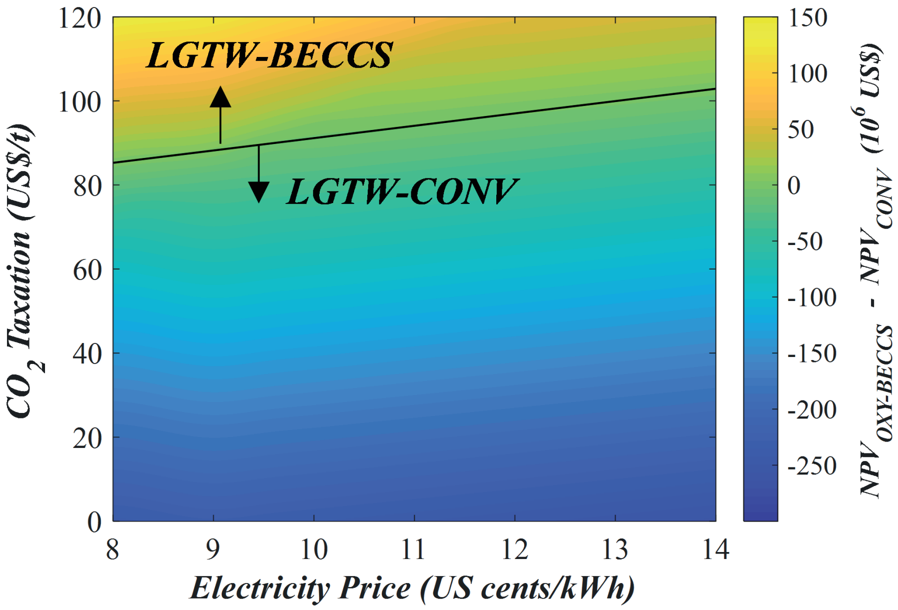

Figure 10 - Delta NPV (*$NPV_{OXY\text{-}BECCS}$–NPV_{CONV}*) as a function of electricity price (¢/kWh) and CO_2 tax level (USD/t). *NPV_{CONV}≡NPV of LGTW-CONV base process. $NPV_{OXY\text{-}BECCS}$≡NPV of LGTW-BECCS base process*

CONCLUSIONS

Assuming fixed large-scale fuel supply as base destination for collected landfill gas, economic viability and competitiveness of LGTW-BECCS based on oxy-combustion combined cycle for zero-emission power generation is presented against CO_2-emitting LGTW-CONV process charged by carbon taxes. Two different oxy-combustion configurations based on CO_2 recirculation to GT are evaluated by process simulation and compared by economic perspective: SCOC-CC (where gas recycle compression is adiabatic) and RIOC-CC (where multistage intercooled compression of gas recycle is adopted). RIOC-CC has greater net efficiency but is economically inferior to SCOC-CC. Therefore, SCOC-CC is selected for LGTW-BECCS application.

Sensitivity analysis on GT combustion pressure evinced highest NPV at ≈20 and ≈8.0 bar in LGTW-BECCS and LGTW-CONV, respectively. Major influence of total capital investment and compression requirements for landfill gas feed to GT are main causes for relatively low GT pressure-ratios. At best operating conditions, 9.2%LHV of efficiency penalty is attained, resulting in ratio of CO_2 capture flow by net power produced of 0.875 kg/

kWh. The comparison of NPV of LGTW-BECCS against LGTW-CONV charged by carbon taxation showed higher profitability of proposed zero-emission alternative when CO_2 tax is above 95 USD/t.

By accounting the life-cycle of the captured CO_2, the proposed solution offers as a sustainable mean of power generation with CDR – since urban solid-wastes typically present substantial content of organic matter from biomass – which makes this concept an effective instrument for climate change mitigation. The solution is profitable and economically feasible in the long-term without need for electricity overpricing and/or government subsidies, with the break-even price for positive NPV being 0.104 USD/kWh. From a stable feed of 1.08 $MMSm^3/d$ landfill gas, LGTW-BECCS is capable of producing 85.33 MW, which is enough power to supply ≈70,000 US average homes (EPA, 2019), which consumption is more than 3 times world average. Besides the advantage of promoting CDR, LGTW-BECCS presents low environmental impacts and is thus demonstrated as a sustainable solution for waste monetization, also capable of promoting health-social benefits and local economic growth.

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ANALYSIS OF OPERATIONAL PERFORMANCE OF CHEMICAL PRODUCTION FROM BIOGAS

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

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

1. INTRODUCTION

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

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

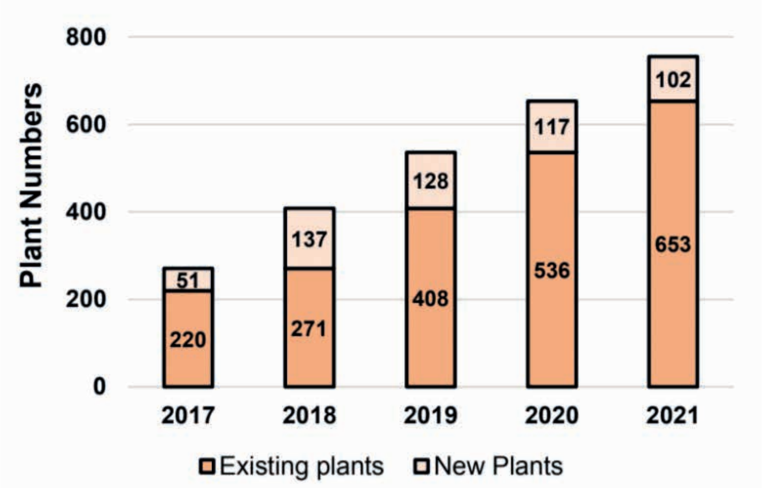

Figure 1 - Biogas plants growth in Brazil between 2017 and 2021 (adapted from CIBiogás, 2021).

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

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

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

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

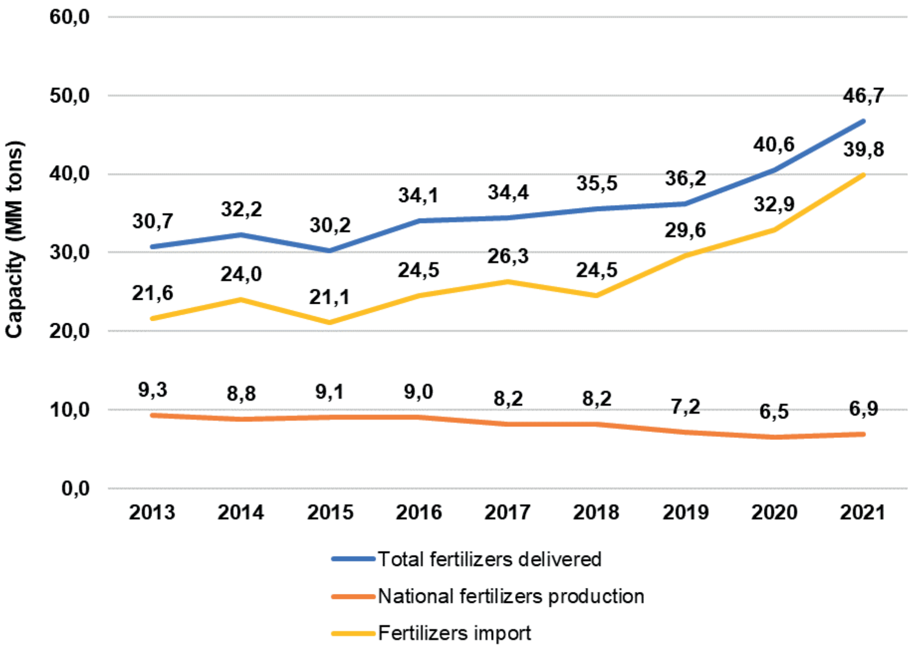

Figure 2 – Sector macro indicators of the fertilizer industry in Brazil according to ANDA.

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

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

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

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

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

2. PROCESS DESCRIPTION & METHODOLOGY

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

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

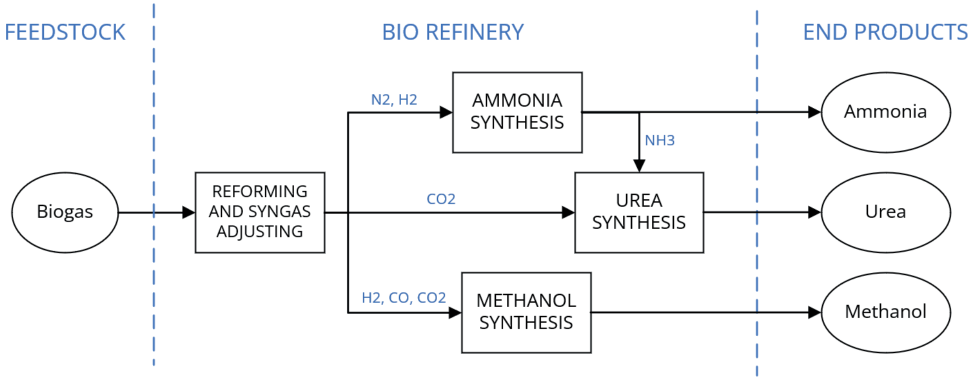

Figure 3 – Block diagram of possible production rotes.

2.1. BIOGAS PURIFICATION

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

2.2. BIOGAS REFORMING

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

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

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

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

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

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

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

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

2.3. SYNGAS UPGRADING

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

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

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

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

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

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

2.4. AMMONIA SYNTHESIS

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

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g) \tag{5}$$

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

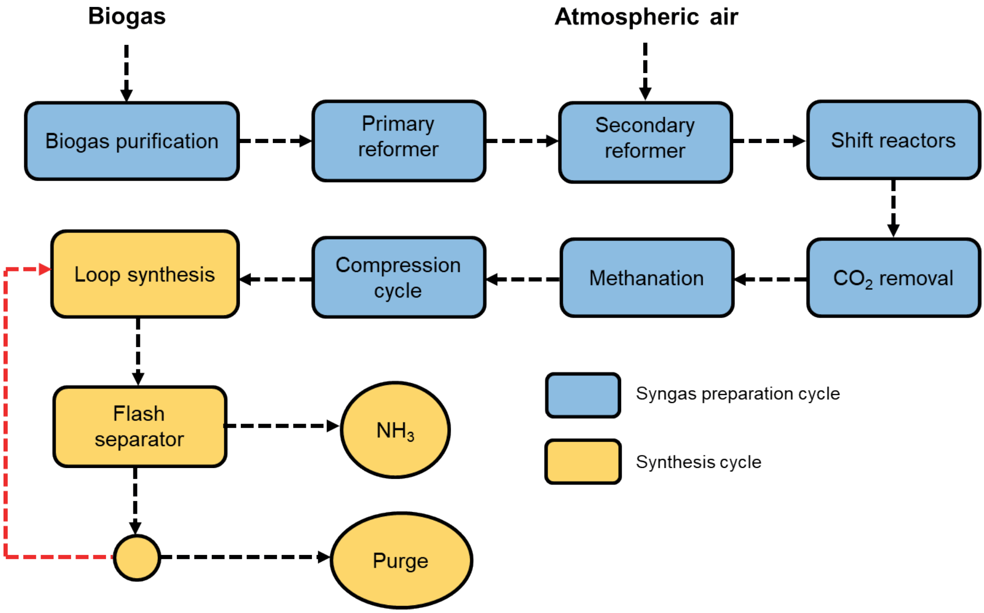

Figure 4 – Ammonia synthesis simplified process flowsheet.

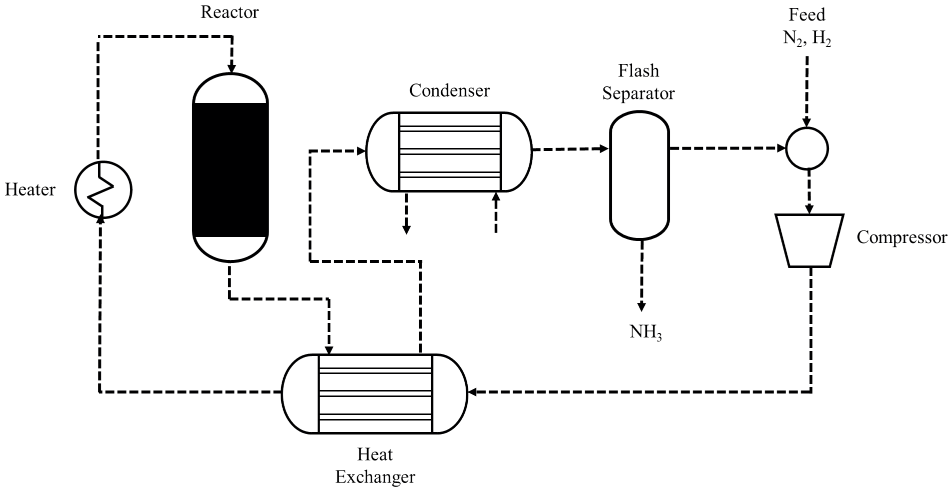

Figure 5 – Simplified schematic of the Haber-Bosch circuit (adapted from Reese et al., 2016).

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

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

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

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

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

2.5. UREA SYNTHESIS – STAMICARBON PROCESS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

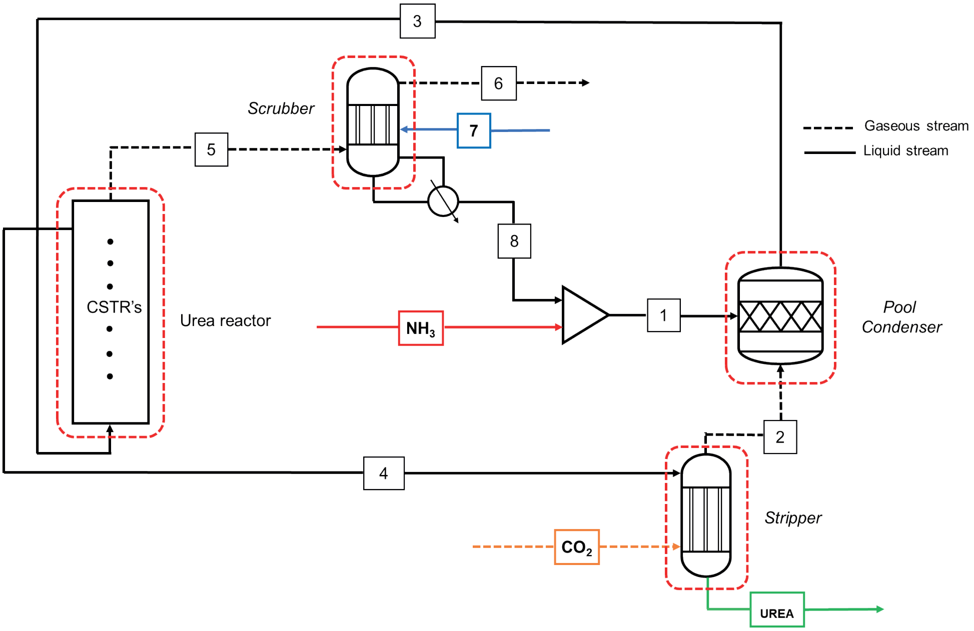

Figure 6 – Urea synthesis process simulation flowsheet (adapted from Chinda, 2015).

