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FERNANDA SANTANA PEITER

Comparative analysis of concentration technologies: designing biorefineries for vinasse resource recovery

Versão corrigida

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Orientador: Prof. Tit. Eduardo Cleto Pires

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RESUMO

Peiter, Fernanda Santana. **Análise comparativa de tecnologias de concentração: design de biorrefinarias recuperação de recursos da vinhaça**. 2018. 167 p. Tese (Doutorado em Engenharia Hidráulica e Saneamento) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2018.

O desenvolvimento de biorrefinarias voltadas à recuperação de recursos é uma tendência crescente que visa promover sistemas alternativos para obtenção de energia e materiais de forma mais sustentável. Dentro deste conceito está o aproveitamento da vinhaça das indústrias de cana-de-açúcar de modo a recuperar água, nutrientes e energia como produtos de interesse. Para isso, é necessário avaliar as possíveis configurações tecnológicas voltadas a este objetivo. No presente trabalho, foram estudados cinco designs de biorrefinaria de vinhaça incorporando uma rota de produção de metano, formada pelo processo de digestão anaeróbia, e uma forma de concentração do efluente. Os métodos para obtenção de água foram evaporação, osmose reversa e osmose direta. Neste último, foram analisadas diferentes formas de regeneração da solução de separação: evaporação, osmose reversa e destilação por membranas. A comparação das alternativas de biorrefinaria foi feita pelo método da análise de exergia, que atua na avaliação da eficiência de conversão dos recursos em sistemas. Esta ferramenta possui como medida base o trabalho útil que pode ser obtido a partir das correntes envolvidas no processo. Desta forma, observou-se que tecnologias que empregam calor como energia de entrada tendem a ser menos eficientes do que as que empregam eletricidade. Neste caso, as alternativas com processo de osmose reversa apresentaram maiores eficiências exergéticas, por exemplo, ao se recuperar 70% de água, sua eficiência seria de 64%. Portanto, sugere-se que a digestão anaeróbia da vinhaça seguida da concentração por osmose reversa seria a configuração mais interessante para concepção de uma biorrefinaria de vinhaça.

Palavras-chave: Biorrefinaria. Vinhaça. Digestão anaeróbia. Concentração. Análise de exergia.

ABSTRACT

Peiter, Fernanda Santana. **Comparative analysis of concentration technologies: designing biorefineries for vinasse resource recovery**. 2018. 167 p. Tese (Doutorado) – Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2018.

Vinasse, a wastewater rich in organic matter, nutrient and water, is commonly used for fertigation of sugarcane plantation. However, this practice is questionable in the environmental sphere because of problems, such as contamination of groundwater and greenhouse gases emission. Researchers have sought for alternatives that use vinasse in a more sustainable way, e.g., biorefineries that recover resources. In general, the pathways considered are the concentration technologies to reclaim water and nutrient, and the anaerobic digestion (AD) to produce biogas. This thesis reports on a study of five designs of vinasse biorefineries that incorporate anaerobic bioreactors followed by a concentration technology (evaporation (EV), reverse osmosis (RO) or forward osmosis (FO)). Different forms of regeneration of the draw solution (DS) namely evaporation, reverse osmosis and membrane distillation (MD) were also analyzed. The alternatives were compared through an exergy analysis, a method that evaluates efficiency in the conversion of resources by systems. The results showed Alternative 2 (anaerobic digestion + reverse osmosis) was the most efficient (64%), since the treatment of 491.76 m^3 vinasse h^{-1} (exergy content of 60513.8 kW) to recover 80% of water reduced 76% of external water requirement and generated 12% more electricity (2601 kW exergy) for the industry.

Keywords: Vinasse biorefinery. Anaerobic digestion. Concentration methods. Exergy Analysis.

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LIST OF SYMBOLS

A: Water permeability constant

B: solute permeability

COD: COD content of the stream

C_{S0}: concentration of the influent COD

$\mathrm{COD}_{\mathrm{CH}_4}$: load of COD removed from the reactor and converted into methane

c_{p}: concentration in permeate

C_{P}: concentration of draw solution

C_0: concentration in the feed

C_{pr}: Retentate specific heat

C_{pF}: Feed specific heat

ΔP: pressure gradient

$\Delta\Pi$: osmotic pressure gradient

$\sum \Delta \mathrm{X}_{out}$: Exergy of the products

$\sum \Delta \mathrm{X}_{in}$:Exergy of the inputs

φ: recovery rate of MD

h: enthalpy of the substance

h_0: reference enthalpy

Jw: water flux

Js: reverse solute flux

K: Solute resistivity for diffusion within the support layer

k: mass transfer coefficient

$\mathrm{K}_{\mathrm{COD}}$: COD corresponding to one mole of CH4

K(t): correction factor for the operational temperature of the reactor

M_{sol}: molar mass

Nr: nutrient requirement

N_{bac}:concentration of nutrient in the bacterial cell

n: number of moles of solute

η: Exergetic efficiency

P: atmospheric pressure

$\mathrm{P_{ctot}}$: Total conductive heat flux

$\mathrm{P_v}$: Latent heat flux for dilute solutions

Q: heat

$\mathrm{Q_{CH_4}}$: flowrate of methane production

$\mathrm{Q_F}$: feed flowrate

$\mathrm{Q_p}$: permeate flow rate

ρ_r: retentate density

R: universal constant of the gases

s: entropy of the substance

s_0: reference entropy

SEC: specific energy consumption

T: temperature of the substance

T_0: reference temperature

TSS/VSS: Total solids/volatile solids ratio for the bacterial cell

$\mathrm{T_{Fa}}$: feed temperature

T_{co}: the cold fluid temperature at the outlet

W: work

x_i^{ch}: chemical standard exergy of a pure component

X_{mass}: Exergy of a matter flow

X^{ph}: Physical exergy

X^{ch}: Chemical exergy

$X_{org,mat}$: Exergy of organic matter

X_{heat}: Exergy of the heat stream

X_{work}: Exergy of the work

y_i: molar fraction

Y: yield coefficient

CONTENTS

1 INTRODUCTION

Since the 1980s, electricity generated from bagasse in cogeneration systems is one of the by-products of sugarcane industries, which nowadays includes the so-called sugar-energy sector. Reusing this by-product creates a sustainable image for these companies as they are devising an alternative source of energy from a material previously considered waste (UNICA, 2018a).

Nevertheless, using vinasse could improve the energy, economic and environmental potential of sugarcane biorefineries. Vinasse is wastewater from alcohol production comprising valuable substances such as water, nutrients and organic matter. However, its use is still limited to fertigation in plantations. Thus, many researchers have been working on developing technologies aimed at recovering resources from this by-product.

The most common methods of using the vinasse include (1) anaerobic digestion as an energy pathway and to produce a supernatant rich in nutrients; (2) concentration processes, such as evaporators and filter membranes, to recycle water and produce a material with a high content of nutrients and organic matter. However, for those technologies to be indeed incorporated into the technical scope, it is important to evaluate which configuration is more interesting for the vinasse biorefinery concept.

Although the literature has discussed these approaches at length, there is a lack of studies that analyse the different possible technological arrangements for vinasse treatment. This analysis is important to help industry decision makers in choosing the configuration to be implemented. Therefore, an assessment of these technologies can provide a comprehensive indication of opportunities and drawbacks in terms of implementing a system designed to reclaim resources from vinasse.

One of the ways to evaluate the efficiency of schemes such as biorefineries and wastewater treatment plants is by using exergy analysis. This is a tool for measuring the sustainability of a system, encompassing not only the quantity, but also the quality of the input and output currents of the processes. Using exergy analysis is important as there is a growing search for the development of more sustainable systems. Considering this, it is possible to achieve not only a reduction in the natural resource consumption, but also to avoid wastes by processes.

In general, this statement shows the need for minimizing environmental impacts, where a better use of resources means less natural resource extraction and less discharge of polluting materials. Therefore, based on that premise this study was developed aiming to compare different technological configurations for a vinasse biorefinery.

1.1 OBJECTIVES

The main objective of this thesis was to evaluate different alternatives for designing a vinasse biorefinery focusing on resource recovery. Anaerobic digestion, evaporation, reverse osmosis, forward osmosis and membrane distillation were the technologies considered. These technologies were arranged in different configurations in order to produce energy, water for reuse and a liquid enriched in nutrients for use in fertigation.

Specific objectives included:

- devising flowcharts to recover energy, water and nutrients, considering different concentration methods;
- performing mass and energy balances for each diagram considered;
- comparing the alternatives regarding exergy efficiency.

1.2 RATIONALE

Increasing exploitation of energy and materials has motivated the search for alternative sources to avoid existing natural resource scarcity. There are social and political incentives for companies to adapt their scope to fit this premise, reducing environmental impacts arising from their processes. In this sense, the concept of biorefinery to recover resources from wastewaters has been gaining increasing attention. If applied to vinasse treatment, a biorefinery can add more value to products from the sugar and alcohol industry (GUPTA; VERMA, 2015; OSAKI; SELEGHIM, 2017).