2.6. METHANOL SYNTHESIS

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

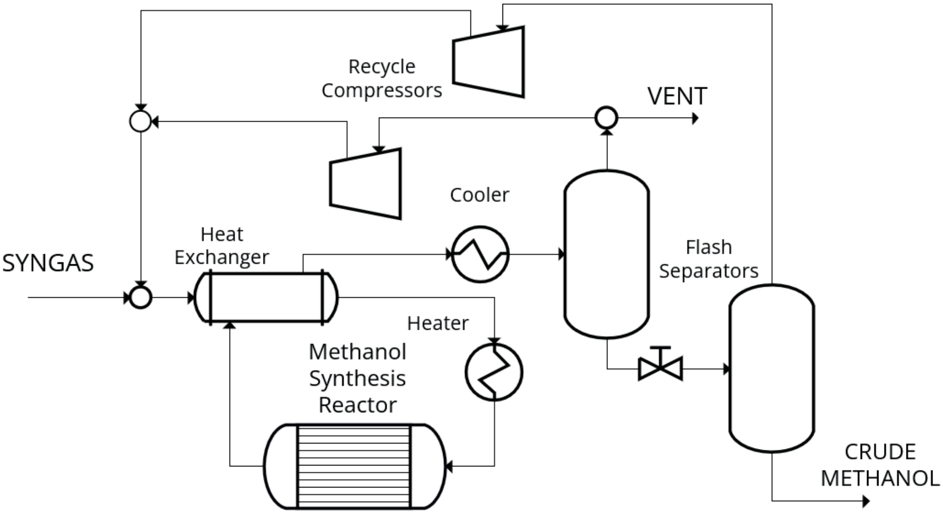

Figure 7 – Methanol synthesis loop flowsheet.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

2.7. CASE STUDIES

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

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

2.7.1. Case A – Ammonia-Urea

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

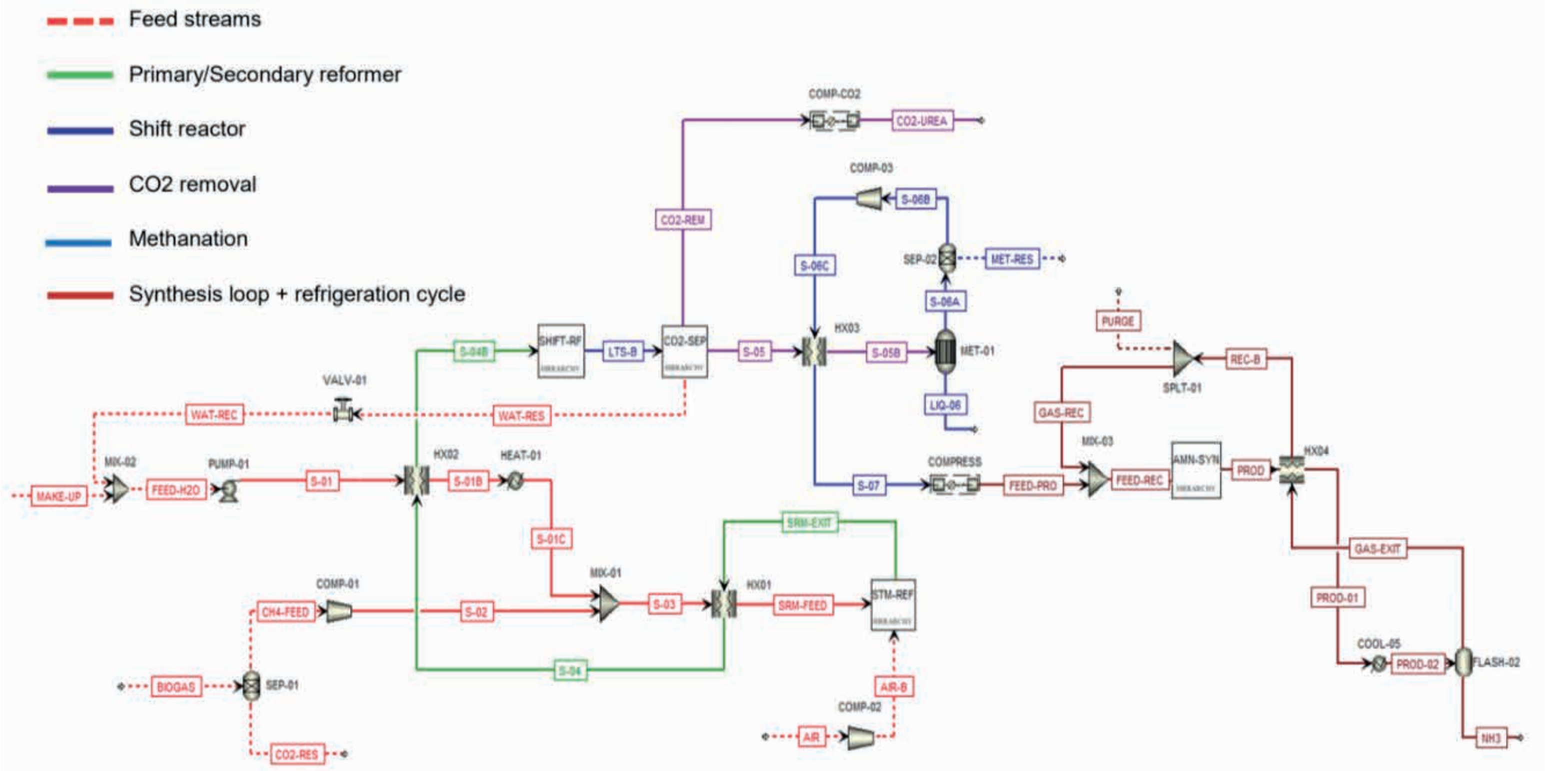

Figure 8 – Ammonia synthesis process flowsheet.

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

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

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

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

2.7.2. Methanol Plant – Case B

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

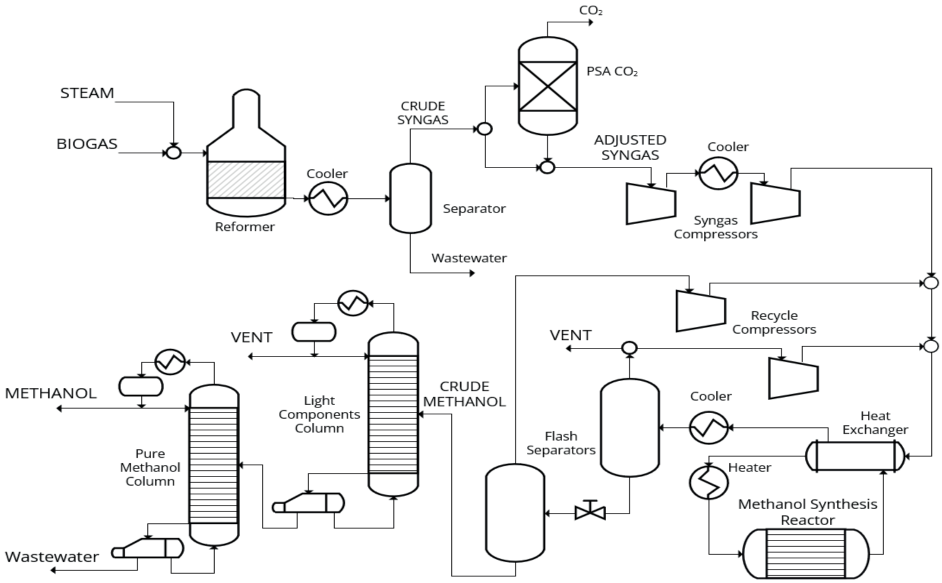

Figure 9 – Methanol synthesis process flowsheet.

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

3. RESULTS AND DISCUSSION

3.1. AMMONIA-UREA PLANT

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

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

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

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

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

Table 1 – Syngas preparation section main results

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

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

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

Table 2- Ammonia synthesis main results

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

[a] Loop synthesis and refrigeration cycle pressure.

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

Table 3 – Urea synthesis main results

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

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

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

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

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

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

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

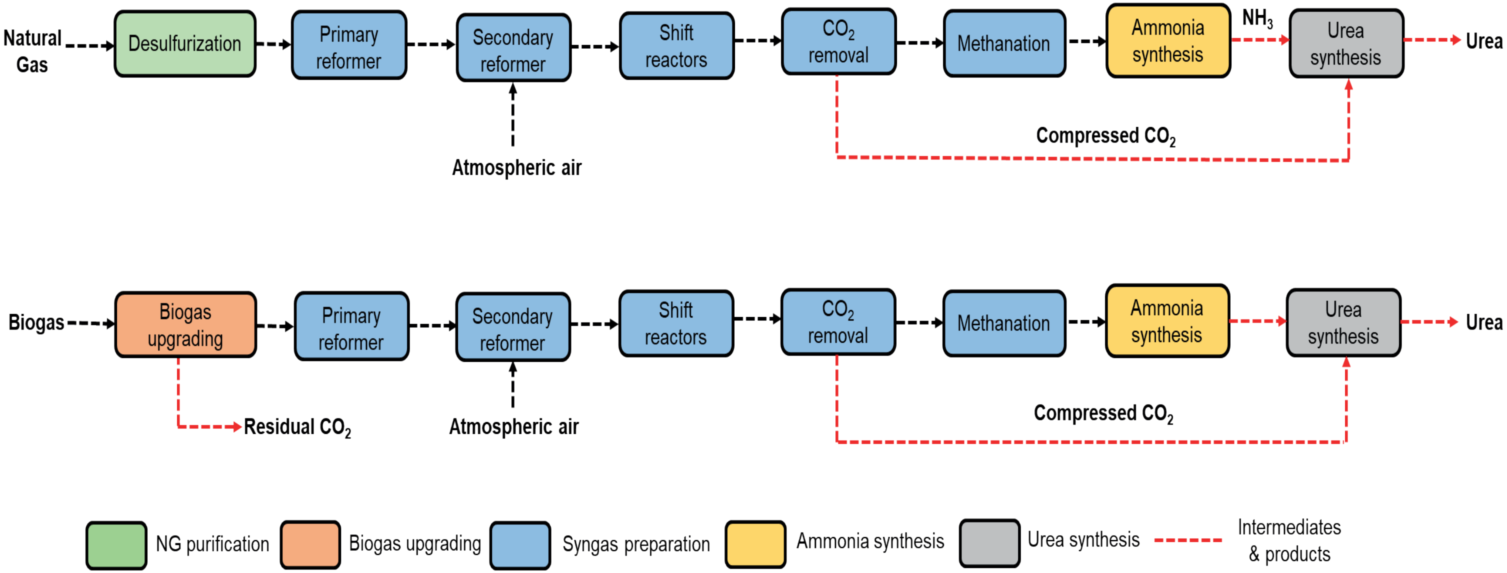

Figure 10 – Conventional and innovative configuration for ammonia and urea synthesis.

3.2. METHANOL PLANT

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

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

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

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

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

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

Table 4 – Methanol synthesis main results

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

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

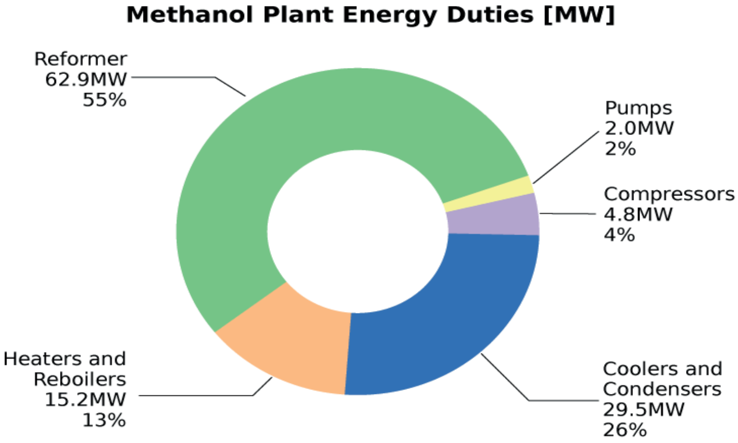

Figure 11 – Energy demand profile of methanol plant.

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

Table 5 – Comparison of methanol synthesis technologies

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

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

CONCLUSIONS

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

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

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

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CHAPTER 7

HYDROGEN PRODUCTION THROUGH REFORMING OF BIOGAS

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ABSTRACT: Biogas has great potential for the production of renewable hydrogen via dry reforming of methane. The primary challenge of this technology is catalyst deactivation, mainly through carbon deposition. In this review, the mechanism of carbon formation is presented, and the different strategies for minimizing carbon deposition are discussed, which include (i) controlling the size of the metallic crystallite and (ii) the use of supports with redox properties. Selection of the catalyst preparation method is essential to control the size of the metallic particles and, consequently, the stability of the catalysts in the dry reforming of methane reaction. Another approach consists of increasing the carbon gasification rate by using supports with high oxygen mobility, based on the role of support in the mechanism of dry reforming of methane reaction. Different examples of catalyst design are discussed involving various preparation methods, such as core-shell, perovskite-type oxide, and spinel phase, to develop a catalyst resistant to carbon deposition. Finally, the perspectives for catalyst design for producing renewable hydrogen through the biogas reforming technology are presented.

KEYWORDS: biogas, carbon formation, catalyst deactivation, dry reforming of methane, hydrogen production.

1. INTRODUCTION

Biomass, particularly in Brazil, has received increasing attention as a renewable energy source. Due to Brazil's large territorial extension and strong agricultural activity, the byproducts of this industry are being studied for their potential in energy generation (Costa *et al.*, 2022). The biogas derived from the anaerobic decomposition of biomass, primarily composed of CH_4 and CO_2, has significant energy potential for producing renewable hydrogen (Yang e*t al.*, 2014).

Hydrogen can be produced by reforming reactions, where methane reacts with water, carbon dioxide, or oxygen to produce syngas. Steam reforming is the conventional method for hydrogen production from hydrocarbons in the industry (Palma *et al.*, 2016). Dry reforming of methane (DRM - Eq. 1) is more appropriate for biogas upgrading due to its high CO_2 concentration and is a promising reaction for hydrogen production while mitigating greenhouse gas emissions. The main limitation of DRM technology remains catalyst deactivation caused by carbon deposition, metal sintering, or metal oxidation under reaction conditions. DRM, being an endothermic reaction ($\Delta H° = 247$ kJ/mol), requires elevated reaction temperatures, thereby promoting many side reactions, notably CH_4 decomposition (Eq. 2); the Boudouard reaction (Eq. 3), which produces coke deposits over the catalyst surface; and the reverse water-gas shift (RWGS) (Eq. 4), which reduces the H_2 yield of the process (Bradford; Vannice, 1999).

$$CH_4 + CO_2 \leftrightarrow 2\ CO + 2H_2 \qquad \Delta H_{25\ °C} = 247\ \text{kJ/mol} \qquad (1)$$

$$CH_4 \leftrightarrow C + 2\ H_2 \qquad \Delta H_{25\ °C} = 75\ \text{kJ/mol} \qquad (2)$$

$$2\ CO \leftrightarrow C + CO_2 \qquad \Delta H_{25\ °C} = -171\ \text{kJ/mol} \qquad (3)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{25\ °C} = 41.2\ \text{kJ/mol} \qquad (4)$$

The catalyst design for DRM reaction has been conducted using diverse approaches for supported metallic catalysts. Catalysts featuring noble metals like Pd, Pt, Rh, and others exhibit high activity and resistance to coke formation due to the low dissolution of carbon in their lattices. Nevertheless, the limited availability of noble metals in the environment has increased research into transition metals such as Ni. Although Ni activity is comparable to noble metals but with costs less, it is prone to coke formation due to its high CH_4 decomposition activity at high temperatures. Additionally, the Ni particle size directly affects the kinetics of CH_4 decomposition, in which larger particles favor the nucleation of carbon at the metal-support interface (Rostrup-Nielsen; Trimm, 1977).

The support plays a key role in preventing carbon formation in the DRM reaction. It can act in two strategies: (i) to increase the thermal stability of the material, avoiding the metal sintering at high temperatures, and (ii) to enhance the oxygen mobility of the support, promoting the rate of carbon gasification at the metal-support interface. A set of new strategies to synthesize Ni-based catalysts with low particle size has been adopted, such as the development of encapsulated metals into the support structure (Marinho *et* *al.*, 2020, 2021). The confined environment led to better thermal stability against metal sintering, in which the shell stabilizes the active metal in the catalyst due to the creation of a physical barrier between different metal particles. Furthermore, an increased interfacial area strengthens metal-support interaction, enhancing the catalytic performance (Marinho *et al.*, 2020, 2021).

Another strategy is the use of reducible supports, where the oxygen vacancies promote the carbon removal mechanism. The main example of this group of oxides is ceria (CeO_2), which can store and release oxygen depending on the environment, following a Mars-van Krevelen mechanism (Kambolis *et al.*, 2010). To optimize the oxygen vacancies on CeO_2-based materials, solid solutions have been developed by inserting metal dopants, resulting in higher resistance to coke formation. Zr is the most used dopant for CeO_2 materials, responsible for promoting the mobility of oxygen species from bulk phase to surface (Bedrane; Descorme; Duprez, 2002) and enhancing the CeO_2 thermal stability (Hori *et al.*, 1998).

Following the recent advances in catalyst design for DRM reaction, this chapter will provide a detailed overview of the thermodynamics and mechanisms of DRM reaction. The focus is on the mechanism of carbon formation and the different strategies used in the Catalysis Group of the National Institute of Technology and the Federal University of Rio de Janeiro to develop catalysts resistant to carbon formation during DRM reaction conditions.

2. THERMODYNAMIC OF DRM REACTION

Figure 1 shows the equilibrium constant value of different reactions occurring simultaneously in the reactor during the DRM process as a function of temperature. The DRM reaction is very endothermic and thus occurs with high CH_4 conversion only at high temperatures. Nevertheless, these conditions promote methane decomposition, as demonstrated in Figure 1. The exothermic nature of the Boudouard reaction prevents its occurrence at high temperatures, while the thermodynamics limits the RWGS reaction above 1000 °C. As can be seen in Eqs. 1–4, carbon formation is attributed to methane decomposition and the Boudouard reaction. However, at high temperatures, only CH_4 decomposition is promoted, and this reaction has been associated with coke formation on Ni-based catalysts. Some efforts have been made to perform DRM at low temperatures to reduce operational costs; however, this condition favors the Boudouard reaction, acting as an additional source of coke on the catalyst.

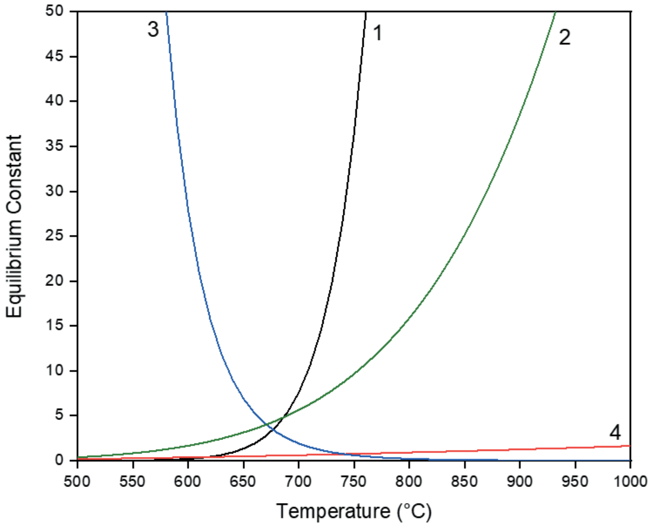


Figure 1 - Equilibrium constant of reactions as a function of reaction temperature: (1) DRM reaction, (2) CH_4 decomposition reaction, (3) Boudouard reaction, and (4) RWGS reaction.

The conversion of CH_4 and CO_2 as a function of temperature for different CH_4/CO_2 molar ratios for the DRM reaction is shown in Figure 2. The conversion increases with the rise in temperature for both reactants due to the endothermicity of the DRM reaction. A CH_4/CO_2 molar ratio exceeding 1.0 favors the CH_4 decomposition reaction, leading to an increase in the H_2/CO molar ratio. However, excess of CH_4 in the gas feed leads to a decrease in the CH_4 conversion and an increase in CO_2 conversion, acting as a limiting reactant in the reactor. Some experimental data have demonstrated high carbon formation derived from CH_4 decomposition on Ni-based catalysts using a feed composition with a CH_4/CO_2 molar ratio higher than 1.0 (Serrano-Lotina; Daza, 2014). Introducing more CO_2 into the feed increases the CH_4 conversion and decreases the CO_2 conversion, highlighting CH_4 acting as a limiting reactant. Furthermore, the H_2/CO molar ratio decreases due to the shifting of the RWGS reaction to the production of CO in an excess of CO_2.

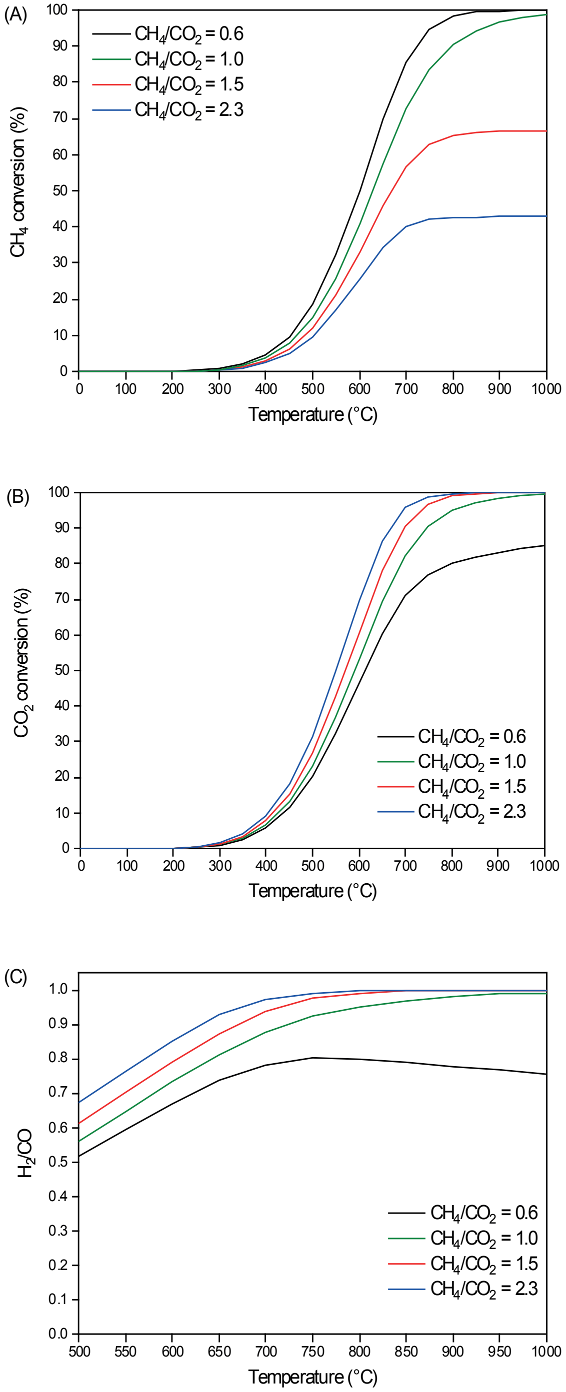


Figure 2 - (A) CH_4 conversion; (B) CO_2 conversion; (C) H_2/CO molar ratio obtained in the DRM reaction as a function of temperature at equilibrium condition.

The use of biogas for the DRM reaction is challenging since the CH_4/CO_2 molar ratio is close to 1.5, promoting a higher rate of carbon formation in equilibrium conditions. Thus, the design of catalysts resistant to coke formation, even under conditions favorable to carbon deposition, is desired for an effective process.

3. REACTION MECHANISM

An ideal catalyst for the DRM reaction is supposed to exhibit both high activity and stability under reaction conditions. Thus, a fundamental criterion for catalyst selection is its ability to decrease or suppress the rate of carbon formation. To achieve this, the mechanism for CH_4 and CO_2 activation in various catalytic systems must be considered (Papadopoulou; Matralis; Verykios, 2012). The mechanism of the DRM reaction has been studied for years as new techniques have been developed for its determination. The consensus in the literature is that methane adsorbs onto the metal surface before the reaction occurs, and the cleavage of the first C-H bond is considered the rate-determining step of the reaction (Wei; Iglesia, 2004). Therefore, the dissociated carbon remains adsorbed on the metallic crystallite. The adsorption of CO_2 can occur on the metal surface as well as on the support, depending on the type of metal and support. The activation of CO_2 is a crucial step as it is responsible for increasing the concentration of reactive oxygen species, thereby enhancing the rate of carbon gasification present in the metallic phase.

A. Methane Activation:

The initial stage involves the adsorption of CH_4 in a dissociative form onto the Ni sites. Methane adsorbs on a metallic site (Eq. 5), followed by successive dehydrogenation steps toward the formation of reactive carbon (Eqs. 6–9).

$$CH_{4\,(g)} + {}^* \rightleftharpoons CH_4^* \tag{5}$$

$$CH_4^* + {}^* \rightleftharpoons CH_3^* + H^* \tag{6}$$

$$CH_3^* + {}^* \rightleftharpoons CH_2^* + H^* \tag{7}$$

$$CH_2^* + {}^* \rightleftharpoons CH^* + H^* \tag{8}$$

$$CH^* + {}^* \rightleftharpoons C^* + H^* \tag{9}$$

B. Carbon Dioxide Activation:

CO_2 may adsorb dissociatively on the metal as well as on the support. CO_2 adsorption on the support leads to the formation of carbonate and bicarbonate species (Eq. 10). In the case of reducible supports, CO_2 adsorbs on the oxygen vacancies, producing lattice oxygen OL and CO (Eq. 11). Therefore, CO_2 replenishes the oxygen vacancies of the support, releasing CO. The lattice oxygen species thus generated may react with C* produced from methane activation (Eq. 12), promoting the removal of carbon from the surface of metal particles, producing CO (Eq. 13). This redox mechanism is characteristic of lanthanides or rare-earth metals and the most studied support is CeO_2. In its ideal stoichiometric state, each O^{2-} ion is coordinated by four Ce^{4+} ions. However, under reducing conditions, specifically in a H_2-rich atmosphere, oxygen is liberated from the CeO_2 lattice, leading to the formation of oxygen vacancies and the generation of Ce^{3+}. The redox property results in high oxygen mobility to CeO_2 via a redox cycle between Ce^{4+}/Ce^{3+} under the Mars-van Krevelen mechanism (Liew; Jalil; Tan, 2022).

$$CO_{2\,(g)} + O^{2-} \rightleftharpoons CO_3^{2-*} \tag{10}$$

$$CO_{2\,(g)} + V_O \rightleftharpoons CO^* + O_L \tag{11}$$

$$C^* + O_L \rightleftharpoons CO^* + V_O \tag{12}$$

$$CO^* \rightleftharpoons CO_{(g)} + * \tag{13}$$

4. MECHANISM OF CARBON FORMATION

The main reactions responsible for the formation of carbon during dry methane reforming are the methane decomposition reaction (Eq. 2) and the Boudouard reaction (also called the CO disproportionation reaction) (Eq. 3). Bengaard *et al.* (2002) proposed that carbon nucleation occurs at the step sites of nickel crystallites. The mechanism of carbon formation in methane reforming reactions is shown in Figure 3 (Trimm, 1997). Initially, the alpha carbon species (C_α) is formed, which is reactive and can be rapidly gasified to CO. However, if the rate of formation of this carbon is much greater than the rate of the gasification reaction, the C_α polymerizes, generating a new species of carbon called beta carbon (C_β). This new species has low reactivity under the reaction conditions and will be deposited on the catalyst. Two processes can occur with an excess of C_β on the catalyst surface:

(i) The encapsulation of the metallic surface, leading to total deactivation of the metallic site;

(ii) Dissolution in the crystallite of Ni, followed by its diffusion and precipitation at the rear of the crystallite, leading to the formation of carbon filaments. Figure 4 illustrates the formation of carbon nanotubes in Ni-based catalysts (Helveg *et al.*, 2011). This is the most common case in Ni-based catalysts. In this case, the formation of carbon does not lead to immediate deactivation of the catalyst, as the Ni particle located at the tip of the filament remains available for the reaction. However, the formation of carbon filaments will lead to increased pressure in the catalyst bed due to catalyst fragmentation and the need for catalyst replacement.

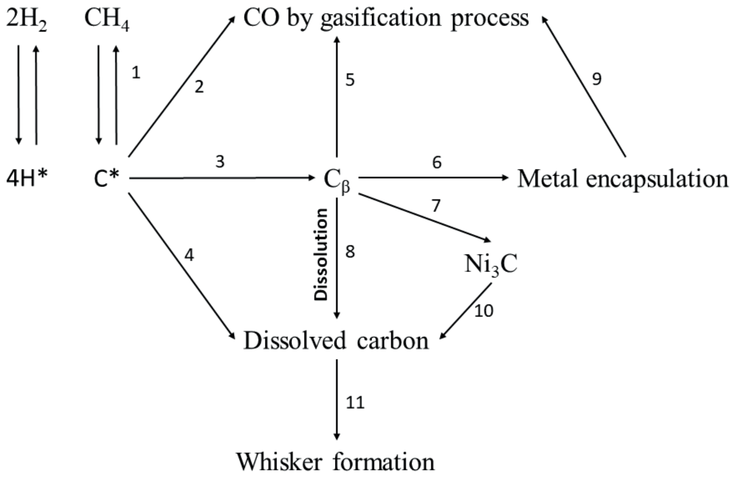


Figure 3 - Mechanism of carbon formation in methane reforming reaction (TRIMM, 1997).

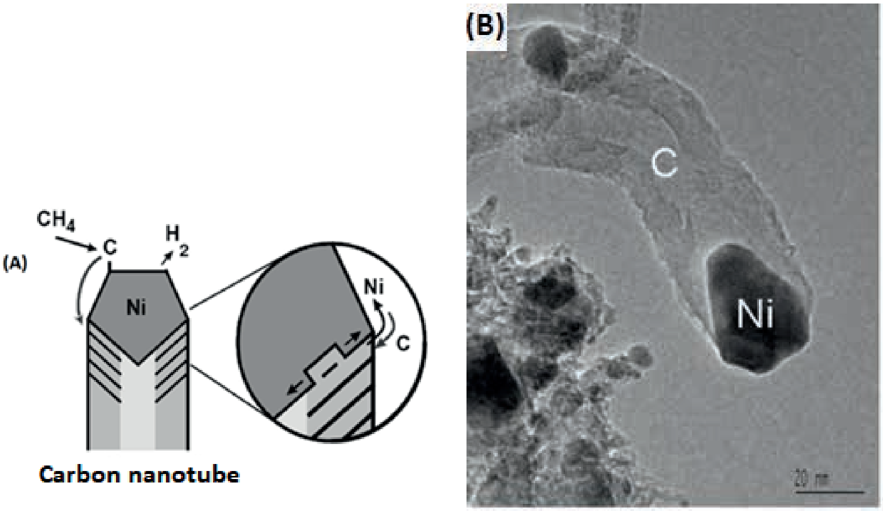


Figure 4 - (A) Scheme of the carbon formation mechanism, especially based on Ni; (B) Transmission electron microscopy image of carbon nanotube (Helveg; Sehested; Rostrup-Nielsen, 2011; Kehlet *et al.*, 2006).

This mechanism explains the low carbon formation on noble metals-based catalysts, as the solubility of carbon in these is much lower than in transition metals. Comparing the tendency of carbon formation during DRM on a series of transition metals supported on Al_2O_3 stabilized with MgO at 500–650 °C and 1 bar, Rostrup-Nielsen and Bak Hansen (1993) found the following order for carbon formation:

Ni > Pd >> Co > Pt > Ru ≈ Rh

5. STRATEGIES FOR MINIMIZING CARBON FORMATION

Carbon formation may be minimized by controlling the rates of carbon nucleation and its gasification. The different strategies proposed to reduce or eliminate carbon formation include (i) controlling the size of the metallic crystallite and (ii) using supports with redox properties.

The CH_x species produced by the decomposition of CH_4 can undergo further dissociation to C and H. According to Trimm (1997), the dissociation of methane requires a defined number of atoms. Rostrup-Nielsen (1977) proposed a critical number of atoms below which carbon formation does not occur. Steam reforming requires ensembles of 3–4 atoms, while carbon formation needs 6–7 atoms. Therefore, the size of the nickel particle significantly influences the rate of carbon nucleation. The initiation step of carbon formation is more difficult at small particle sizes (Helveg *et al*., 2011). Controlling particle size is a strategy for reducing or suppressing the rate of coke formation. Thus, selecting the catalyst preparation method is essential to control the size of the metallic particles and, consequently, the stability of the catalysts in the dry methane reforming reaction.

The catalyst synthesis method must lead to the formation of small and stable metallic particles. This can be achieved by methods that promote the interaction between the metal and the support. However, depending on the characteristics of the support, the reduction of metal oxides (e.g., especially Ni and Co oxides) may be difficult due to the strong interaction with the support. The formation of non-reducible mixed oxides, such as nickel aluminate, during the calcination or activation steps can also hinder reduction. The presence of these phases can result in loss of activity because the metal is considered the active site for the dry reforming of methane reaction. Therefore, appropriate preparation method that minimizes carbon formation has to be a compromise between obtaining small metal particles and the reducibility of the metal oxide. The different catalyst preparation methods proposed to obtain highly dispersed metallic particles include (i) sol-gel; (ii) the incorporation of metallic particles within the microporous and mesoporous channels of materials such as zeolites and SBA-15; (iii) the confinement of metallic particles in a core-shell structure; and (iv) the use of supports that promote the dispersion of the active phase.

Another approach consists of increasing the carbon gasification rate employing supports with high oxygen mobility, which can alternate the oxidation state of the metal present in the oxide to donate and receive oxygen in its structure. This strategy is based on the role of the support in the methane dry reforming reaction mechanism.