Few publications have accessed full-scale plants or configurations aimed at full recovery of water, energy and nutrients from vinasse. In general, research on vinasse biorefineries addresses specific improvements of technologies, such as the anaerobic digestion process to produce biogas or membrane separation processes to recover water. However, studies that compare various techniques aiming to recover multiple resources are still scarce (BARRERA et al., 2016; CARTHERY et al., 2012; FUESS et al., 2017; OJHA et al., 2015).

This study considered the anaerobic digestion process as an energy pathway, given the growing evolution of research in the use of this technology. Investigations have demonstrated success in operating anaerobic reactors as can be seen in studies carried out by Inaê Alves (MSc), Valéria Del Nery (PhD) and Professor Eduardo Cleto Pires. The study group operated a pilot UASB (Upflow Anaerobic Sludge Blanket) reactor producing suitable amounts of biogas (5-8 $L_{methane}$ $L^{-1}_{reactor}$ day^{-1}) from vinasse degradation. A project entitled "Biogas production by sugarcane vinasse anaerobic degradation" is underway in the Biological Process Laboratory, at the São Carlos School of Engineering (University of São Paulo). The success of this research shows that it is valid to consider anaerobic bioreactors as suitable technologies for vinasse processing and biogas production enriched in methane (ALVES, 2015).

Therefore, the novelty of the present work is to analyse different effluent concentration technologies of anaerobic bioreactors for designing vinasse biorefineries. The different arrangements studied included using evaporators, traditionally adopted in the sugarcane industry, and membrane processes as the most recent technologies. Thus, the advantages of the association between anaerobic reactors and concentration technologies for resource recovery are emphasized. Moreover, the opportunities in this type of configuration must be studied, as they may entail environmental and economic gains for the sugar and alcohol sector.

1.3 SCOPE OF THE THESIS

This thesis is organized as follows:

- Chapter 2 presents a literature review on vinasse, technologies for handling this effluent and the exergy analysis method in systems evaluation;
- Chapter 3 presents the methodology used;

- Chapter 4 shows the results and discussion during the development of this research;
- Chapter 5 draws the conclusions and makes suggestions for future studies.

2 LITERATURE REVIEW

The Environmental Company of the State of São Paulo (Companhia Ambiental do Estado de São Paulo, *in Portuguese*) was the first Brazilian government sector to abolish the launching of vinasse in water bodies, established in 1976. In 1978, this prohibition was extended to the Federal level. Therefore, on account of restrictions imposed by Brazilian environmental standards, ever since then industries have been using this effluent as a fertilizer in sugarcane plantations (BRASIL, 1980, 2005; SÃO PAULO (ESTADO), 1976).

Nonetheless, the characteristics that make vinasse a rich material to supply the needs of plants are the same that make it an effluent with a high pollutant load. There are still doubts about the environmental safety of fertigation practice in soil, groundwater and atmosphere. From an economic perspective, there are problems with the high cost of large volumes of this liquid even in sugarcane growing areas (RABELO; COSTA; ROSSEL, 2015).

Thus, concentration and anaerobic digestion are other ways of handling vinasse to mitigate the above issues. Concentration aims at a decrease in vinasse volume by using technologies such as evaporation and membrane filtration, while anaerobic digestion reduces the organic matter load and produces methane gas that can be used as fuel. Concerning implantation in industries, the advantages and disadvantages of each of these processes should be considered.

Therefore, the systems design to use vinasse should entail studying technologies that promote the treatment of this wastewater more efficiently. Considering that the objective is to promote resource recovery, this efficiency is related to obtaining valuable products such as water, energy and fertilizers, requiring less input resources. That is, producing more resources with less resource depletion.

Depending on the chosen alternatives, system balances can entail higher or lower losses, which can be accounted for using an exergy analysis. This tool considers the currents involved in the process using the common measure of exergy, as will be explained later. (OLIVEIRA JUNIOR, 2013).

Thus, this chapter deals with the general characterization of vinasse and offers some technological options to process this effluent, clarifying the advantages and disadvantages. Moreover, the literature review discusses the concept of exergy analysis and in which ways this method is used as an environmental indicator of the biorefinery proposed in the current research.

2.1 VINASSE AND FERTIGATION

Alcohol, as well as sugar and electricity from cogeneration systems, is one of the main products of the sugarcane industry in Brazil. Ethanol can be manufactured by using juice, molasses or a mixture of both as input. Fermentation of these components generates wine, which is processed into distillation columns. The latter process results in the generation of ethanol as the main product and vinasse as wastewater (ENSINAS et al., 2007; VASCONCELOS, 2015).

Vinasse is a dark brown liquid generated in an approximate proportion of 10 to 15 litres for each litre of ethanol produced. This volume varies according to the market demand in the harvest period, where the industrial route can be targeted at sugar or alcohol production. For example, in the 2015/2016 harvest, São Paulo state manufactured $21,567 \cdot 10^6$ tons of sugar and $14,577 \cdot 10^6$ m^3 of ethanol, according to the Brazilian Sugarcane Industry Association (UNICA, *in Portuguese*). In the next harvest in 2016/2017, the sugar demand was higher, producing $24,248 \cdot 10^6$ tons of sugar and less ethanol, $13,197 \cdot 10^6$ m^3, consequently producing smaller amounts of vinasse (CORTEZ; FREIRE; ROSILLO-CALLE, 1998; UNICA, 2018a; VAN HAANDEL, 2005).

As well as volume, the composition of vinasse also varies throughout the harvests. Its content depends on the type of sugarcane, environmental factors, feedstock used and the sort of ethanol produced (anhydrous or hydrated). Table 1 and Appendix A (page 131) present some characteristics of sugarcane vinasse.

Vinasse mainly consists of water (93%), organic solids and minerals (7%). Due to the significant levels of nutrients, mainly potassium, wastewater is used as soil amendment and fertilizer in the sugarcane plantation. This liquid can be transported to the plantation areas using trucks, canals or pipes. It can be applied directly to the soil or can be spread by spraying using sprayers or sprinklers (CARRILHO; LABUTO; KAMOGAWA, 2016; RABELO; COSTA; ROSSEL, 2015).

Table 1 – Characteristics of vinasse from sugarcane.

Parameter	**Molasses**	**Juice**	**Molasses and juice mix**
pH	4.2 – 5.0	3.7 – 4.6	4.4 – 4.6
Temperature (°C)	80 – 100	80 – 100	80 – 100
BOD (mg O_2 L^{-1})	25000	6000 – 16500	19800
COD (mg O_2 L^{-1})	65000	15000 – 33000	45000
Total solids (mg L^{-1})	81500	23700	52700
Volatile solids (mg L^{-1})	60000	20000	40000
Nitrogen (mg N L^{-1})	450-1610	150-700	480-710
Phosphorus (mg P_2O_5 L^{-1})	100-290	10-210	9-200
Potassium (mg K_2O L^{-1})	3740-7830	1200-2100	3340-4600

Source: Carrilho et al. (2016).

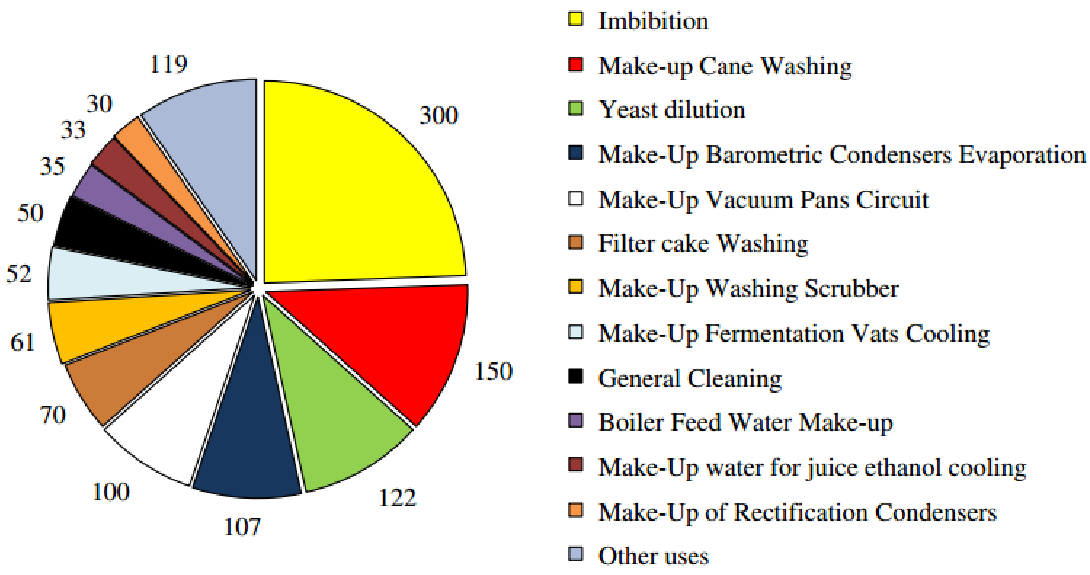
This practice, namely fertigation, not only supplies nutrients to the plant, but also improves soil aggregation and increases pH, as demonstrated by Barros et al. (2010). The authors evaluated the effect of using vinasse in sugarcane farms over ten years. They observed that adding vinasse to the soil had altered its chemical properties, with an increase in organic matter content and cation-exchange capacity (CEC). Generally, the higher the soil CEC, the better its fertility and the lower the nutrient leaching (HUNSIGI, 1993; RONQUIM, 2010).

Fertigation is initially adopted as a more viable alternative for the sugar and alcohol industry as the technique is simple to carry out, savings can be made from fertilizers and it is easy to dispose of vinasse. However, there are environmental concerns about this practice. Continuous application of high volumes of vinasse culminates in lixiviation of mineral elements and soil and groundwater contamination. Moreover, storage, transportation and application practices contribute to greenhouse gas (GHG) emissions, such as carbon dioxide, nitrous oxide and methane (DE OLIVEIRA et al., 2013; FUESS; RODRIGUES; GARCIA, 2017; MOORE; NOGUEIRA; KULAY, 2017; MORAN-SALAZAR et al., 2016; OLIVEIRA et al., 2017).

In general, the amount of vinasse applied in soil is higher than the recommended dose. Furthermore, because of the significant amount of produced effluent, it incurs high transport costs as most of it is transported in tanker trucks. Considering this, some industries concentrate the vinasse, decreasing its volume and recovering water that could be used for different applications in the industry (RABELO; COSTA; ROSSEL, 2015).

Currently, the sugarcane sector accounts for approximately 7% of water withdrawals in São Paulo state. According to the National Confederation of Industry, water withdrawal in the sugarcane industry, mainly in plants in south-central Brazil, is approximately 1-2 m³/tons of sugarcane. Although sectors achieve 95% of reuse, the water balance is still negative and requires a significant amount of imports from natural sources. Taking this into account, water recovery would be advantageous as many processes within the industry entails using this resource, as shown in Figure 1 (BRASIL, 2013; FILHO et al., 2018; PINA et al., 2017).

Figure 1 – Water demanded by the processes in kg/t sugarcane.



Source: Chavez-Rodriguez et al. (2013).

Therefore, there are two approaches generally considered for vinasse concentration and water production for recycling: evaporation, as a traditional method of sugarcane industries; and membrane filtration, representing a novel technology within this sector. Considering these points, the next sections discuss these methods.

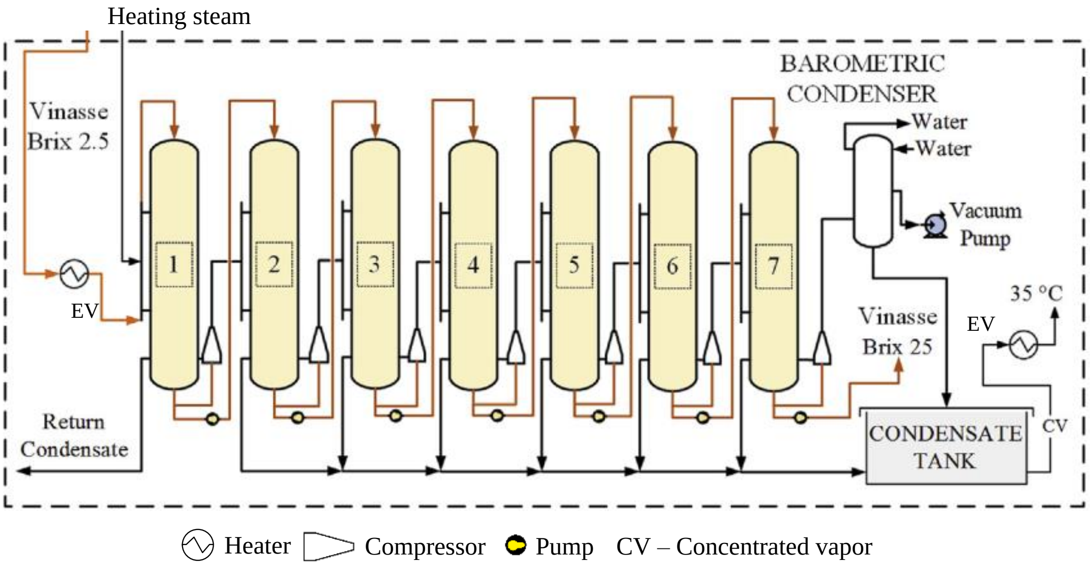
2.2 EVAPORATORS

Evaporation is a technology commonly used in sugarcane mills to concentrate juice to produce sugar and can be extended to vinasse as it is well-established in the sector (MADAENI; ZERESHKI, 2010; PINA et al., 2017).

On the other hand, the obstacle of evaporation technology is the high requirement of steam, as it is one of the operation units that consume more energy in sugar and alcohol plants. These systems bring significant additional thermal dissipation to distilleries. To reduce this depletion, several strategies are used, such as implementing multiple-effect evaporators (CARVALHO; SILVA, 2011; MADAENI; ZERESHKI, 2010; NETO, 2016).

In a multiple-effect evaporator (Figure 2), the evaporators are assembled in sequence, where the evaporated vapor from the first effect is the energy source for the second effect and so on. The evaporated water from the last effect passes through a condenser, finishing the process (CARVALHO; SILVA, 2011; CORTES-RODRÍGUEZ et al., 2018).

Figure 2 – Example of a multi-effect evaporator to concentrate vinasse.



Source: adapted from Cortes-Rodríguez et al. (2018).

The first effect is where raw steam is fed and in which the pressure in the vapor space is the highest (about 1.69 bars). The last effect is where the vapor-space pressure is the minimum. Appendix B (page 133) presents the balances involved in a multi-effect evaporator unit (FOUST et al., 1960; MCCABE; SMITH; HARRIOT, 1985).

The amount of energy saved is defined by the ratio between the total evaporated water and the steam provided for the first effect. The multiple effect configurations can also save refrigerated water in the condenser because this equipment operates only for condensing the vapor generated in the last effect. In contrast, a significant number of effects cause lower temperature gradients, which means more areas for heat exchanges, increasing the capital costs. However, the choice in the number of effects is defined by an economic balance between the amount of steam saved, the chilled water and the investment costs (CARVALHO; SILVA, 2011; CORTES-RODRÍGUEZ et al., 2018).

In a study evaluating a multi-effect evaporator to concentrate vinasse, Carvalho and Silva (2011) showed some characteristics of a traditional configuration for the system. Table 2 presents average values of brix, temperature and heat transfer coefficient and area requirement for a plant with five effects. The authors observed that it is possible to recover 78% of the water contained in the vinasse, reaching 21% solids in the concentrated liquid.

Table 2 – Values for typical vinasse evaporation plant.

	1st effect	**2nd effect**	**3rd effect**	**4th effect**	**5th effect**	**Concentrated**
Temperature (°C)	115	94	91	84	78	62
Brix (°Bx)	4.5	5.4	6.55	8.4	11.92	21.44
U (kW m^{-2} K^{-1})	2.50 - 3.27	2.12 - 3.03	1.92 - 2.95	1.50 - 2.85	0.70 - 2.57	
A (m²)	165 - 126	1460 - 1422	707 - 460	1130 - 595	956 - 261	

U: heat transfer coefficient; A: area of each effect of evaporation.

Source: adapted from Carvalho and Silva (2011).

There is a relatively small body of literature that is concerned with evaporators to concentrate vinasse. For example, Larsson and Tenberg (2014) state that it is possible to evaporate vinasse with initial 10.2°Bx up to a dry solid content of 72%, which is considered high. The authors evaluated an evaporator with 7 effects, which could remove 97% of the water in raw wastewater. Based on the experiments conducted, the authors suggested that it is essential to map the trends in fouling formation in the evaporators.

Challa (2015) reported that fouling formation rates in the evaporator increased as the vinasse went through the first stages (effects). This also emphasizes that vinasse evaporation has problems concerning fast incrustation and spontaneous crystallization.

As can be observed, the requirement of large areas, vast energy consumed and fouling are the primary technical problems related to evaporator systems. Instead of these aspects, some researchers have proposed using membrane filtration as an alternative because they require smaller areas and less energy to promote water separation. Thus, an overview of membrane technologies is presented below.