The decomposition of CH_4 and the dissociation of CO_2 occur via two independent pathways (Figure 5) (Stagg-Williams *et al*., 2000; Noronha *et al*., 2001; Rabelo-Neto *et al*., 2018). The first path involves the decomposition of CH_4 on the metal particle, resulting in the formation of hydrogen and carbonaceous deposits. The carbon formed can partially reduce the support near the metal particle, producing CO. In the presence of an irreducible support, carbon deposits remain on the surface, leading to catalyst deactivation. The second path is the dissociative adsorption of CO_2 onto the support, producing CO and oxygen. This oxygen replenishes oxygen vacancies, establishing a continuous cleaning redox mechanism. The balance between the methane decomposition rate and the cleaning rate determines the stability of the catalyst. In this two-way mechanism, the role of support is very important because it participates in the dissociative adsorption of CO_2 near metal particles, transferring oxygen to the surface of the metal particle containing carbon deposits, thus promoting the mechanism that removes carbon from the metal.

Cerium oxide has a high oxygen exchange capacity due to its ability to easily change its oxidation state, which leads to the formation of oxygen vacancies. Considering that the presence of oxygen vacancies close to the perimeter of the metallic particle is fundamental to the cleaning mechanism, one approach to improving the stability of the catalyst is to increase the reducibility of the support. This can be done by doping the ceria with different metals, such as zirconia. Therefore, the addition of zirconium oxide to ceria increases its reducibility and oxygen transfer capacity from the support by formation of a ceria-zirconia solid solution. Next, different examples of catalytic systems developed for the dry methane reforming reaction will be presented, aiming to obtain catalysts that are more resistant to deactivation.

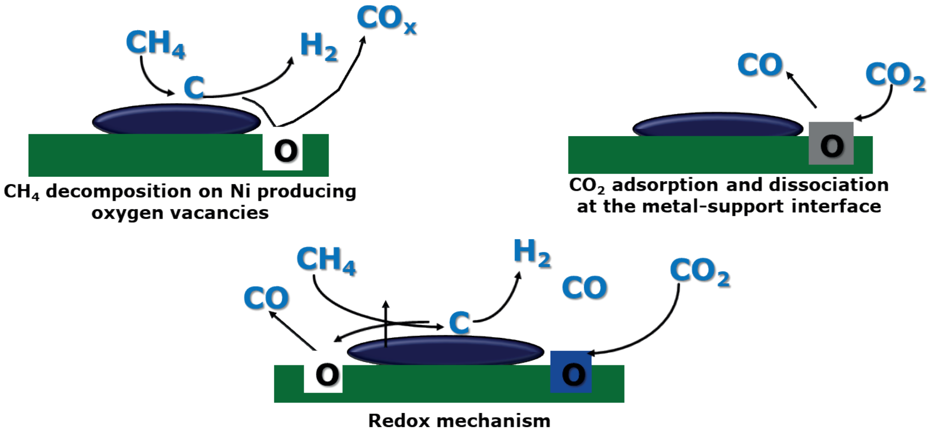


Figure 5 - Scheme for the dual path mechanism for DRM over Ni supported on ceria and ceria mixed oxides (Rabelo-Neto *et al.*, 2018).

6. DEVELOPMENT OF CATALYSTS RESISTANT TO CARBON FORMATION IN DRM

Da Fonseca *et al.* (2022) investigated the effect of Ni crystallite size and oxygen vacancies of the support on carbon formation over Ni/CeO_2 catalysts for the DRM at 1073 K. A large range of crystallite size was achieved using different Ni contents (5 and 10 wt%) and calcination temperatures (673, 873, 1073, and 1473 K). *In situ* XRD and XANES experiments at the L_{III} edge of Ce revealed that the increase in calcination temperature caused an increase in Ni crystallite size, while the amount of oxygen vacancies decreased. The Ni/CeO_2 catalysts were tested for the DRM at 1073 K for 24 h. Bulk NiO was also used as a reference. The 5Ni/CeO_2_673, 10Ni/CeO_2_673, 10Ni/CeO_2_873, and 10Ni/CeO_2_1073 catalysts suffered a small drop in conversion over the 24 h of time on stream (TOS), while a higher loss of activity was observed at the beginning of the reaction for the 10Ni/CeO_2_1473 and bulk NiO. Scanning electron microscopy images of the catalysts after the reaction revealed the presence of carbon filaments in the catalysts calcined at 673 and 1073 K, with the formation of carbon nanotubes not being observed in the 10Ni/CeO_2_1473 and bulk NiO catalysts. The rate of carbon formation was determined through temperature-programmed oxidation (TPO) of the spent catalysts. The carbon formation rate (mgC/(gcat.h)) followed the order: 10Ni/CeO_2_673 (20.9) > 10Ni/CeO_2_873 (10.6) > 10Ni/CeO_2_1073 (5.9) > 5Ni/CeO_2_673 (1.6) > 10Ni/CeO_2_1473 (0.3) ≈ NiO (0.2). Figure 6 shows the variation of the carbon formation rate for the Ni/CeO_2 catalysts after the DRM reaction at 1073 K for 24 h as a function of the Ni crystallite size. The rate of carbon formation increased as the Ni crystallite size increased, reaching a maximum of around 20–30 nm and then continuously decreasing to 133 nm. Therefore, there is a critical size of the Ni crystallite for carbon formation during the DRM reaction over Ni/CeO_2 catalysts, in which the maximum amount of carbon is formed. Figure 6 illustrates the window for carbon formation during DRM, as carbon deposition below 10 nm and above 100 nm is negligible. For catalysts with very large Ni^0 crystallite sizes (10Ni/CeO_2_1473 and bulk NiO), the CH_4 dissociation rate was probably so low that the carbon species formed react, and carbon accumulation does not occur. Furthermore, supports with redox properties such as ceria play a fundamental role in the DRM reaction, participating in the mechanism of carbon removal from the metal surface (Figure 3). However, the effectiveness of the carbon removal mechanism also depends on the metal-support interaction and, thus, on the size of the metal particle. A larger metal-support interface favors the oxygen migration from the support to the metal surface, thus eliminating or reducing carbon accumulation. Therefore, this mechanism is promoted in highly dispersed metallic particles on supports with redox properties, such as ceria or mixed oxides ceria-zirconia. Then, the higher amount of oxygen vacancies of the cerium oxide support calcined at 673 K and the smaller Ni crystallite size on the 5Ni/CeO_2_673 catalyst led to a lower carbon formation rate. Increasing the Ni crystallite size to 20 nm reduced the metal-support interface and increased the rate of carbon formation. For the 10Ni/CeO_2_673 catalyst, the oxygen transfer rate from the support to the metal surface was insufficient to counterbalance the methane decomposition rate, and carbon accumulates on the surface despite the large number of oxygen vacancies observed in this catalyst. For the 10Ni/CeO_2_1473 catalyst, the large crystallite size probably led to a low methane decomposition rate, in which the carbon species formed had time to react with CO_2 in the feed, preventing carbon deposition even on a support with low oxygen vacancy density.

The so-called core-shell catalysts represent a strategy for controlling the size of metal particles and has been extensively studied. Core-shell catalysts are classified according to their composition, morphology, properties, and applications. The current classification of its morphology is much broader, as shown in Figure 7 (Das *et al.*, 2020).

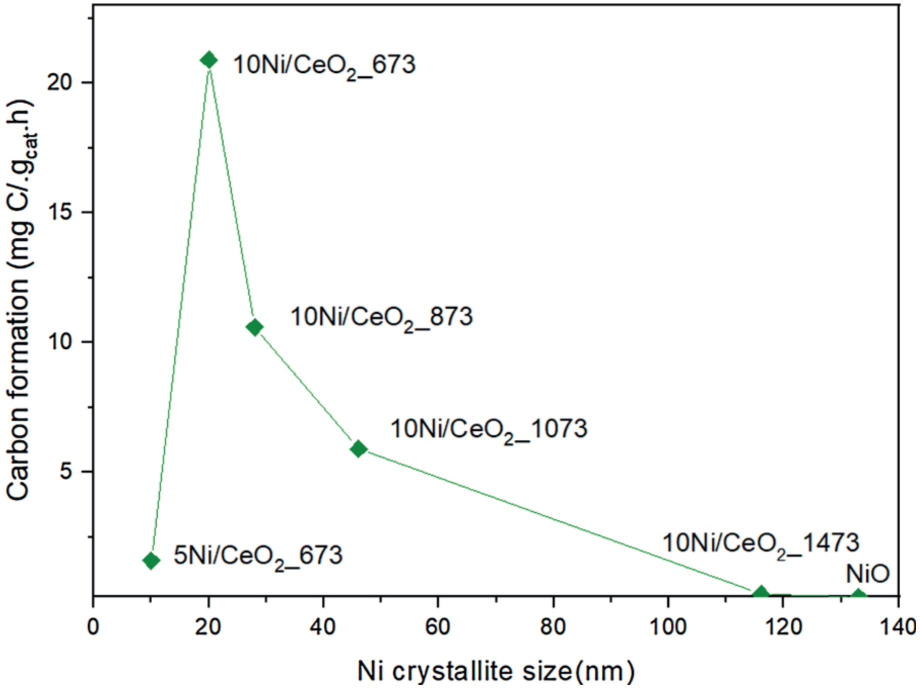


Figure 6 - Rate of carbon formation in the DRM reaction during 24 h of TOS as a function of Ni crystallite size. (Da Fonseca et al. (2022)).

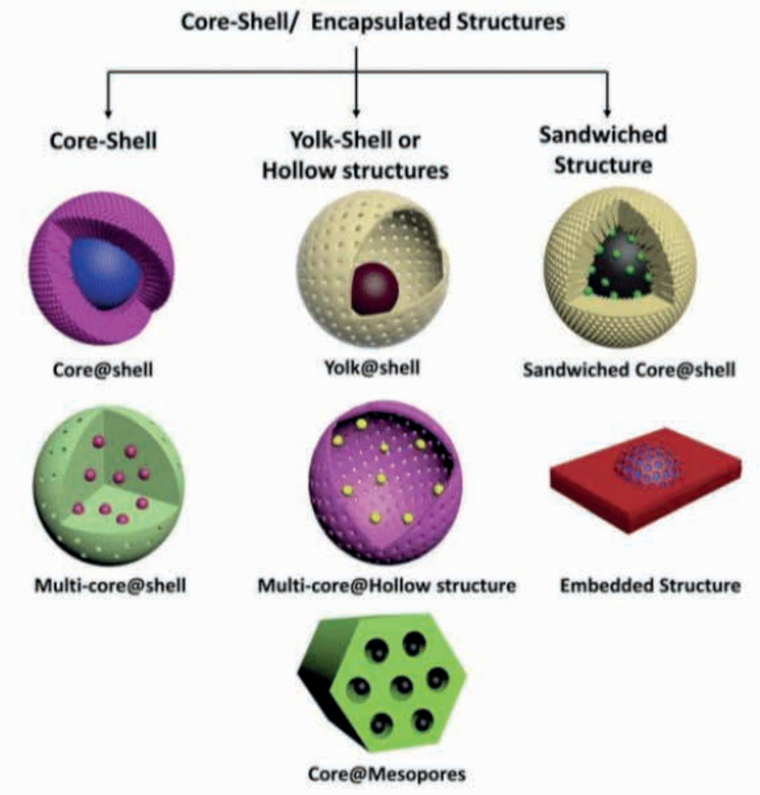


Figure 7 - Types of core-shell structures based on morphology (Das *et al*., 2020).

Ni nanoparticles embedded in CeO_2 (Ni@CeO_2) and $CeZrO_2$ (Ni@$CeZrO_2$) were synthesized by sol-gel method and compared with a Ni/CeO_2 prepared by support impregnation (Marinho *et al*., 2020). The performance of the catalysts was investigated for DRM reaction. The TEM images of the reduced Ni/CeO_2, Ni@CeO_2, and Ni@$CeZrO_2$ catalysts are shown in Figure 8. For the Ni/CeO_2 catalyst, the TEM image displays large Ni particles segregated on the surface of the sample, with an average particle size of around 30 nm. The TEM image of Ni@CeO_2 and Ni@$CeZrO_2$ catalysts reveals the presence of small Ni nanoparticles embedded in the ceria matrix formed during reduction. Segregated Ni particles could not be observed on the TEM images of Ni@CeO_2 and Ni@$CeZrO_2$ catalysts. Ni-embedded catalysts presented smaller metal particles than Ni/CeO_2. For Ni@CeO_2 and Ni@$CeZrO_2$, the Ni particle sizes were around 13 and 6 nm, respectively. Therefore, TEM found that Ni embedded in CeO_2 improved the resistance to sintering along the reduction at 800 °C. *In situ* XANES and XRD experiments showed that the embedded Ni particles in the ceria matrix were more difficult to reduce than the segregated particles characteristic of the impregnated catalyst. The strong interaction between Ni and CeO_2 improved the dispersion and avoided metal sintering at high temperatures. More oxygen vacancies were also generated on the catalysts containing Ni nanoparticles embedded in the support, as demonstrated by the isotopic exchange experiments. The initial CH_4 and CO_2 conversions were approximately the same for all catalysts and remained quite constant during 24 h of TOS. Figure 8 shows TEM images of spent catalysts. The image of the Ni/CeO_2 catalyst exhibits the presence of Ni nanoparticles located inside the carbon filaments. For the $Ni@CeO_2$ catalyst, TEM images reveal the presence of Ni nanoparticles into the bulk of CeO_2, but sintering is observed (Ni particle size around 20 nm). This higher interaction inhibits the detachment of Ni particles from CeO_2 and the growth of carbon filament. The TEM images of $Ni@CeZrO_2$ show Ni nanoparticles embedded into a ceria matrix with very small particle sizes (around 8 nm) after 24 h of TOS. Furthermore, carbon filaments were not observed, which demonstrated that inhibiting Ni sintering in the presence of a support with oxygen mobility suppressed the formation of carbon filaments. The rate of carbon formation was calculated through TG analysis of the used catalyst. Ni/CeO_2 catalyst exhibited the highest amount of carbon deposits (9.7 $mg_C/(g_{cat}.h)$) but the carbon formation rate was significantly reduced for the catalysts containing Ni nanoparticles embedded in the ceria structure. For the $Ni@CeO_2$ catalyst, the carbon formation rate was 1.6 $mg_C/(g_{cat}.h)$) whereas the $Ni@CeZrO_2$ catalyst did not show evidence of carbon formation after DRM reaction. Therefore, the control of Ni particle size and the high oxygen mobility of the $Ni@CeZrO_2$ catalyst inhibited carbon deposition and favored the mechanism of carbon removal, promoting catalyst stability.

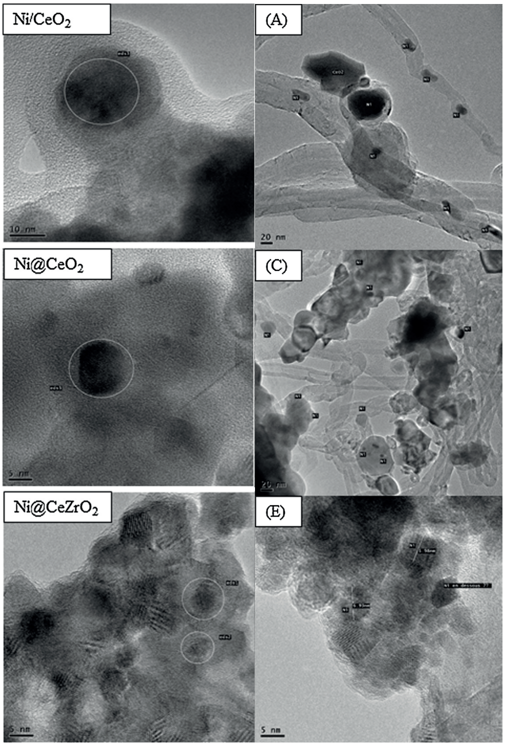
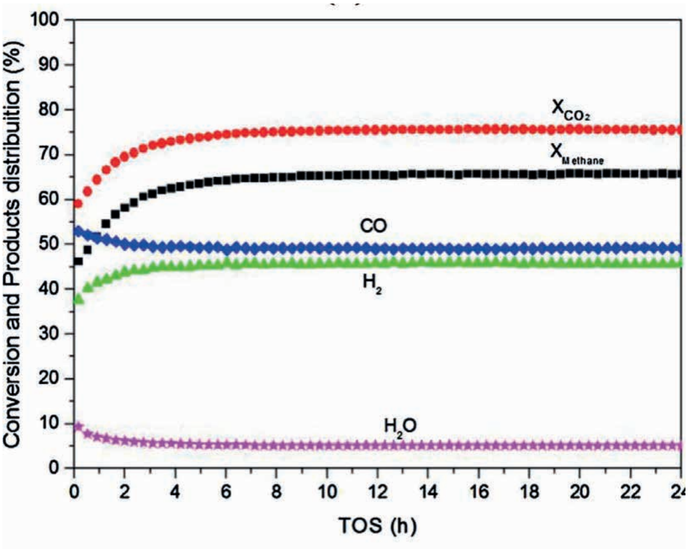


Figure 8 - TEM images of Ni/CeO_2, $Ni@CeO_2$, and $Ni@CeZrO_2$ catalysts before and after DRM reaction at 800 °C for 24 h of TOS. (Marinho et al. (2020)).