2.3 MEMBRANE PROCESSES

Resource recovery using membranes is not novel as this type of technology is widely used for separating solutions, obtaining water as a product. More recently, researchers have also explored nutrient recovery using this method. The opportunities are widespread, especially when these are coupled to other types of processes, such as crystallization, distillation, biological processes, among others (ANSARI et al., 2015, 2016, 2017; HOU et al., 2017; SUN; WANG; LI, 2013; XIE et al., 2014, 2016; YANG et al., 2010).

Regarding distillery effluents, a wide range of publications can be found on the topic, as shown in Appendix C (page 137). In general, researchers conclude that the application of membranes to treat vinasse offers advantages such as (PRODANOVIĆ; VASIĆ, 2013):

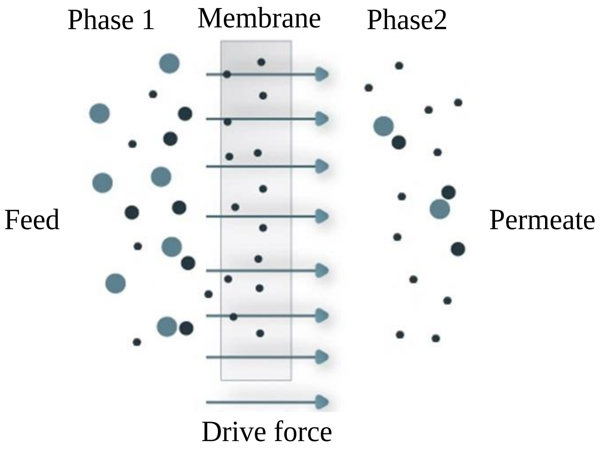
- Recycling water;
- Liquid production enriched in nutrients suitable for use as fertilizer, recycling for fermentation processes or microorganism cultivation. Production of concentrate in organic matter feasible for biogas generation;
- Reducing the volume of effluent to be discharged.
- Purifying wastewater.

Conversely, the major drawback of membrane technologies is the incrustation that blocks the water flux. A brief explanation of the main aspects regarding membrane processes is presented in the next section.

2.3.1 Overview of membrane processes

Membranes are filtering barriers between two similar phases that allow the passage of certain elements contained in a solution, while the others are retained (Figure 3). In principle, the degree of retention depends on the relationship amongst the dimension of the component to be filtered and the membrane pore size. The coarser ones prevents the passage of particulate matter while the more selective ones retain even isolated ions (JUDD; JUDD, 2011; MULDER, 1996).

Figure 3 – Schematic representation of membrane separation.



Font: adapted from Mulder (1996).

On the whole, membranes are categorized according to their morphology. If the membranes have a structure with interconnected and randomly distributed pores, they are called porous. However, if they are formed by a film consisting of interstices of insignificant size, they are designated as dense. There is also the possibility of the coexistence of two types of morphology, with a thick and a porous part. In this case, the classification needs to be extended and should be isotropic (symmetrical) or anisotropic (asymmetric) (BAKER, 2012; HABERT; BORGES; NOBREGA, 2006).

Various types of materials are available for manufacturing membranes, including polymeric, ceramic and metal, as well as a combination of these, such as ceramically coated metal membranes. The material used depends largely on the performance required, dictated by the feeding properties and the separation objectives. For example, if the feed contains significantly high amounts of aggressive solvents and should be processed at temperatures higher than 140 °C, a polymer-based membrane would not be suitable. However, most layers are made from synthetic polymers. Interest in ceramic materials has also increased, as they tend to be very robust and withstand harsh operating and cleaning conditions (FOLEY, 2013; ZHANG et al., 2012).

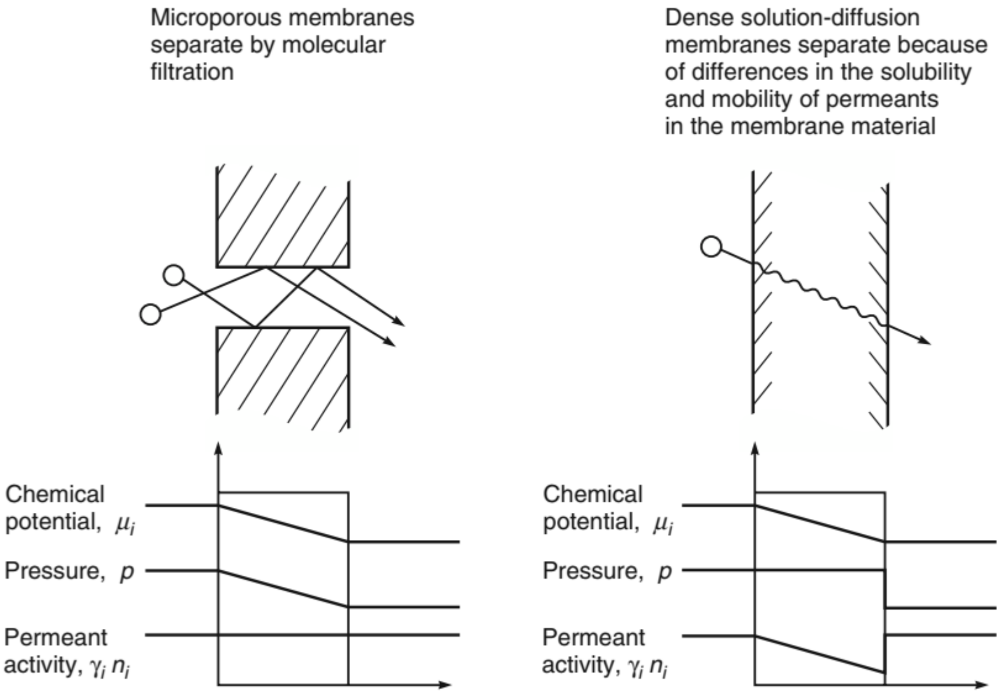
In addition to the physical properties, membrane processes are usually characterized by the driving force used during species separation. Commercial membrane separation methods use concentration, pressure and electric potential gradient as driving forces (HABERT; BORGES; NOBREGA, 2006).

Just as the temperature difference causes heat transfer, the potential chemical gradient is the motivating factor of mass transfer in membranes. This premise is grounded in the science in which driving forces that govern their transportation motivates the natural flow of entities such as energy, mass, momentum and electricity. Substances are spontaneously transported from the highest to lowest chemical potential until they reach the equilibrium. That is, in a membrane system, the passage of components occurs as long as there is a difference of chemical potential between the feed and permeate sides (BASMADJIAN, 2007; ÇENGEL, 2007; TAYLOR; KRISHNA, 1993; THEODORE, 2010).

Figure 4 shows a comparison between the mass transport that happens on porous and dense membranes. In the capillary medium, pressure-driven convective flows are assumed. In this case, the permeate concentration within the membrane is uniform, and the chemical potential gradient is dependent only on the pressure gradient. For dense membranes, the pressure inside the membrane is considered to be uniform and the chemical potential gradient is represented only by the concentration gradient. Transport through the membrane, permeate fluxes and membrane lifetime can be primarily affected by the concentration polarization and fouling phenomena (GOOSEN et al., 2004).

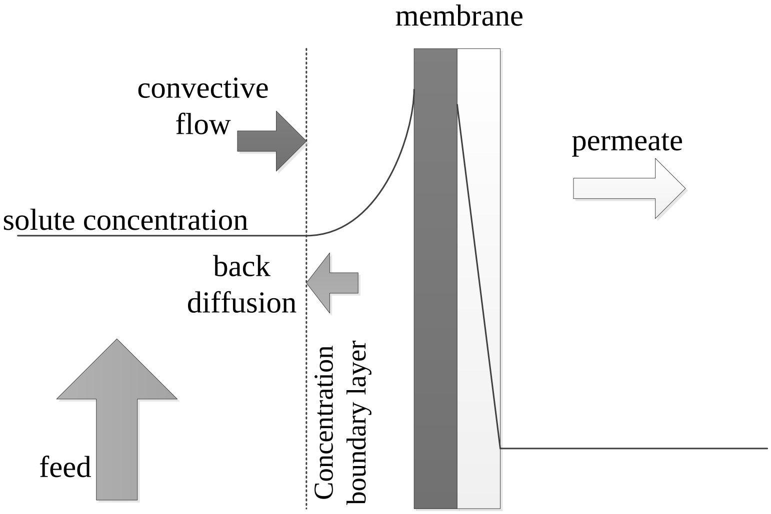
Concentration polarization is mostly the cause of the initial rapid decline of flux in the first few minutes of processing. Since the components present in the feed permeate at different rates, concentration gradients can be formed on both sides of the membranes. It happens because the convective flow of the solute to the membrane surface is more prominent than diffusion backflow to the bulk solution. As a consequence, an accumulation of the rejected component takes place at the membrane surface, as shown in Figure 5 (BAKER, 2012; BHATTACHARYA; HWANG, 1997; D’SOUZA; MAWSON, 2005; MATTHIASSON; SIVIK, 1980).