The perovskite-type oxide (ABO_3) is an interesting class of material. These mixed oxides can produce very small metal particles upon reduction (Lima *et al.*, 2006; Valderrama *et al.*, 2005). Therefore, carbon formation could be decreased or inhibited on these highly dispersed metal particles. However, unsupported perovskite-type oxides have a low surface area, impacting their activity. One solution is to support the perovskite-type oxides on a high surface area oxide. Rabelo-Neto *et al.* (2018) deposited a perovskite-type oxide ($LaNiO_3$) over alumina and silica doped-ceria supports and tested them for the DRM reaction at 800 °C. Supported Ni catalysts were prepared by reducing $LaNiO_3$ perovskite precursors, producing Ni/La_2O_3. The stability of the unsupported $LaNiO_3$, $LaNiO_3/Al_2O_3$, and $LaNiO_3/SiCeO_2$ catalysts for the DRM reaction at 800 °C was evaluated for 24 h. However, the test with the unsupported $LaNiO_3$ catalyst was stopped after 10 h due to a strong increase in pressure in the catalytic bed. For the $LaNiO_3/Al_2O_3$ catalyst, the CH_4 and CO_2 conversions increased and stabilized after 4 h of reaction (Figure 9). The performance of the $LaNiO_3/SiCeO_2$ catalyst was quite different. In this case, methane and CO_2 conversions increased only slightly during the first 6 h of reaction and then remained constant during 24 h. The higher CO_2 conversion than methane conversion, H_2/CO ratio values less than 1.0, and water formation were probably due to the RWGS. This behavior, i.e., the increase in CH_4 and CO_2 conversions at the beginning of the DRM reaction, was also observed in the literature and attributed to the oxidation of metallic particles by CO_2 in the feed. Then, the synthesis gas produced during the DRM reaction reduces the NiO particles formed, generating metallic Ni particles and increasing the conversion of CH_4 and CO_2 (Faria *et al.*, 2014; Takanabe *et al.*, 2005). To study the oxidation state of Ni during the DRM reaction, *in situ* XPS experiments were carried out. The intensity of the band corresponding to the binding energy of Ni 3p at 66 eV decreases continuously during the reaction in the $LaNiO_3/Al_2O_3$ catalyst while it remained approximately constant in the $LaNiO_3/SiCeO_2$. These results confirm the oxidation of metallic Ni particles by CO_2 in the feed at the beginning of the DRM reaction for the $LaNiO_3/Al_2O_3$ catalyst. TG analyses of the used catalysts were performed to investigate carbon formation. The TPO profiles of the $LaNiO_3$ and $LaNiO_3/Al_2O_3$ catalysts showed peaks at 625 and 643 °C, respectively, while no peak was observed in the TPO profile of the $LaNiO_3/SiCeO_2$ catalyst. These results demonstrated the formation of carbon filaments in the bulk and alumina-supported $LaNiO_3$ catalysts. The largest amount of carbon was formed on unsupported $LaNiO_3$. Supporting the $LaNiO_3$ phase significantly decreased the amount of carbon deposited. For alumina, the amount of carbon was approximately one third of that for the unsupported $LaNiO_3$. The deposition of $LaNiO_3$ on $SiCeO_2$ practically eliminated carbon formation. The operando XPS experiments showed the presence of a high fraction of Ce^{3+} species during the reaction, demonstrating that the redox cycle (Figure 5) was operational during the DRM reaction on the $LaNiO_3/SiCeO_2$ catalyst, which contributed to the removal of carbon deposits, promoting catalyst stability. Furthermore, *in situ* XRD measurements showed that the metal-ceria interaction also inhibited metal sintering during the reaction.

The growth of Ni crystallite size during DRM was lower in the $LaNiO_3/SiCeO_2$ catalyst, which also contributed to the lower carbon formation.

(A)



(B)

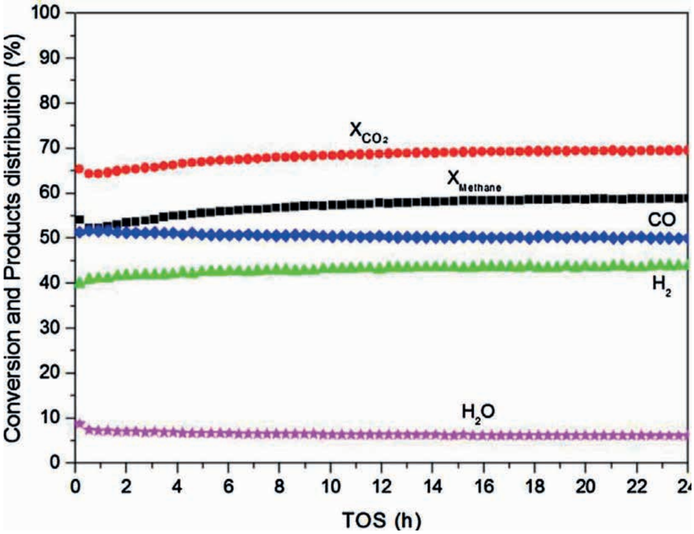


Figure 9 - CH_4 and CO_2 conversion and product distribution for DRM at 800 °C for 24 h of TOS over: (A) $LaNiO_3/Al_2O_3$; (B) $LaNiO_3/SiCeO_2$. (Rabelo-Neto et al. (2018)).

In addition to the perovskite-type oxides, the spinel phase has also been used to control Ni sintering during reduction at high temperatures, providing a high metal dispersion on the catalyst (Xu *et al.*, 2001). The Evaporation Induced Self-Assembly (EISA) method was used to obtain highly dispersed Ni particles due to the formation of $NiAl_2O_4$ spinel structure (Marinho *et al.*, 2021). The high dispersion of Ni results from the reduction of $NiAl_2O_4$, as observed from the XRD experiments, which prevents sintering at high temperatures. After reduction, small-size metallic Ni particles were observed (< 5 nm) for the catalyst prepared by EISA (10-Ni-CeAl). The catalyst synthesized by traditional impregnation of CeAl support exhibited a larger Ni crystallite size (11.3 nm). The 10Ni-Al and 5Ni-CeAl catalysts exhibited low initial CH_4 and CO_2 conversions that significantly increased during the first 2 h of TOS, and then they leveled off. For the 10Ni-CeAl and 10Ni/CeAl catalysts, the CH_4 and CO_2 conversions remained constant from the beginning of the reaction. However, the test was interrupted after 24 h of TOS for the 10Ni/CeAl catalyst due to the significant increase in the pressure drop on the reactor. The induction period observed for the 10Ni-Al and 5Ni-CeAl catalysts was attributed to the oxidation of Ni particles by CO_2 when the catalysts are initially contacted with the feed, resulting in a loss of activity. Nevertheless, the partially oxidized Ni particles were reduced again by the syngas produced during the reaction, increasing the conversion of reactants. The spent catalysts were characterized by TEM and TG analyses to investigate the formation of carbon deposits. No carbon filaments are observed on the TEM images of the 10Ni-CeAl catalyst. The average Ni particle size is around 10 nm, which indicates a slight increase compared to the reduced sample (4–5 nm according to the XRD and TEM results). The TEM images of the 10Ni-Al and 10Ni/CeAl catalysts after the DRM reaction reveal high carbon formation, with the presence of many carbon filaments. The Ni particle size is higher than the ones observed for the 10Ni-CeAl catalyst (around 20 nm for both catalysts). TG analysis did not detect carbon deposits on the 5Ni-CeAl and 10Ni-CeAl catalysts prepared by the EISA method. However, carbon was formed over the catalyst prepared by impregnation (10/Ni/CeAl: 2.0 mgC/(gcatal.h)). The presence of Ce in the structure increased the oxygen mobility and acted as sites for CO_2 adsorption, promoting the carbon removal mechanism. Therefore, the Ni-based CeO_2-Al_2O_3 catalysts prepared by the one-pot EISA method exhibited high activity and stability for the DRM due to the confinement of Ni particles and the inhibition of carbon deposition by the Ce in the structure.

Table 1 summarizes the rate of carbon deposition during DRM over different Ni-based catalysts from the literature and developed in the Catalysis group of the National Institute of Technology (INT). The different strategies used to develop catalysts resistant to carbon deposition were successful.

Table 1 - Rate of carbon formation on Ni-based catalysts from the literature after DRM.

Catalyst	Reaction Conditions	Rate of carbon deposition ($mg_C/g_{catal}/h$)	Reference
5Ni-CeAl	800 °C, $CH_{4:}CO_2$ = 1:1	0.0	(Marinho *et al.*, 2021)
10Ni-CeAl	800 °C, $CH_{4:}CO_2$ = 1:1	0.0	(Marinho *et al.*, 2021)
10Ni/CeAl	800 °C, $CH_{4:}CO_2$ = 1:1	2.0	(Marinho *et al.*, 2021)
10Ni-Al	800 °C, $CH_{4:}CO_2$ = 1:1	0.8	(Marinho *et al.*, 2021)
Ni/CeO_2	800 °C, $CH_{4:}CO_2$ = 1:1	9.7	(Marinho *et al.*, 2020)
Ni@CeO_2	800 °C, $CH_{4:}CO_2$ = 1:1	1.6	(Marinho *et al.*, 2020)
Ni@$CeZrO_2$	800 °C, $CH_{4:}CO_2$ = 1:1	0.0	(Marinho *et al.*, 2020)
$LaNiO_3$	800 °C, $CH_{4:}CO_2$ = 1:1	27.0	(Rabelo-Neto *et al.*, 2018)
$LaNiO_3/SiCeO_2$	800 °C, $CH_{4:}CO_2$ = 1:1	0.3	(Rabelo-Neto *et al.*, 2018)
Ni/0Ce-AlO	800 °C, $CH_{4:}CO_2$ = 1:1	3.7	(Chen *et al.*, 2013)
Ni/05CeAlO	800 °C, $CH_{4:}CO_2$ = 1:1	2.8	(Chen *et al.*, 2013)
Ni/10CeAlO	800 °C, $CH_{4:}CO_2$ = 1:1	1.8	(Chen *et al.*, 2013)
Ni/15CeAlO	800 °C, $CH_{4:}CO_2$ = 1:1	1.2	(Chen *et al.*, 2013)
NiCu/$Ce_{0.9}Gd_{0.1}O_2$	800 °C, $CH_{4:}CO_2$ = 1:1	12.2	(Bonura; Cannilla; Frusteri, 2012)
Ni/CeO_2	800 °C, $CH_{4:}CO_2$ = 1:1	4.8	(Luisetto *et al.*, 2019)
Ni/CZ100	700 °C, $CH_{4:}CO_2$ = 1:1	0.4	(Kambolis *et al.*, 2010)
Ni/CZ75	700 °C, $CH_{4:}CO_2$ = 1:1	3.5	(Kambolis *et al.*, 2010)
Ni/CZ44	700 °C, $CH_{4:}CO_2$ = 1:1	1.7	(Kambolis *et al.*, 2010)
Ni/CZ28	700 °C, $CH_{4:}CO_2$ = 1:1	0.7	(Kambolis *et al.*, 2010)
Ni/CeZr(8.5)	700 °C, $CH_4:CO_2$ = 1:1	15	(Donphai *et al.*, 2023)
20Ce/Ni@SiO_2	700 °C, $CH_4:CO_2$ = 1:1	2.2	(Zhou *et al.*, 2022)
Ni/$Ce_{0.95}Zr_{0.05}O_2$	800 °C, $CH_4:CO_2$ = 1:1	0.0	(Zou *et al.*, 2023)

The carbon deposition in the DRM reaction strongly depends on the type of metal being used (Noronha *et al.*, 2001). In general, Group VIII metals are less prone to coking than Ni and Co, but their ability to operate with low carbon deposition in CO_2 reforming of methane is strongly related to their activity for CO_2 dissociation. For example, Ru and Rh are very active in CO_2 dissociation, and they can perform the CO_2 reforming of CH_4 without carbon deposition. Although the type of support used can affect the methane-reforming activity of metals like Ru or Rh, which are efficient for dissociating CO_2, those effects are much less crucial than in the case of Pt and Pd. This difference is due to the different abilities of the metals for CO_2 dissociation. A metal able to dissociate CO_2 can efficiently eliminate carbon produced by methane decomposition. In contrast, Pt or Pd require the assistance of the support to keep their surface free of carbon. Therefore, Pt supported on ceria and ceria mixed oxides catalysts have been extensively tested for DRM. However, ceria generally exhibits low surface area, which leads to low metal dispersion. A solution to overcome this problem is to deposit the ceria on high-area supports such as alumina (Azevedo *et al.*, 2022; Da Fonseca *et al.*, 2020a, 2020b).

Da Fonseca *et al.* (2020a) investigated how the nature of the dopant (Pr, Nb, and Zr) affects the performance of Pt supported on cerium-based oxides deposited on alumina for DRM. *In situ* XRD and XANES experiments showed that the catalyst doped with Pr achieved the highest reducibility of ceria (23%). Furthermore, the addition of Pr improved the resistance to metal sintering during the dry reforming reaction. The catalysts were tested for DRM at 800 °C for 24 h. For undoped catalyst (Pt/Al_2O_3), a strong deactivation occurred during the reaction due to the absence of support reducibility and the highest Pt sintering. However, adding Pr, Zr, and Nb to cerium oxide significantly decreased the loss of catalytic activity, mainly for the sample containing Pr. TPO analyses of the spent catalysts showed that the presence of dopants decreased carbon accumulation on the Pt surface. Moreover, for doped samples, a change of ceria oxidation states between Ce^{4+} and Ce^{3+} was observed during reduction treatment, as revealed by *in situ* XRD and XANES experiments. This effect was more significant for Pt/CePr/Al_2O_3, indicating that this sample presented the highest oxygen storage/release capacity, promoting the carbon removal mechanism from the metallic surface. In addition to carbon formation, metal sintering also occurred on the Pt/CeNb/Al_2O_3, Pt/CeZr/$Al_2O_{3,}$ and especially the Pt/Al_2O_3 catalyst. The decrease in metal dispersion also contributed to the deactivation of these catalysts during DRM. Among the doped-ceria samples, Pt/CePr/ Al_2O_3 exhibited the highest activity and stability. These results were attributed to (i) the oxygen mobility of the supports containing ceria, mainly for the sample doped with Pr, which favors the carbon removal mechanism, and (ii) the absence of Pt sintering during the reaction.

CONCLUSIONS AND PERSPECTIVES

Development of a biogas reforming technology is a potential route for hydrogen production in Brazil. Among the reforming processes, DRM benefits from using CO_2 as an oxidizing agent, decreasing associated costs to steam production with simultaneous CO_2 valorization. Despite its environmental promise, DRM technology has not yet reached industrial-scale operation, mainly because of the high coke formation and metal sintering, which occur in harsh reaction operations, leading to catalyst deactivation.

Research and development in this field are highly active, with Ni-based materials as one of the most common catalysts. Catalysts with small particles, often incorporating mixtures of elements (CeO_2 and Ce-doped materials), showed promising results in achieving high methane conversion and resistance to deactivation. The development of supports with high oxygen mobility promotes coke gasification during reaction. In addition, new catalyst structures with confined Ni nanoparticles have been developed to control the CH_4 decomposition. The development of such materials is crucial to highly dispersed Ni nanoparticles at high temperatures. The results showed that a balanced combination of well-dispersed metal on a support with high oxygen mobility could be a successful approach for DRM reaction.