Figure 4 – Mass transport in porous and dense membranes.



Source: Baker (2012).

Figure 5 – Concentration polarization phenomenon.



Source: adapted from Stephenson et al. (2000).

Fouling formation in membranes is related to the deposition of particles, colloids, macromolecules, salts and biomolecules on the surface of the membrane or the wall of the pores that constitutes it. Biofouling is one of the major problems, which destroys the structural integrity of the membrane, and this leads to subsequent irreversible membrane damage, shortened membrane life, increased operational and maintenance costs, as well as reduced efficiency (AKHONDI et al., 2017; HILAL et al., 2005; KUMAR; ISMAIL, 2015).

Chemical cleaning is an integral part of a membrane process operation that must be regularly carried out to remove fouling and ensure continued satisfactory operation and product safety (AL-AMOUDI; LOVITT, 2007; D’SOUZA; MAWSON, 2005).

Indeed, the membrane performance depends on several factors, briefly shown in Table 3. Information on the manufacturing principle, operation, transport mechanisms and types of membrane applications can be easily found in the literature. Therefore, the present section only covers the main aspects relevant to understanding this thesis (BAKER, 2012; HANKINS; SINGH, 2016; JUDD; JUDD, 2011; MULDER, 1996; SEADER; HENLEY, 2006; STEPHENSON et al., 2000).

In summary, there is a wide range of configurations and types of developed industrial membrane separation processes. The well-established and readily available ones on the market are microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and electrodialysis (ED). However, forward osmosis (FO) and membrane distillation (MD) have been highlighted as promising and innovative processes in the area of membranes (MD) (BAKER, 2012; HANKINS; SINGH, 2016).

All the above factors, from the module type to the transport mechanism, are essential in developing the membrane system. Each membrane process has individual characteristics that must be considered when choosing the technology. Among the many alternatives of membrane processes, the present work deals only with reverse osmosis and forward osmosis for vinasse biorefinery design. In addition, the membrane distillation is also approached as a regeneration method of the draw solution, a stage complementary to forward osmosis. A brief description of these methods is presented in the following topics.

Table 3 – General characteristics of membrane processes.

Characteristic		Importance
Membrane process	Microfiltration; Ultrafiltration; Nanofiltration; Reverse Osmosis; Electrodialysis; Membrane degasification; Forward Osmosis; Membrane Distillation.	There are many types of membrane processes, which differ in terms of nominal pore size and the driving-force applied. The choice of the process should initially consider the characteristics of the feed solution and the product desired.
Driving force	Pressure gradient; Electrical potential gradient; Concentration gradient; Vacuum; Partial pressure gradient.	Force that motivates the transmembrane flux.
Mass transport model	Pore-flow model; Solution-diffusion model.	These models describe the permeation mechanism of in membranes.
Modules	Plate and frame; Spiral-wound; Tubular; Hollow-fiber.	Structure that covers the membrane. It must meet the mechanical, hydrodynamic and economic requirements of the system.
Separation operating modes	Cross-flow; Dead-end.	Determines if the feed solution flows tangentially or perpendicular to the membrane surface.
Membrane system operation control	Constant flux; Constant pressure.	Determines if membrane systems operate in constant flux (implying variable feed pressure) or constant pressure (implying variable water flux) mode.
	Critical flux.	If the flux is kept below the critical flux, no particles will deposit on the membrane and the flux will remain constant at the clean-membrane value.

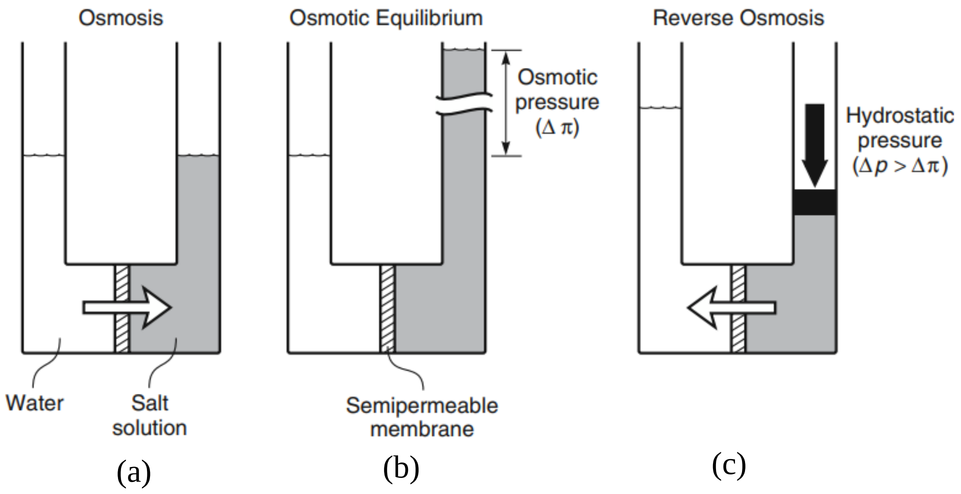
Source: based on information from Hankins and Singh (2016), Foley (2013) and Baker (2012).

2.3.2 Forward Osmosis and Reverse Osmosis

The equilibrium state of two liquid mixtures (or solutions) separated by a membrane, is considered, particularly a solute-solvent system in which only the solvent is able to cross the membrane. Osmosis is a phenomenon in which the pure solvent has higher free energy than in the solution, and so it will tend to flow in the direction of the most upper concentration cell (CUSSLER, 2000; SANDLER, 1989).

The osmosis follows the second law of thermodynamics as the mass transport through the interphase occurs spontaneously until reaching the thermodynamic equilibrium (Figure 6 – a, b), i.e., chemical potential of the solvent is the same on each side of the membrane (ATKINS; PAULA, 2010; SANDLER, 1989).

Figure 6 – Relationship between osmosis, osmotic equilibrium and reverse osmosis.



Source: Baker (2012).

The chemical potential (*μ*) refers to Gibbs (*G*) partial molar energy and depends on the composition, pressure and temperature of the mixture. According to Atkins and Paula (2010, p. 137):

> When an infinitesimal amount dn of the substance is transferred from one location to the other, the Gibbs energy of the system changes by $-\mu_1 dn$, when material is removed from location 1, and it changes by $+\mu_2 dn$ when that material is added to location 2. The overall change is therefore

> $dG = (\mu_2 - \mu_1)dn$. If the chemical potential at location 1 is higher than that at location 2, the transfer is accompanied by a decrease in G and so has a spontaneous tendency to occur. Only if $\mu_1 = \mu_2$ there is no change in *G*, and only then is the system at equilibrium.

Therefore, this process characterizes the forward osmosis (FO) membrane system. In this system, solvent molecules move naturally from a low to a high concentration solution (referred to as the draw solution) to equilibrate their overall chemical potential (CATH; CHILDRESS; ELIMELECH, 2006; GE; LING; CHUNG, 2013).

The forward osmosis process is used in wastewater treatments and food processing. Among the numbers of studies and applications, FO seems to be a novel technology for separation and recovery of nutrients from different kinds of wastewater (ANSARI et al., 2016; GAO et al., 2018; HUANG; LEE; LAI, 2015; QASIM et al., 2015; QIU et al., 2016; SOLER-CABEZAS et al., 2018; XUE et al., 2016).

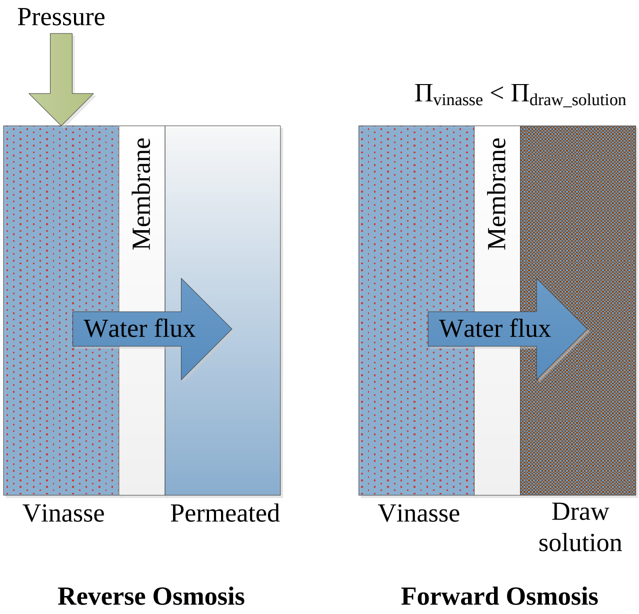
Meanwhile, reverse osmosis (RO) is a widely and well-established membrane process. As can be seen in Figure 6 (c), the objective, contrary to osmosis, is to force water to move through the membrane in the direction of the less concentrated cell. Mass transfer occurs when a pressure higher than osmotic pressure is applied. Reverse osmosis is the most selective among the pressure-driven membrane processes, which apply hydraulic pressure to accelerate interphase transport. The difference between reverse osmosis and forward osmosis can be observed in Figure 7 (KUCERA, 2010).