Several key future research directions are top priorities in advancing biogas reforming technology:

1. **Tailoring of Metal-Support Interaction:** The rational design of DRM catalysts should focus on studying metal-support interaction. Parameters such as oxygen vacancies, oxygen mobility, and support-induced effects can significantly enhance the resistance against deactivation by coke formation or metal sintering.
2. **Advanced Synthesis Methods for Ni particle size control:** The utilization of advanced synthesis methods capable of fine-tuning the Ni crystallite size is crucial. This sintering control allows the design of DRM catalysts with remarkable resistance to coke formation. New studies should be conducted in this direction, such as developing single-atom catalysts.
3. **High-Pressure DRM Investigation:** Very few works have explored the development of catalysts to operate at high pressure during DRM reactions. Although high-pressure DRM has been considered to have lower costs than ambient pressure conditions, it has been relatively unexplored due to challenges such as enhanced coke formation, higher temperature requirements, and the formation of coke precursors. The catalyst design under high operating pressures is an important way to reduce costs in realistic DRM processes.
4. **Application of Advanced Operando Techniques:** DRM reaction occurs at high temperatures, and the catalyst can undergo changes during the reaction. Understanding the relationships between structure and activity at the atomic level is important to improve catalyst design techniques. Advanced *operando* techniques can be crucial in addressing the challenges outlined above. These techniques, including FTIR, XPS, or EXAFS spectroscopy, can provide valuable insights into the identity of key reaction intermediates, reaction pathways, and the effects of temperature and pressure on both mechanisms and coke formation on catalyst surfaces. Applying these techniques will contribute to a comprehensive understanding of variations in reaction mechanisms and kinetics of DRM reactions.

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SUSTAINABILITY ANALYSIS OF BIOGAS PRODUCTION AND ITS BARRIERS WITHIN THE BRAZILIAN LEGISLATIVE FRAMEWORK

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ABSTRACT: In Brazil, production growth and the transition to renewable energy have been driven by specific government policies, environmental regulations, and tax incentives. Biogas is considered a promising alternative for renewable energy development, making it crucial to analyze standards and regulations for its production. This chapter presents an exploratory, descriptive, and bibliographic review of the government policies development in Brazil related to the dissemination of biogas production technology and how these regulations directly affect sustainability aspects. The results reveal several lacks of clarity and standardization within the biogas legislative framework, potentially leading to uncertainty, misunderstandings, and misinterpretations. Economically, costs impact biodigester development, with lacking government financial mechanisms affecting farmers, especially small agricultural and small-scale biogas producers. On the other hand, fiscal incentives are crucial for renewable energy. Socially, limited awareness hampers biogas technology acceptance and performance, hindering public and political support. Environmentally, biogas offers cleaner energy and emission reduction, so its non-implementation can affect the country's goals. Thus, the gaps within the legislative framework strongly affect the sustainability pillars of the biogas and biomethane production system.

KEYWORDS: barriers, biogas, legislative framework, sustainability.

1. INTRODUCTION

The interest and importance of global warming and the reduction of greenhouse gas (GHG) emissions have grown (Etminan *et al.*, 2016). These issues occupy prominent positions on the political agendas and regulatory frameworks of several countries worldwide (Rogelj *et al.*, 2016), leading many scientists to call for immediate changes in existing energy systems (Nevzorova and Kutcherov, 2019). Thus, the search for and acquisition of new renewable energy sources and biofuels has intensified.

The three main gases that contribute to GHG emissions are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Worldwide, anthropogenic activities cause 50% of the total methane emitted, which is released by the decomposition of biogenic material from landfills, municipal wastewater, and agricultural and industrial activities (Nevzorova and Kutcherov, 2019).

Methane is the main gas in biogas (Hajjaji *et al.*, 2016; Poeschl *et al.*, 2012). Biogas can be produced through anaerobic digestion, a bioconversion process of organic substances, especially biomass residues (Yu and Schanbacher, 2010; Singh *et al.*, 2020).

Biogas is considered a promising alternative for the development of renewable energies (Rose *et al.*, 2014; Thrän *et al.*, 2020) and can be burned in heating systems (Abanades *et al.*, 2021) or when purified into biomethane, used as fuel in vehicle engines (Robin *et al.*, 2014). Furthermore, cogeneration plants can use biomethane to generate electricity, which can be used directly by the producer to meet their internal demand or sold (Sukun *et al.*, 2020. Kucher *et al.*, 2022).

Although it has several applications and is an important source of renewable energy, the full potential of biogas can only be exploited sustainably if its production and use are properly regulated (Popp *et al.*, 2014; Abanades *et al.*, 2021).

Biogas production has environmental, economic, and social benefits. However, it can affect other aspects, such as quality, global carbon and nitrogen cycles, competitive uses of raw materials, land use conversion in areas less suitable for sustainable agriculture, and land use changes (Thrän *et al.*, 2020).

Worldwide, the barriers study to implement biogas production technology has been growing rapidly. Mukeshimana *et al.* (2021) addressed the gaps in the literature focusing on the main barriers for the adoption of family biodigesters in Rwanda. Nevzorova and Kutcherov (2019) conducted a comprehensive barriers assessment of biogas wider adoption, aiming to understand the main challenges that currently hinder the adoption of biogas as an energy source. On the other hand, a comprehensive review about the recent progress in biogas technologies focuses on the advances in waste conversion to produce electricity, heat, and other forms of energy was performed by Abanades et al. (2021). Alvarez *et al.* (2019) investigated the hypothesis that more flexible and up-to-date regulations on renewable energy would have a positive impact in Peru. Their research considered the disparity between the slow advancement of regulations and the faster progress of science and technology. Thrän *et al.* (2020) investigated how sustainable has been managed during the German development, the biogas market.

Most resources used for biogas production are from the agricultural sector (Nevzorova and Kutcherov, 2019). In Brazil, livestock is one of the main economic activities of the country and the main source of environmental pollution in rural areas (Potenza *et al.,* 2021). Therefore, legislation for producing biogas and biomethane as a renewable energy source is related to different economic sectors.

However, a study has not been published focused on the failures of the legal framework in Brazil regarding the production of biogas and biomethane. Thus, this chapter explores the development of government policies in Brazil that relate to the dissemination of biogas production technology and how these regulations directly affect social (agribusiness: farmers and producers of raw materials), economic, and environmental aspects, putting their sustainability at risk.

2. METHODOLOGY

In the Brazilian context, a comprehensive analysis of the norms and incentives for the biogas sector over decades is essential to understand its legislative evolution, development, and challenges. The trajectory from the 1970s to the present day allows for a panoramic view, highlighting both the progress and the gaps in legislation related to this biofuel.

The research methodology includes an exploratory, descriptive, and bibliographic review to collect political information and the legislative framework related to biogas production in Brazil.

Initially, a systematic literature review on Brazilian legislation was developed using the databases of Google Scholar, Capes Journals, Web of Science, government and official websites of different institutions, websites of legally established Brazilian companies and associations, and leaders in research related to biogas and biomethane. The following keywords were used separately and in random combinations in Portuguese: *"Histórico", "Historia", "Leis Brasileiras", "legislação", "Brasileira", "Biogás", "biofertilizantes", "Brasil"*; and in English: "Brazilian", *"Brazil", "Laws", "Legislation", "Biogas", "Biofertilizer", "Historical"*.

To understand the evolution of Brazilian laws, a time interval from the 1970s to 2022 was considered. All statutes, normative resolutions, decrees, and bills that could directly or indirectly influence the development of the biogas market and its effect on the sustainability of the process were analyzed. Direct influence includes those standards that textually name biogas or its production process and affect its entire chain. Indirect influence refers to those standards that affect the use, sale, and distribution of products, such as the sale of energy from renewable sources. State and government regulations on the production of renewable energy, electricity, solid waste, and the environment were considered, as they are correlated with the production of biogas.

After exploring the national legislation trajectory, the shortcomings and failures of existing legislation to encourage the biogas production were analyzed. In addition, efforts were made to understand how the development of government policies in the country related to the dissemination of biogas production technology as well as the federal legal framework and state regulations directly affect the pillars of sustainability (Rogelj *et al.*, 2016).

3. EVOLUTION OF BRAZILIAN BIOGAS LEGISLATION

Since the 1970s and 1980s, highlighted by the Stockholm Declaration in 1972 and the First World Climate Conference in 1979, the severity of climate change has been recognized, and global concern has grown about the implementation of the Clean Development Mechanism and the reduction of GHG emissions. According to Johon (2010), the 1970s also witnessed a renewed emphasis on the energy issue, driving change in the world energy model toward greater diversification through the use of alternative and renewable energy sources.

In Brazil, the oil crisis beginning in 1979 aroused the government's interest in biogas production due to the low cost of deploying biodigesters (CIBiogás, 2023a). This emerging technology, internationally highlighted for the mitigation of environmental impacts and waste treatment, led to the creation of the Energy Mobilization Program (PME – *Programa de Mobilização Energética*), approved by Decree No. 87,079/1982. Biogas and biomass were mentioned as a second priority and a local solution for power generation, aiming to progressively replace petroleum products with alternative fuels produced in Brazil. However, due to the lack of technical knowledge about biodigester technology and the shortage of specialized labor, operational problems arose, leading to the abandonment of the technology a few years later (CIBiogás, 2023).

In the 1990s, the National Program for Family Agriculture (PRONAF – *Programa Nacional para a Agricultura Familiar*) was created by Decree No. 1,946/1996 to promote sustainable development in family farming. Offering the lowest interest rates on rural financing and having low default rates, the PRONAF is implemented by public and private banks, the National Bank for Economic and Social Development (BNDES – *Banco Nacional de Desenvolvimento Econômico e Social*) and rural credit cooperatives. It is present in almost all Brazilian municipalities. Within PRONAF, the Technical Assistance and Rural Extension subprogram (ATER - Assistência Técnica e Extensão Rural) seeks to foster income generation through activities that encourage farmers to produce biofuels, among other activities.

In the 21st century, the Brazilian agricultural sector has shown significant interest in biogas production, driven by the enormous generation of manure, especially in pig farming (Lima, 2007), and by the opportunity to participate in the carbon credit market. The second edition of the National Environmental Program (PNMA II, 2000 - edition II – *Programa Nacional do Meio Ambiente*) was established in 2000. This program facilitated the implementation of environmental projects in pig production, exemplified by the Santa Catarina Pig Farming project, which constructed two biodigesters on pig-producing properties to demonstrate and encourage the adoption of this technology (Lima, 2007).

In this century, biogas production technologies have gained momentum in Brazil, with rapid growth evidenced by several studies (Kunz *et al.*, 2016; CIBiogás, 2021; ABEEólica, 2020). These technological advances stimulated research, structured government policies, development of laws, programs, and finally, economic and tax incentives. A notable example of this interest in the energy sector is Statute No. 9,991/2000, which promotes investments in research and development, as well as energy efficiency by companies in the electricity sector. In addition, the legislation encourages research into systems that generate renewable energy.

In 2002, the Incentive Program for Alternative Energy Sources (PROINFA – *Programa de Incentivo* às *Fontes Alternativas de Energia*) was established to increase the participation of renewable sources, such as small hydroelectric plants, wind power plants, and biomass thermoelectric projects, in the production of electricity. The program, governed by Statute No. 10,438/2002, favors entrepreneurs without corporate ties with generation, transmission, or distribution companies. According to Eletrobrás (2023), PROINFA is considered the largest global program to encourage alternative sources of electricity.

Through the program, a significant improvement in biogas production occurred in 2004. However, this renewable source still played a secondary role behind conventional sources, such as hydroelectricity and fossil fuel thermal power plants (Correa, 2015). Even with an improvement in the biogas production sector, until 2005, no state had created regulations that facilitated the development of this technology.

In 2006, the National Agroenergy Plan (*Plano Nacional de Agroenergia*) was established to promote less use of fossil fuels, expand the production and consumption of biofuels, protect the environment, explore the international market, and contribute to social inclusion (MAPA, 2006).

The pioneering Solid Waste Policy of the state of São Paulo (Statute 12,300/2006) encouraged and increased interest in using solid waste to generate energy and fuel from renewable sources. With this policy, the treatment and final disposal of the various wastes generated by society began to boost the development of new technologies, research, and regulations involving biogas and other renewable sources.

In the field of renewable energy, the state of São Paulo (SP), through Decree No. 51,736/2007, which established the Special Bioenergy Commission of the State of São Paulo sought to organize the necessary attributions and governmental actions for the development of renewable energy generation activities in the state, including subsidies, evaluations, research, and the preparation of the State Bioenergy Plan. This decree prioritized the production of renewable energy from biodiesel and ethanol; however, it did not directly cover biogas due to the greater volume of studies, development, production, and marketing of these biofuels (Sánchez *et al.,* 2017; REN21, 2020).

The company Paranaense de Energia (COPEL) in the state of Paraná began to be interested in distributed micro- and mini-generation. It constructed a plant connected to the low-voltage network that generates and distributes electricity from biogas generated by properly managing organic waste from animals raised on small farms (Sapatel, 2020). Furthermore, through Resolution No. 1,482/2008, a pioneer in Brazil in recognizing biogas as an energy source, the Distributed Generation Program with Environmental Sanitation (*Programa de Geração Distribuída com Saneamento Ambiental*) was authorized, presented by COPEL as a pilot project for the implementation of low voltage distributed generation (DG) lasting six months, marking incursions by the sector.

In 2009, the state of Maranhão instituted Statute No. 8923/2009. This regulation encourages the use of energy from any potential source linked to the services, including energy from biogas resulting from sanitary sewage treatment and treatment or final disposal of solid waste.

In the same year, a partnership was formalized between the Itaipu Technological Park (PTI - Parque tecnologico de Itaipu) and the Brazilian Agricultural Research Corporation (Embrapa – *Empresa Brasileira de Pesquisa Agropecuária*) to develop the Biogas Laboratory (CIBiogás, 2023a). PTI implemented the program of energy applications from renewable sources in DG for biogas, validated by Authorizing Resolution No. 1,482/2008 of the National Electric Energy Agency (ANEEL– *Agência Nacional de Energia Elétrica*) (CIBiogás, 2023a). Another pilot project, approved through this resolution, is the *Granja São Pedro* project of the Colombari family. This innovative project in Brazil uses biogas as a raw material to generate electricity for DG (CIBiogás, 2023a; Sapatel, 2020).

Until that time in the history of biogas, most of the advances made in the country had been developed in the south region. The regulations related to renewable energies emphasized the individual support of each state, and biogas was not considered a primary energy source. Thus, in the period between 2000 and 2010, Brazil gained a better understanding and learned about biogas production technology.

After 2010, more specific policies for generation of biogas and renewable energy emerged, such as the creation of the Renewable Energy Observatory for Latin America and the Caribbean (*Observatório de Energias Renováveis para América Latina e Caribe*), resulting in the formation of the Center for Biogas Studies (CEB *Centro de Estudos do Biogás*), through a technical partnership between the United Nations Industrial Development Organization (UNIDO), Itaipu Binacional, and Eletrobrás (FIERP, 2023).

The Low Carbon Agriculture Program (ABC - *Plan Centro de Estudos do Biogás*) was established and approved, as defined in Decree No. 7,390/2010. This program aimed to organize and plan the adoption of sustainable production technologies. It was designed to meet the country's commitments to reduce GHG emissions in the agricultural sector (MAPA, 2012). With national coverage and valid from 2010 to 2020, the ABC Plan is recognized as the largest plan to promote sustainable technologies in the agricultural and forestry sectors worldwide. Due to its successes, the program was extended for another 9 years from 2021 to 2030 (GovBr, 2021).

The ABC Plan consists of several programs. However, according to Embrapa (2021), the program for the recovery of degraded pastures and the treatment of animal waste (pig and dairy farming), despite technological advances, has faced challenges in its development, installation, and improvement because its improvement goals have not been met.

The year 2012 was important for electricity from renewable sources, including biogas. The ANEEL prepared Normative Resolution No. 482/2012, to establish the general conditions for the access to electricity distribution systems by micro- and mini-generation. With the implementation of this resolution, considerable advances occurred in the field of micro- and mini-generation of energy. The Electricity Compensation System enabled Brazilian consumers to generate their own electricity from renewable sources (Sapatel, 2020). Furthermore, the surplus could be supplied to the local distribution network in exchange for energy credits (Correa, 2015). Thus, the system further motivated the production of energy from biogas, because when generated in decentralized areas and its surplus marketed, it is considered a sustainable solution and compliant with the circular economy, transforming an environmental liability into an energy asset.

In Paraná, under Statute No. 17,188/2012, rural landowners could sell to COPEL the electric energy generated by small generators using renewable energy sources. In the state of São Paulo, the São Paulo Biogas Program and its Managing Committee Program were established by Decree No. 58,659/2012. The objective of this program was to encourage and expand the participation of renewable energies in the state's energy matrix, highlighting the positive externalities of generating fuel gases from biomass. The state of Rio de Janeiro created a state renewable natural gas policy in Statute No. 6361/2012, which provides incentives for generating fuel from organic waste by transforming it into biogas to help reduce the production of greenhouse gases in the state.