As pointed out by Hankins and Singh (2016, p. 55):

> Compared with FO, RO is a more familiar and established process. It uses hydraulic pressure to overcome the natural osmotic pressure gradient and squeezes the water back in the opposite direction through a membrane. The two main differences are that (1) RO uses hydraulic pressure to drive the process rather than using the natural osmotic pressure in FO, and (2) the product is the purified water in RO rather than the diluted draw solution in FO. These two differences lead to a higher energy consumption for the stand-alone RO process, but a more directly usable product. The stand-alone FO also has some niche applications, such as fertilizer dilution and fruit juice concentration, but in the main one is regarded as a pretreatment for the

subsequent process in which purified water is recovered from the diluted draw solution.

Figure 7 – Comparison between Forward Osmosis and Reverse Osmosis processes.



Source: Present author.

Reverse osmosis is applied mainly in desalinization and studies have been conducted on the use of this technology for water reclamation from wastewater plants. Nonetheless, energy consumption in the system’s operation is a major drawback when RO is used. For this reason, forward osmosis is considered instead as it achieves the same separation objectives with fewer energy requirements. This is possible because osmotic pressure itself is the driving force for mass transport (CATH; CHILDRESS; ELIMELECH, 2006; LI, 2011; ZHOU et al., 2011).

However, obtaining significant water flow and consequent liquid concentration in forward osmosis processes are highly dependent on the draw solution applied. Some criteria must be considered in selecting a suitable draw solution for FO applications. It should be able to significantly reduce the water chemical potential, and consequently generate a high osmotic pressure. Furthermore, it should show minimized internal concentration polarization (CAI; HU, 2016; ZHAO et al., 2012).

The draw solution regeneration step largely determines the energy consumption of the FO process. Therefore, for an ideal FO draw solution, it is also desired to have active regeneration with low energy requirements. However, if the draw solution separation and recovery are not necessary after the FO process, fertilizer-drawn forward osmosis for sustainable agriculture and water reuse is suggested. Instead of separating the draw solution from desalinated water, the diluted fertilizer draw solution could be directly applied for fertigation (CHEKLI et al., 2017; NGUYEN et al., 2013, 2017; PHUNTSHO et al., 2011).

Johnson et al. (2018) provide an overview of the current literature regarding the different types of draw solutions investigated and their respective benefits and detriments, as shown in Table 4.

Table 4 – Summary of draw solutes described in the scientific literature for FO tests.

Solute	**Osmotic pressure/ concentration**	**Advantages**	**Disadvantages**	**Regeneration methods**
		Inorganic solutes		
NaCl	4.8 MPa/1.0 M	Low viscosity, low cost, high osmotic pressures achievable	High reverse salt diffusion	RO, MD
KCl	4.46 MPa/1.0 M			
$MgCl_2$	7.3 MPa/1.0 M			
		Inorganic solutes (fertilizers)		
$Ca(NO_3)_2$	4.94 MPa/1.0 M	Diluted draw solute can be re-used for fertigation, therefore recovery is not required	Reverse solute flux can be high; reverse solute flux increases nutrient concentration on the feed side of the membrane, encouraging biofouling	Dilution before use in fertigation
KH_2PO_4	3.70 MPa/1.0 M			
$(NH_4)_2HPO_4$	5.13 MPa/1.0 M			
K2SO$_4$	2.8 MPa/0.58 M			
NH_4Cl	4.41 MPa/1.0 M			
$NaNO_3$	8.22 MPa/2.0 M			
KNO_3	3.77 MPa/1.0 M			
$(NH_4)_2SO_4$	4.67 MPa/1.0 M			
NH_4NO_3	3.41 MPa/1.0 M			
$NH_4H_2PO_4$	4.44 MPa/1.0 M			
		Simple organics		
Sucrose, glucose, fructose	2.4 MPa/1.0 M	High solubility	Lower osmotic pressure than inorganic salts; may act as nutrient if mixing with feed side occurs	RO, NF, MD

Source: adapted from Johnson et al. (2018).

In a study evaluating forward osmosis to pre-concentrate wastewater for subsequent anaerobic digestion, Ansari et al. (2015) assessed the performance of different draw solutions. The results showed that ionic organic draw solutes such as sodium acetate were the most appropriate for that application. However, the reverse flow of solute (sodium chloride) caused a small but obvious inhibition in methane production. This factor shows the sensitivity of anaerobic processes, which can be affected when a pre-concentration step is used.

Singh et al. (2018) examined the vinasse concentration by forward osmosis using magnesium chloride hexahydrate ($MgCl_2.6H_2O$) for the draw solution. It was concluded that higher water recovery could be obtained from FO of distillery wastewater as compared to RO at first. The authors suggested that a shortcoming in this method is the small molecules that are not rejected and can pose as a challenge for draw solution reuse, and both reversible and irreversible membrane fouling occur. Moreover, they recommended further investigations to confirm if the combined FO-RO process for distillery wastewater treatment could be a better option than RO alone.

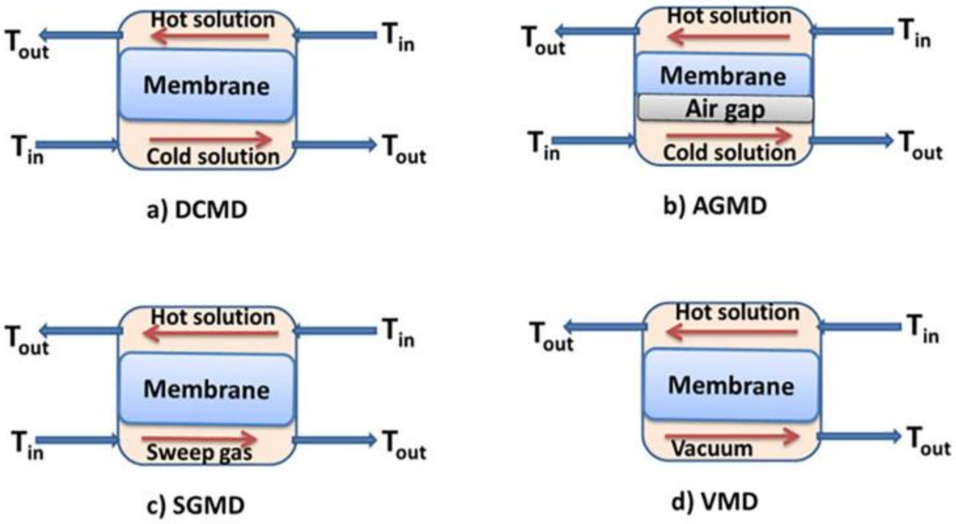
2.3.2.1 Membrane distillation as a regeneration method

The forward osmosis-membrane distillation (FO-MD) integrated system is a newly developed membrane-based hybrid technology. Membrane distillation is a complementary step in the FO process, used to regenerate the draw solution (LIU et al., 2016; ZHANG et al., 2014).

In membrane distillation (MD), water vapor is transported through the pores of a hydrophobic micro-porous membrane via the temperature gradient-induced vapor pressure difference across the membrane. The MD process can offer complete rejection of non-volatile substances in the feed solution, and its efficiency is relatively independent of salt concentration in the feed solution (DRIOLI; ALI; MACEDONIO, 2015; HUSNAIN et al., 2015).

Membrane distillation is divided into four main configurations, depending on the method used to derive its driving force, as presented in Figure 8 (SANMARTINO; KHAYET; GARCÍA-PAYO, 2016).

Figure 8 – Principal membrane distillation configurations.



a) Direct contact MD; b) Air Gap MD; c) Sweep Gas MD; d) Vacuum MD.

Source: Ullah et al. (2018).

The main difference amongst the configurations is the condensation method of the vapor permeated:

- Direct Contact Membrane Distillation (DCMD) – An aqueous solution colder than the feed is maintained in direct contact with the permeate side of the membrane; it is the most straightforward configuration, and the disadvantage is heat loss by conduction;
- Air Gap Membrane Distillation (AGMD) – Stagnant air is introduced between the membrane and the condensation surface; this configuration reduces heat loss by conduction, but increases mass transfer resistance;
- Vacuum Membrane Distillation (VMD) – A pump is used to create a vacuum in the permeate membrane side; in contrast to both DCMD and AGMD configurations, condensation takes place outside of the membrane module;
- Sweeping Gas Membrane Distillation (SGMD) – A cold inert gas sweeps the permeate side and carries away the evaporated molecules; the drawback is the larger condenser required due to the small volume of permeate diffusing in a broad sweep gas volume (ALKHUDHIRI; DARWISH; HILAL, 2012; JACOB et al., 2015; SANMARTINO; KHAYET; GARCÍA-PAYO, 2016).