The state of Minas Gerais passed legislation directly related to biogas production, Decree No. 46,296/2013, dealing with the Mineiro Renewable Energy Program and establishing measures to encourage the production and use of biogas and biomethane as renewable energy. In Paraná, the International Renewable Energy Center (CIBiogás – *Centro Internacional de Energias Renováveis*) was incorporated, becoming a center of competence at the PTI. In Pernambuco, Decree No. 39,059/2013 granted incentives to the company Gases Renováveis do Brasil LTDA. In São Paulo, Decree No. 59,038/2013 established the São Paulo Biofuels Program. In Espírito Santo, Decree No. 3,453/2013 provided a state policy to encourage renewable energies, including wind, solar, biomass, and other renewable sources, and aimed to appropriately adapt the treatment of organic waste and economically exploit biomethane generated in landfills. It also sought to integrate biomethane into the natural gas network to distribute this resource in the state.

The Brazilian Association of Biogas and Biomethane (ABiogás – *Associação Brasileira de Biogás e Biometano*) was created in 2013 to foster the country's potential production of energy and fuel from agricultural waste, landfills, sanitary effluents, and animal waste from slaughterhouses and dairy products. Currently, ABiogás is a consolidated science and technology institution that drives the sustainability of the sector and makes it more competitive, covering regulatory environment analysis and public policies (Abiogás, 2023).

In 2014, Paraná implemented Decree No. 11,671/2014, which established the Paraná Renewable Energy Program – Illuminating the Future (*Programa Paranaense de Energias Renováveis – Iluminando o Futuro*) and includes measures to stimulate the production and use of renewable energy. Simultaneously, the CIBiogás association launched the Biomethane Mobility Project to reduce GHG emissions using biomethane as a vehicle fuel (CIBiogás, 2023b).

Enacted in 2015, National Agency of Petroleum, Natural Gas, Biofuels (ANP *Agência Nacional do Petróleo, Gás Natural e Biocombustíveis*) Resolution No. 8 specified the characteristics of Brazilian-produced biomethane intended for commercialization throughout the country. Subsequently, Normative Resolution No. 687/2015 was implemented to improve the guidelines established by Resolution No. 482/2012, enabling the installation of small generating plants and allowing the credits to be attributed to producers when the amount of energy they produce exceeds the energy consumed (SUNENERGIA, 2017).

Santa Catarina, in Decree No. 233/2015, created the Santa Catarina Clean Energy Program (SC+ENERGIA Program – *Programa Catarinense de Energias Limpas*), whose main objective was to provide guidelines for using waste, such as feces and urine from livestock, especially in pig farming, to generate energy through biodigesters. In addition to solve environmental issues, this new policy aimed to provide farmers with an additional source of income and diversify the energy matrix in Santa Catarina.

In 2016, the Biogasfert project was implemented by a consortium composed of Embrapa, PTI, CIBiogás, and the International Hydroinformatics Center (CIH - *Centro Internacional de Hidroinformática)*, currently known as the Territorial Intelligence Center (*Núcleo de Inteligência Territorial*). The objective of the project was to promote studies and technological solutions for the integrated use of biogas, biofertilizers, and other organic minerals derived from animal waste from different agricultural production systems, concentrating these advances mainly in Brazilian South region (CIBiogás, 2023a).

In the state of Rio Grande do Sul, Statute No. 14,864/2016 established the Institute of State Policy on Biogas and Biomethane as well as the Gaucho Program to Encourage the Generation and Use of Biogas and Biomethane (RS-GÁS – *Programa Gaúcho de Incentivo à Geração e Utilização de Biogás e de Biometano*). This was the first specific law to promote the generation, production, marketing, transport, and use of biogas and biomethane; energy production; and vehicular fuel to care for the environment and reduce GHG emissions. In the state of Piauí, Statute No. 6901/2016 created the Piauí Clean Energy Development

Incentive Program (PROPIDEL – Programa Piauiense de Incentivo ao Desenvolvimento de Energias Limpas), aiming to encourage biogas production in the state of Piauí through the installation of biodigesters on rural properties. In Roraima, Statute No. 1109/2016 created the State Policy to Encourage the Generation and Use of Solar, Wind, and Biomass Energy. The main objective of both these laws is to encourage the production and use of clean energy sources in the respective states, promoting economic development and environmental sustainability.

Thus, between 2010 and 2016, Brazil made significant progress in the biogas sector, with notable advances in technologies, regulatory frameworks, research, and project development (EPE, 2017a). The share of biogas in the Brazilian energy matrix grew from 0.01% to 0.05%, representing an increase of 400%. In 2016, biogas accounted for 1% of the total energy supply in the country, standing out compared to other energy sources derived from biomass (EPE, 2017a)

In 2017, the federal RenovaBio program was implemented, characterized as the National Biofuels Policy, an initiative of the Ministry of Mines and Energy (MME – *Ministério de Minas e Energia*). This program aimed to "encourage and expand the production and participation of biofuels in the transport energy matrix of the country, based on environmental, economic, and social predictability and sustainability, establishing annual national decarbonization targets" (EPE, 2017b). Statute No. 13,576/2017 established the program and provided specific incentives for the large-scale biogas production (Stilpen *et al.*, 2018).

The ANP established Resolution No. 685/2017, which defines rules for the quality control and specifications of biomethane produced from landfills and wastewater treatment plants, intended for use in vehicles and residential, commercial, and industrial facilities throughout the national territory. This measure allows appropriate parameters for the commercialization of biogas nationwide.

The implementation of regulations, programs, plans, and incentives for biogas production in Brazil marks a new phase for the sector, enabling its commercialization as a substitute for natural gas. These measures boost the development of a new economic activity and the entry of new agents into the market while promoting sustainable practices.

In 2018, the state of Paraná sanctioned the new State Policy on Biogas, biomethane, and other by-products generated from the decomposition of organic matter through biodigestion in Statute No. 19,500/2018. The main objective of this law is to establish principles, rules, obligations, and instruments for the organization, encouragement, supervision, and support of integrated or non-integrated productive chains, addressing climate change and promoting regional development sustainably. The regulation establishes the production chain for biogas, biomethane, and products related to the decomposition of organic matter (biodigestion) as a set of activities and endeavors interconnected by contractual relations.

In the same year, Santa Catarina instituted its State Biogas Policy based on Statute No. 17,542/2018. Santa Catarina's state policy is comprehensive, including incentives to reduce GHG emissions, purify biogas, use biomethane as a vehicle fuel, and manage the by-products of anaerobic digestion. In addition, Statute No. 302/2018 aimed to encourage companies that produce biogas, methane, and electricity from solid waste in landfills in Santa Catarina. The state of Minas Gerais, in Statute No. 5,240/2018, established the State Biogas and Biomethane Policy and the state of São Paulo with Decree No. 46,476 regulates Law No. 16,001, which establishes the state policy to encourage the development of the productive chain in the biogas and biomethane.

In Rio Grande do Norte, Statute No. 10,338/2018 guides the State Policy on Distributed Generation with Renewable Energies (GDER- Política Estadual de Geração Distribuída com Energias Renováveis). The project Applications of Biogas in the Brazilian Agroindustry, aims to reduce GHG emissions and dependence on fossil fuels. This project promotes the use of biogas in energy generation and mobility solutions in agroindustrial chains in southern Brazil, strengthening the value chain of biogas technology nationwide.

The Panorama of Applied Technologies in the Agribusiness of Biogas and Biomethane (*Panorama de Tecnologias Aplicadas no Agronegócio de Biogás e Biometano*) (MARTINEZ; BÜHRING; MÜLLER, 2019) was released in 2019, providing data on five specific plants, their biodigestion systems, and the technologies used to treat biogas. In addition, the first report on the Biogas Production Potential in Southern Brazil was presented in collaboration between CIBiogás, Embrapa, the UNIDO, the Global Environment Facility (GEF), Itaipu Binacional, the Ministry of the Environment (MMA *Ministério do Meio Ambiente*), the MME, the Ministry of Agriculture, Livestock, and Food Supply (MAPA – *Ministério da Agricultura, Pecuária e Abastecimento*), and the Ministry of Science, Technology, Innovations, and Communications (MCTIC – *Ministério da Ciência, Tecnologia, Inovações e Comunic*ações). The state of Mato Grosso proposed Bill No. 640/2019, addressing the State Policy for Biogas and Biomethane, with additional measures.

In 2020, many of the legislative procedures to incentivize biogas incentives were impacted by the COVID-19 pandemic, resulting in delays. However, both the federal government and the state of Goiás enacted significant initiatives: Bill No. 2193/2020 and Statute No. 20,710/2020, respectively, establishing the Biogas and Biomethane Policy. In addition, the ANP Resolution No. 828/2020 provided information contained in the quality documents and the sending of quality data of fuels produced nationally or imported.

In 2021, Paraná stands out in creating regulations to boost the biogas and biomethane production. Ordinance 118/2021 established technical guidelines for the Paraná Renewable Rural Energy (RENOVAPR – *Paraná Energia Rural Renovável*) program, an integral part of the state agricultural policy for economic and social development. This program plans to promote the DG of electricity, encouraging the production of biogas and biomethane in the state's rural production units.

The state of Maranhão proposed Bill No. 542/2021 to institute its State Biogas Policy. In Rondônia, Bill No. 3791/2021 sought to establish incentives for the energy utilization of biogas originating from sewage and solid urban waste management activities. In Minas Gerais, Bill No. 3865/2021 includes the Incentive Program for the Production and Use of Biogas, Biomethane, and Associated Co-products (PIBB – Programa de Incentivo à Produção e ao Aproveitamento de Biogás, Biometano e Coprodutos Associados), including indication of co-products, such as digestate. São Paulo also proposed Bill No. 3865/2021 to establish its PIBB.

The recently approved Statute No. 14,134/2021 expanded the regulatory standards originally intended to advance natural gas projects to cover other gases, including biogas. This inclusion aligns with the strategic plan to boost the natural gas sector. In addition, Decree No. 10,712/2021, which regulates the new Gas Law, stipulates that all gases interchangeable with natural gas must receive equivalent regulatory treatment.

Following the lockdowns during the pandemic, the resumption of activities highlighted the importance of renewable energies. Cozzi et al. (2020) noted that this period emphasized the search for fuels, technologies, and structural and governmental changes, including the implementation of new legislation to regulate energy production.

Following the post-pandemic transition phase, several measures were implemented to boost the renewable energy sector, especially regarding biogas and biomethane production. They include Statute No. 14,300/2022, which established the legal framework for distributed micro-generation and mini-generation, the Electric Energy Compensation System (SCEE – *Sistema de Compensação de Energia Elétrica*) and the Social Renewable Energy Program (PERS – *Programa de Energia Renovável Social*), mechanisms that are based mainly on renewable energy production, including biogas.

The National Methane Emission Reduction Program (Metano Zero – *Programa Nacional de Redução de Emissões de Metano*) (MMA ordinance No. 71/2022), the Federal Strategy to Encourage the Sustainable Use of Biogas and Biomethane (*Estratégia Federal de Incentivo ao Uso Sustentável de Biogás e Biometano*) (Decree No. 11,003/2022), and the temporary authorization for the company Cocal Energia S.A. to market biomethane with different specifications (ANP Authorization No. 547/2022) were established. ANP Resolutions No. 886/2022 and No. 906/2022 define specifications and rules for quality control of biomethane from landfills, sewage treatment plants, and organic products and waste, intended for vehicular and residential use, respectively, aimed at their commercialization throughout nationwide.

Pernambuco established a state policy to encourage the generation of renewable energy by rural producers in Statute No. 18,111/2022. Ceará addressed its biogas production and use with Resolution No. 16/2022. Rio Grande do Sul, through Decree No. 56,348/2022, established the Incentive Program for the Generation and Use of Biogas for Electricity Generation (BIOGÁS-RS – *Programa de Incentivo à Geração e Utilização de*

Biogás para Geração de Energia Elétrica). The state of Goiás established the state policy to encourage the use of biomass for the generation and cogeneration of renewable energy through Statute No. 21,737/2022. The state of Mato Grosso do Sul implemented the State Program to Encourage the Development of Renewable Sources of Electricity Production (MS Renovável- *Programa Estadual de Incentivo ao Desenvolvimento das Fontes Renováveis de Produção de Energia Elétrica*) through Decree No. 16038/2022.

3.1. BRAZILIAN TAX INCENTIVES

In addition to the legislation, tax incentives are also needed to encourage the installation and use of new technologies such as biogas and biomethane production. In Brazil, the decrees that present these incentives began in the 2010s.

In Piauí, Decree No. 14,861/2012 defined the guidelines for granting the Environmental Seal to municipalities in line with Ordinary Statute No. 5,813/2008, recognizing biogas production as an alternative for waste treatment and energy generation.

With Tax on Circulation of Goods and Services (ICMS - *Imposto sobre Circulação de Mercadorias e Serviço*s) Agreement No. 112/2013, economic incentives began to be provided to the states of Bahia, Mato Grosso, Rio de Janeiro, and São Paulo that reduced the calculation basis of the ICMS for internal biogas and biomethane outputs.

Several states have adhered ICMS Agreement No. 16/2015 of the National Council of Finance Policy (*Conselho Nacional de Política Fazendária*), which exempts internal electricity-related operations to encourage bioenergy production, especially from biomass and biogas.This agreement aims to ensure equitable conditions between companies importing products and those producing them domestically (Rosa, 2018).

ICMS Agreement 6/2016 authorized the states and the Federal District to grant exemption from ICMS in biogas operations when used as fuel in internal combustion engines or gas turbines.

The creation of ICMS Agreements led different Brazilian states to join the implementation of these agreements and to create their own regulatory frameworks that exempt biogas, as shown in Table 1.

These agreements and regulations reduce the ICMS tax base for internal biogas and biomethane outputs, establishing a tax burden of 12% on the value of the operation; defer the ICMS in operations with machinery and equipment for capturing solar energy; exempt biogas from landfills from the ICMS; and reduce the ICMS tax base for internal biogas and biomethane outputs.

Year	State	Regulation
2016	Bahia, Mato Grosso, Rio de Janeiro, and São Paulo	ICMS Agreement No. 24
2018	Ceará	Decree No. 32,600
2019	Rio Grande do Sul	ICMS Agreement No. 13
2019	Pará	ICMS Agreement No. 19
2019	Paraíba	Decree No. 39,110 and ICMS Agreement No. 06
2022	Mato Grosso do Sul	Decree No. 16,027
2022	Goiás	Statute No. 21,555

Table 1. Regulatory exemptions for biogas by state.

4. LEGISLATION ANALYSIS

Roitman (2018) highlights that there is no established worldwide standard or ideal model for public and private policies in the renewable energy sector. Brazil also does not present a model. This scenario is even more apparent when it comes to biogas and biomethane production, as in Brazil, this renewable energy source has been growing and developing with significant advancements only since 2010.

In Brazil, the production growth and the transition to renewable energy have been driven by specific government policies, environmental regulations, and tax incentives (EBA, 2017). The standards or regulations are important for developing and implementing these policies. Regulatory Agencies play a fundamental role in establishing these standards by regulating, controlling, and supervising the activities in specific sectors, ensuring appropriate application (Desclaux, 2019). The policies creation and standards about the issue is influenced by the context, needs, and territory maturity (Mito, 2022). The country is advancing in its energy transition to reduce dependence on fossil fuels by increasing renewable energy matrixes. Between 1970 and 2022, approximately 175 regulations related to the generation of energy from renewable sources were identified, of which 29 are specific to the production of biogas, and 8 bills are still under evaluation.

The biogas sector lies within the legal frameworks of renewable energy (electricity and natural gas sector), sanitation (management of urban solid waste and effluents), the environment, and climate change. It is also subject to some regulations related to the agricultural sector. The biogas legislative trajectory evidences that the growth in the number of standards and regulations related to renewable energies, especially those associated with biogas, is correlated with the significant increase in the implementation and this resource production. This increase is primarily attributable to the growing awareness of the population about the importance of sustainability and the environmental impacts resulting from the inadequate organic waste disposal, which has considerable potential as raw materials for the bioenergy production (Bharathiraja *et al.*, 2018).

Interest in biogas production in the country is being driven by the low cost of implementing biodigesters, an innovative technology internationally adopted to mitigate environmental impacts and providing benefits in waste and byproduct treatment (Esteves *et al.*, 2019).

In the twenty-first century, biogas production technologies have spread rapidly in Brazil, boosting research, policy development, and implementation of economic and fiscal incentives. Between 2000 and 2009, the interest and expansion of biogas production increased in Brazilian agriculture. However, specific regulations for biogas were not established, as it was not seen as a significant source of energy production, maintaining a subordinate position compared to traditional sources such as hydroelectricity and thermoelectric plants powered by fossil fuels. Thus, between 2007 and 2010, decrees related to the production of renewable energy prioritized biodiesel and ethanol. This occurred due to a larger volume of studies in the research, development, and production of these sources, which were also the most traded in the Brazilian and global markets (Sánchez *et al.*, 2017). However, regulations on renewable energy emphasize the individual support of each state, giving them autonomy to establish their own energy policies.

Since 2010, the transition through a gradual reconfiguration of legislation has been motivated by the development of renewable energies and as a solution to local issues, emission reduction, and waste management. In this scenario, the growing interest in biogas was driven by projects financed by several non-governmental institutions to acquire new knowledge and the global sharing of information in the sector. A notable example is the project developed by UNIDO, Itaipu Binacional, and Eletrobrás with the objective of preventing eutrophication in the Itaipu lake. Important events in 2010 include the World Energy Conference in Vienna and the launch of the first Refresher Course on Biogas Energies (CIBiogás, 2023). In turn, this year, the National Solid Waste Policy (PNRS) was instituted through Statute No. 12,305. Brazil has been slightly behind in enacting legislative to regulate the proper treatment and final disposal of waste, as other Latin American countries issued the corresponding laws years earlier: Mexico (2003), Colombia (2008), Peru (2000), and Argentina (2003). The delay in the creation and establishment of these statutes can be considered a barrier to the development of cleaner technologies, the production of renewable energy from waste, and the reduction of waste generated by society.

In turn, the government created the Electricity Compensation System (SCEE – *Compensação de Energia Elétrica*) that authorized Brazilian consumers to generate their own electricity from renewable sources (SAPATEL, 2020). This begins to further open the market for energy produced from renewable energies.

In state terms, the first specific regulation for biogas was created in 2012 in São Paulo through Decree No. 58,659/2012, establishing the São Paulo Biogas Program.

The legal economic incentives began with the creation of the ICMS Agreement 112/2013. This agreement allowed for a reduction in the tax burden for projects, connections, transportation, and electricity generation from biogas and biomethane (LIMA, 2022). Other states, including Goiás, Minas Gerais, and Bahia, have created specific laws related to ICMS taxation and special tax regimes to benefit biofuel producers.

However, agreements can generate a distortion in competition between companies in the sector, as not all have access to the same tax incentives, which can favor some to the detriment of others (GOV, 2022). The agreements are not clear and specific about who can obtain the tax benefits and do not establish amounts and percentages related to the acquired benefit. In this sense, regulatory frameworks provide greater clarity in defining who can participate in the markets, how they can participate, and under what conditions.

No statute guarantees that the government grants the benefits to the producer or buyer for a specific time. In addition, there is a risk that companies will use these incentives only to reduce costs and not to invest in technological and environmental improvements, compromising the quality and sustainability of biogas and biomethane production. Another point to consider is that these agreements are only temporary and can be revoked or modified at any time, which can generate legal uncertainty for investors (PCD, 2020; GOV, 2022). All these points are examples of the ambiguity in the legislation becoming important barriers to the development of the sector, causing negative impacts on competition, quality, and sustainability of the production of this bioenergy and legal certainty.

This chapter highlights that several statutes, decrees, and agreements in Brazil regulate biogas production, but the lack of standardization at both the state and federal levels is evident. The generalization of the term “renewable energy” in standards and programs makes it difficult to determine which technologies or resources are included in the definition when sources are not specified, which may result in gaps or inconsistencies in the implementation and compliance with energy policies. The lack of clarity could create uncertainty for investors, developers, and others interested in the industry. Therefore, renewable energy-related standards and programs must specify which technologies and resources are covered by the definition to provide a solid foundation for consistent implementation of related policies and regulations and to avoid misunderstandings or misinterpretations. Regulatory frameworks are fundamental to define the business environment and market models. This aspect is considered a challenge that prevents the biogas use as an energy source (Santos *et al.*, 2018).

According to BEP (2021), the diversity of the legal framework can lead to a lack of standardization and harmonization between standards. Therefore, it is crucial to identify which standard to apply and understand how it ensures compliance with all project requirements. Some state or federal standards have limited reach and scope, resulting in conflicts with other standards or not meeting the specific demands of each region or sector. In addition, the standards may have different technical requirements, administrative procedures, jurisdictions of the agencies responsible for the license, and mitigating and compensatory measures required for the environmental licensing of biodigesters with energy recovery from biogas.

From 2019 to the end of 2020, the years of the COVID-19 pandemic were stagnant years for many sectors, including the legislative sector. This period helped in understanding the importance of renewable energies, with an increase in regulations related to the area encouraging their generation.

In 2020, the Bill 2193/2020 was proposed, aiming to establish the Federal Policy for Biogas and Biomethane, seeking to encourage the production, research, and consumption of gases produced from organic waste (PCD, 2020). This bill is considered one of the most relevant for biogas and biomethane in the country until today. However, there is still a long way to go because, after more than 20 years of technological development in the country, the statute has only been proposed but not approved yet. Approval by the National Congress may result in changes or vetoes of the original text, which means that it is unknown when it may be approved, delaying the process of institutionalizing biogas production in subsequent chains.

Considering the provisions of Complementary Statute No. 205/2017, ARSESP Resolution No. 744/2017, Bill No. 3865/2021, Statute No. 5420/2021, Statute No. 2656/2022, Statute No. 11,190/2022, and Resolution No. 16/2022, the biogas that can be injected into the gas network and commercialized is exclusively biomethane. Thus, only facilities with a biogas purification process and access to the natural gas distribution network can sell the excess gas produced. This can cause economic problems for farmers, as many are in decentralized areas without access to gas pipelines, electricity, studies, and knowledge of technologies that can improve the current situation to meet the basic needs of the farm.

Power plants that can sell excess biogas or energy to the national distribution network are mostly considered large-scale enterprises because these systems require the integration of anaerobic digestion plants with the biogas purification steps and transformation into energy. This implies substantial investments in this production chain to achieve these products and economic benefits through the sale of energy, biomethane, and biofertilizer, in addition to obtaining environmental gains by avoiding the consumption of products from the national network.

On the other hand, farmers with low raw material production or more rudimentary and less technological biogas production technology could not reap an economic benefit from the sale of their products. In turn, their location far from centralized areas or gas pipeline and electricity grid connections makes it difficult to distribute biomethane and energy produced.

The projects developed on a large and small scale with farmers have faced a common difficulty – the lack of technical knowledge about the production process and skilled labor. Brunel (2023) identified that political instability, the lack of motivational factors, and limited environmental awareness are global causes for the shortage of professionals with skills to work in the energy sector. Although there are initiatives in Brazil to enter, enhance, and delve into the biogas sector, it is crucial to invest in the training and improvement of knowledge among the workforce, farmers, and the interested population, as well as allocate economic resources for this purpose. Technological knowledge stands out as one of the most relevant aspects in the decision-making process for its implementation.

For the different investments made in the area, national development banks have been the major loan providers for the large-scale development of renewable energy in some Latin American countries, offering particularly attractive conditions and covering a large part of the funding required by project developers (Brunel, 2023). According to Lonnqvist *et al.*, 2018, the desired scale for implementation includes macroeconomic and macro-political factors, such as energy prices and plant infrastructure. The abolition of fossil fuel subsidies, which lower the costs of generated energy and purchased material, would put pressure on the socio-technical system of biogas production.

Evaluating the installed capacity of small biogas power plants is crucial. Larger power plants generally have lower relative installation and maintenance costs (Lima *et al.*, 2018), generally making their economic feasibility higher. This is why investments of resources are mostly made for large-scale production projects rather than small projects, especially not micro and mini power generators from biogas. Legislation for the latter is more focused on other renewable sources. An example of this is Decree No. 16027/2022, which grants ICMS deferral in operations involving machinery and equipment for the capture, generation, and transmission of solar or wind energy, as well as for the energy generation from biogas. Thus, it was not written for small producers, as technologies purchased outside the country may be more expensive than more basic technologies created in the national territory.

Usually, small-scale production is the least developed in the legal framework. However, this is precisely where the potential biogas producer is in Brazil. If small producers had access to the national energy distribution and transmission system, they could acquire greater socioeconomic benefits, considering that 79% of Brazil's total registered power plants are small (CIBiogás, 2021).

Thus, the legislation related to the production of biogas and biomethane in the country is still in transition to a suitable configuration. With this transition, different legislation must undergo transformations. This type of change is increasingly focused on properly educated energy producers with stable production. This could be considered an aspect that has direct environmental effects for the country, because the most abundant raw material comes from the agricultural sector, which is the second-largest generator of GHG emissions in the country. Thus, small and medium-sized farms and ranches could reduce their emissions with adequate waste management to reach the emission reduction targets, consequently increasing the participation percentage of renewable sources from biomass in the Brazilian energy matrix, as well as providing benefits from the co-products generated from the production of biogas (energy and biofertilizer).

On the other hand, biogas and biomethane production in the country could also be a strength by using raw materials from landfills and sewage treatment. This production is mainly linked to large-scale production, because the production of these raw materials is higher and continuous throughout the year.

Prior to the distribution stage of the surplus energy generated and the barriers that this stage covers, the acquisition of technology to purify biogas into biomethane or transform it into energy can be considered one of the main barriers due to its economic viability (dos Santos *et al.*, 2018).

Before addressing the distribution phase of the surplus energy generated and the barriers associated with this stage, it is essential to highlight that the technology acquisition for the biogas purification into biomethane or its conversion into energy can be considered one of the main barriers and is influenced by its economic viability (dos Santos *et al.*, 2018) and the purchasing power of the producer.

According to the biogas panorama report of CIBiogás (2021), Brazil has 811 biogas plants, of which 755 are currently in operation. In comparison, developing countries such as China, India, Bangladesh, and Nepal have achieved remarkable success in their biogas programs with the installation of millions of domestic digesters (Mukeshimana *et al.*, 2021). This is due to key factors, including favorable government policies, adequate financial support, technological advances, training, efficient quality control, raw materials availability, financial and technical support from donors, and effective coordination between institutions and partners (Mukeshimana *et al.*, 2021). In essence, well-designed policies make the biogas market prosper as a source of renewable energy. Along with maintaining these long-term policies, fixed objectives, and continuous review and evaluation for the commercialization of biogas and biomethane is necessary.

5. BARRIERS AND SUSTAINABILITY OF THE SYSTEM

The sustainability of the biogas production system currently depends on different factors and the main economic activities in each country. Although countries may face some common barriers. The adoption of biogas systems can also be influenced by specific geographic location, climate, culture, and economic situation (Mukeshimana *et al.*, 2021).

Legislation has a direct influence on the sustainability of the biogas and biomethane production process. The **sustainability economic aspect** (Mukeshimana *et al.*, 2021) includes the costs associated with acquiring the equipment and materials necessary to install biodigesters, and these costs are reflected in the construction, operation, and maintenance of the technology. Another economic aspect is the lack of clear financial mechanisms from the government (tax exemptions, discounts, and subsidies), including a framework that regulates prices and maintains price stability, preventing price fluctuation from directly affecting the economy of the farmer or energy producer (Lonnqvist *et al.*, 2017). According to Thrän *et al.* (2020) fiscal incentives, subsidies, and financing to shape renewable energy generation are essential for its development.

Due to the lack of price stability and standardization (Nevzorova and Kutcherov, 2019), products from the biogas production chain entails high economic risks, with long periods and low rates of return on the amount invested. This is a delicate aspect, as not all farmers, ranchers, or rural producers have the same purchasing power to buy and maintain the plants in operation.

In general terms, the uncertainties and instability that the legislation generates (Martin, 2015; Ammaenberg *et al.*, 2018) are among the reasons why project financiers related to renewable energies are not interested in this type of renewable source

Finally, a barrier directly linked to the economic and social aspects is the lack of knowledge about the economic benefits of acquiring the technology and possible sale of products obtained from anaerobic digestion (Yasar *et al.*, 2017; Scheftelowitz *et al.*, 2018). Energy from biogas can supply the energy demand of small properties, reducing the energy consumption from the national grid and fossil fuels (Oehmichen *et al.*, 2017) and consequently increasing family income, generating savings in the annual budget.

Beside this, considering **sustainability social aspect**, there is lack of awareness, social acceptance, knowledge of biogas production technology and the benefits that its installation can provide directly affect the performance of installed plants (Mukeshimana *et al.*, 2021). In turn, this lack of knowledge affects national scopes related to increasing the percentage share of renewable energy sources in the energy matrix, consequently reducing greenhouse gas emissions from the proper management of waste generated by human activities, and thereby boosting the national economy through small-scale production units.

The lack of acceptance, awareness, and knowledge about biogas production technology directly affects public and political support, directly influencing decision-making on implementation of the technology at different levels. To correct this barrier, the government must provide the necessary support to the community so that this lack of knowledge and acceptance ceases to be a hindrance.

For the **sustainability environmental aspect**, the generation of GHG emissions from inadequate management of agriculture should be considered where no anaerobic digestion technology has been implemented**.** Thus, implementing technologies for the agricultural waste use in the production of agro-energy would also help the country meet its emission reduction targets (Hollas *et al.*, 2022). Finally, the non-implementation of the system in rural areas with a large production of organic waste from potentially polluting activities keeps the producer from having a more sustainable production chain. Biogas production is an opportunity to produce cleaner energy, earn environmental seals, sell carbon credits, and consequently reduce GHG emissions (Oehmichen *et al.*, 2017). The latter is a critical characteristic that directly affects the economic and social aspects of the Brazilian industrial and agricultural production chains.

In general terms, the three pillars of sustainability are correlated in different aspects, which can easily and directly affect the sustainability of the biogas production system (Thrän *et al.*, 2020).

CONCLUSIONS

The biogas sector in the country is covered in the legal contexts of renewable energy (electricity and natural gas sector), sanitation (management of urban solid waste and effluents), the environment, and climate change. The analysis of the legal framework revealed the enormous interest of the country in this renewable energy source. Thus, biogas technology has been driven and disseminated by government initiatives in collaboration with various organizations, but it is still in the process of development and transition. Therefore, crucial factors must be better structured and analyzed to obtain better results in the adoption of biogas in the Brazilian energy matrix, such as clear and detailed government support policies, technical training of the community about the technology, its benefits, and its regulations, and technological standardization for small- and large-scale operations.

Legislation strongly influences the sustainability of the biogas and biomethane production system, as the gaps within each regulatory framework can directly affect any of the three pillars of sustainability.

In the economic aspect, the costs of acquiring biodigester equipment impact its construction, operation, and maintenance. The absence of clear government financial mechanisms, like tax exemptions and subsidies, leads to price instability, affecting farmers. Fiscal incentives and financing are crucial for renewable energy development. Additionally, the lack of price stability and standardization in biogas products poses high risks and low returns on investment.

In the social aspect, the lack of knowledge about the economic benefits of biogas technology and its potential sale impacts social acceptance and the performance of installed plants. In turn, the lack of awareness and social acceptance of the technology affects public and political support, hindering decision-making on its implementation.

In the environmental aspect, the use of agro-pastoral waste in agroenergy reduces greenhouse gas emissions. However, not implementing the system in rural areas with significant organic waste misses the chance for a more sustainable production chain. Biogas production offers opportunities for cleaner energy, environmental certifications, and reduction of greenhouse gas emissions.

The legal framework related to biogas favors large-scale renewable energy producers, facilitating the equipment acquisition and inputs (national and international) for their generation. However, this benefit is less accessible to small-scale agricultural producers located in decentralized areas of the country, which represent the majority of production. This discrepancy slows the development of the sector and prioritizes the production of other renewable energy sources, such as solar and hydroelectric.

Despite initiatives in Brazil to improve and strengthen the biogas sector, the state and federal governments need to enhance mechanisms to improve the knowledge of the workforce, farmers, or the interested population, as well as directing fixed and detailed economic funding for this purpose. Therefore, the transition of the sector will take longer than expected, even though Brazil is one of the richest countries in raw materials for biogas production.

The legislative framework for biogas and biomethane should undergo continuous evaluation and renewal to keep pace with evolving technologies and practices. Specific parameters need to be established for biogas and biomethane production in rural areas, given the often-precarious conditions, as these sources of energy directly impact the country's economy.

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