Regardless of the type of configuration adopted, several authors consider membrane distillation as a suitable technology for the recovery of draw solutions. (HUSNAIN et al., 2015; LIU et al., 2016; MARTINETTI; CHILDRESS; CATH, 2009; WANG et al., 2011; XIE et al., 2013, 2014; ZHANG et al., 2014).

In general, forward osmosis discards most contaminants and foulants from the feed solution, decreasing the fouling and wetting problem for the downstream MD process. MD then recovers the draw solution for the FO process, enabling a constant water flux for FO. The benefits of the integrated process include ambient pressure operation and the potential use of renewable low-grade heat as the energy source (HUSNAIN et al., 2015).

Further understanding of membrane processes can be obtained by analysing mathematical models. In this research, a set of equations includes the determination of water flux for reverse osmosis, forward osmosis and membrane distillation, considering the effects of concentration polarization, as summarized in Appendix D (page 139).

2.3.3 Membrane bioreactors

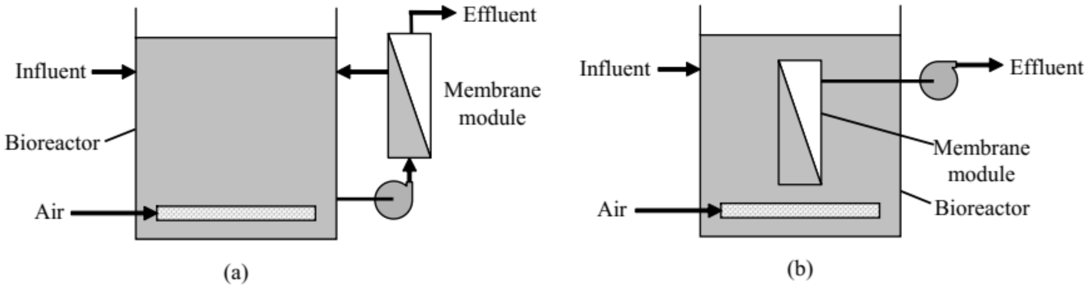
Membrane processes can be coupled with biological reactors in a technology known as membrane bioreactors (MBR). This framework is often used in wastewater treatment as a replacement for sedimentation, i.e., for biomass separation. Besides that, they are used for the controlled transfer of nutrients into a bioreactor or extraction of pollutants from wastewater which are untreatable by conventional biological processes (JUDD; JUDD, 2011; PARK; CHANG; LEE, 2015; STEPHENSON et al., 2000).

Membrane bioreactors have limitations regarding membrane fouling induced by activated sludge, suspended solids, organics and inorganics during the filtration process. Physical rinsing and chemical cleaning have to be frequently applied when operating an MBR, which increases the operation cost and shortens the life of the membrane (PARK; CHANG; LEE, 2015; WANG; LI; HUANG, 2007).

The original concept of the membrane bioreactor was developed in 1960, combining ultrafiltration with the conventional activated sludge process for treating sewage on ships. From then until now, several hydrodynamic, chemical and biological alterations have been made. That is, the academic community is constantly trying to improve the process in order to develop new membranes that are less susceptible to the fouling problem (JUDD; JUDD, 2011; KHAN; HANKINS; SHEN, 2016).

Membrane modules can be kept inside (submerged) or outside (sidestream) the biological reactor (Figure 9). In the sidestream, the feed flows tangentially to the surface of the membrane High crossflow velocities can be used as a fouling control strategy with hydraulic scour of the membrane surface reducing membrane fouling. However, sidestreams are generally used to promote external loops, which can be problematic because the cells/enzymes are unnecessarily subjected to shear stress and fluctuations of the reaction process. In contrast, submerged membranes have good flux values and require no extra pumps. They avoid additional shear stress and allow tightly controlled reaction conditions, but are more susceptible to fouling formation (AL-MALACK, 2007; CARSTENSEN; APEL; WESSLING, 2012; JUDD; JUDD, 2011; MORROW et al., 2018).

Figure 9 – Schematic diagrams of basic membrane bioreactor configurations.

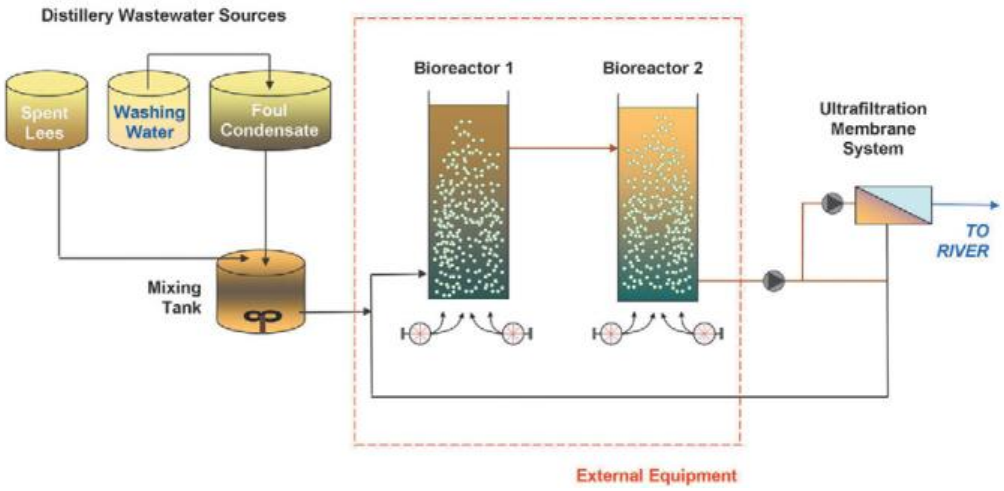


(a) Sidestream configuration; (b) Submerged configuration. Source: Ng and Kim (2007).

An example of a distillery in Scotland installed a plant to treat vinasse using a membrane bioreactor. The distillery comprises a membrane bioreactor treatment system incorporating sidestream cross-flow ultrafiltration to treat 144 m^3/day of wastewater. Figure 10 illustrates this process (ROBINSON, 2009).

Nonetheless, an external submerged configuration was described by Smith et al. (2012). This arrangement facilitates membrane cleaning and replacement by allowing isolation of the membrane unit in an external chamber. In this system, the membrane would not be in contact with the biomass, avoiding problems with formation of fouling. In addition, it would not be necessary to pump the effluent and prevent the shear stress problem in the microorganisms.

Figure 10 – Process flow schematic of MBR system in a Scottish distillery.



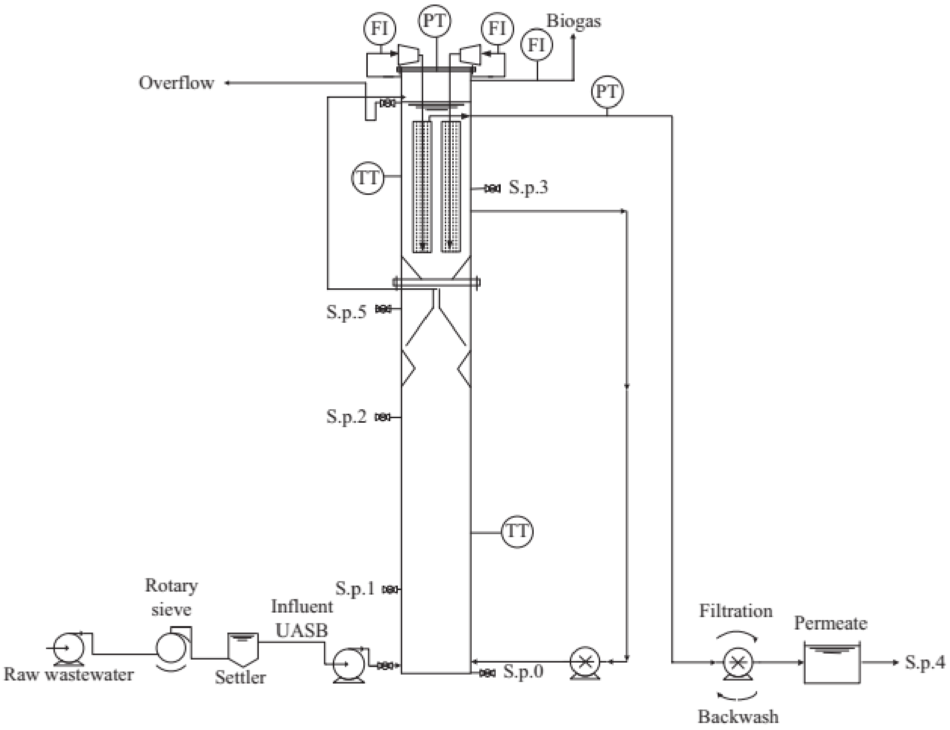
Source: Robinson (2009).

Considering that aerobic processes are more prone to sludge formation, whose net biomass production is ten times higher than anaerobic treatment, anaerobic membrane bioreactors (AnMBR) were developed. The AnMBR configuration has the advantages of dissociation between the sludge retention time (SRT) and the hydraulic retention time (HRT) and it also allows energy to be recovered. Furthermore, a study carried out by Li et al. (2016) showed that mesh fouling in the AnMBR operation was mitigated by in-situ biogas sparging (CHARFI et al., 2017; CHEN et al., 2016; LIN et al., 2013).

An example of external membrane and anaerobic treatment is the promising design developed by Gouveia et al. (2015) shown in Figure 11. The pilot scale anaerobic submerged membrane bioreactor (AnSMBR) was equipped with an ultrafiltration unit, treating municipal wastewater, and inoculated with a mesophilic inoculum without acclimation. During the three- year continuous operation, the membrane was not physically or chemically cleaned.

The performance of an AnMBR system was also evaluated by Mota et al. (2013) and Santos et al. (2017). The authors designed a two-stage submerged anaerobic membrane bioreactor to treat sugarcane vinasse. The reactor showed the high capacity of removing organic matter and producing biogas. Reducing the HRT, the average mass of soluble microbial products and extracellular polymeric substances per mass of mixed liquid volatile suspended solids increased. Consequently, the transmembrane pressure rate and fouling resistance rose. Despite the fouling effect, physical and chemical cleaning processes were able to recover operational permeability.

Figure 11 – AnSMBR pilot plant flow scheme.



Flowrate indicator (FI); pressure transmitter (PT); temperature transmitter (TT); sampling points (S.p).
Source: Gouveia et al. (2015).

Although many MBR configurations are possible, anaerobic membrane bioreactors seem to be the most interesting in the context of this work. This configuration was considered because it represents a potential technology for the vinasse biorefinery, integrating energy production and water recycling. Thus, an overview of the anaerobic digestion process is discussed next.

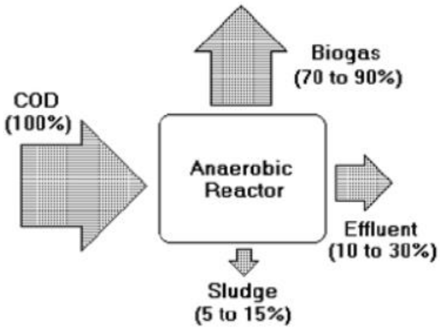
2.4 ANAEROBIC BIOREACTORS

Anaerobic digestion (AD) is an efficient biological process to remove organic matter. If the start-up of the bioreactor (an adaptation of the biomass to the effluent to be treated) and the maintenance of active biomass are adequate, suitable biogas can be generated. In general, this technology uses investments in industrial plants related to the installation and operation of the bioreactor and associated with the treatment of the biogas generated. Anaerobic digestion has demonstrated technical effectiveness, and for this reason, researchers have been working on the continuous improvement of the process. Therefore, this technology is a promising source of energy for industrial plants (DEL NERY et al., 2016; FUESS; GARCIA, 2017; MORAES et al., 2014; RABELO; COSTA; ROSSEL, 2015; SANTOS; BARROS; TIAGO FILHO, 2016).

According to Fuess and Garcia (2017), when anaerobic digestion is applied, bioenergy generation from biogas can fully supply sugarcane-based plants, so that vinasse may be characterized as a highly energetic biofuel. Thus, many researchers have shown that vinasse treatment by anaerobic digestion results in an improvement of the energy potential of biorefineries (AKRAM et al., 2015; FUESS; GARCIA, 2017; JOPPERT et al., 2017; MORAES; ZAIAT; BONOMI, 2015; NAIR et al., 2018; SALOMON; LORA, 2009; SILVA DOS SANTOS et al., 2018).

Anaerobic systems are advantageous mainly for producing biogas, requiring low energy for operations and generating small amounts of solids. Most of the organic content in the feed is converted into biogas, and a small fraction of COD leaves the reactor in sludge form. A schematic balance in the anaerobic digestion unit is presented in Figure 12 (CHERNICHARO, 2007).

Figure 12 – Biological conversion in anaerobic system.



Source: Chernicharo (2007).

As can be observed, biogas is produced and can be used as fuel for energy production. This process also has sludge as output, which is formed by concentrated biomass and water, and must be treated due to the high presence of organic matter. Anaerobic digestion supernatant is a mixture of partially degraded organic matter, anaerobic biomass and inorganic matter (including nutrients). Besides the metabolism that combines carbon and hydrogen producing methane, AD processes facilitate the mobilization of nutrients from the organic matter to the liquid phase. Thus, N is converted into ammonium, and organic phosphorus is hydrolyzed to soluble P. The fundamental principle of anaerobic digestion conversion is explained in the next section.

The balances for an anaerobic digestion unit, including biogas, sludge and effluent streams are described in Appendix E (page 145).

2.4.1 Overview of the anaerobic digestion process

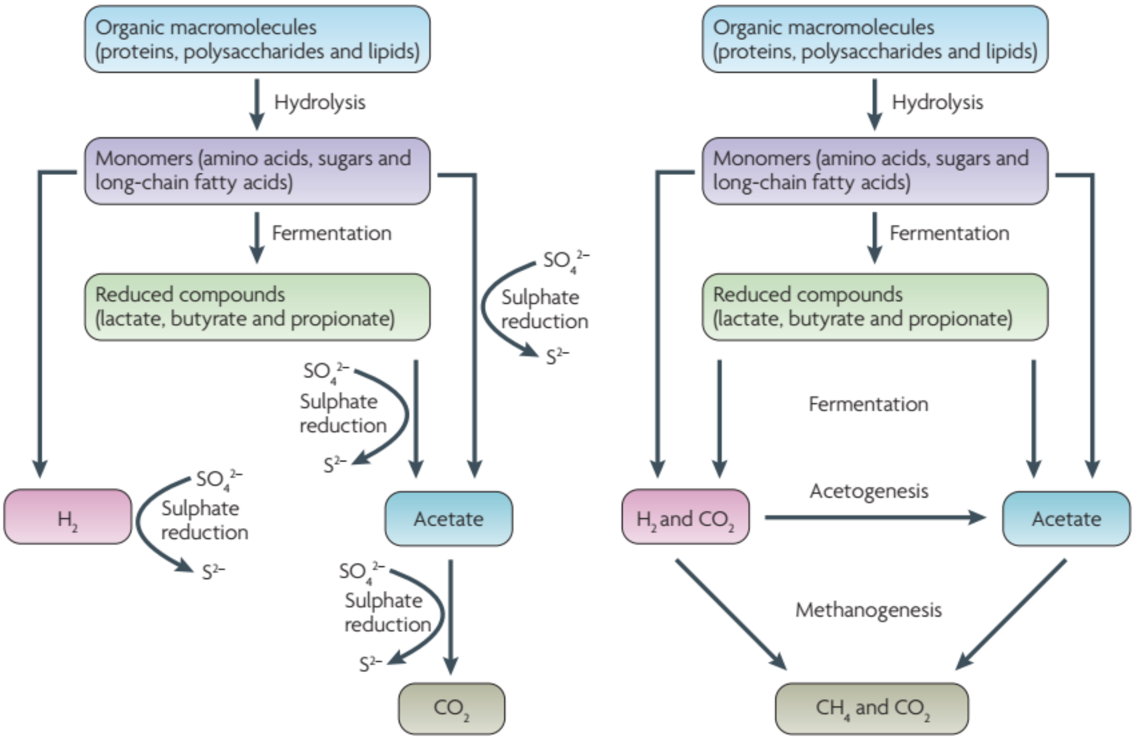
In anaerobic digestion processes, biological degradation of organic components is achieved with no requirement of molecular oxygen. Most of the carbon atoms originating in the waste material are reduced to methane (CH_4). However, conversion of organic pollutants may be achieved without methane formation, when denitrifying and sulfate-reducing organisms utilize nitrate and sulfate as terminal electron acceptors. Sulfate-reducing bacteria are obligating anaerobes and convert sulfate to sulfide (ANDERSON; SALLIS; UYANIK, 2003; METCALF; EDDY, 2003).

The complexity of the conversion process in anaerobic digestion, including sets of biochemical and physical-chemical reactions, is shown in Figure 13. In the presence of sulfate, sulfate-reducing bacteria consume fermentation products (acetate, propionate, butyrate, lactate, and hydrogen) and produce sulfide, which can be toxic to methanogenic bacteria. However, in the absence of sulfate, the hydrogen and acetate formed in the fermentation and acetogenesis steps are consumed by the archaea methanogenic generating methane and carbon dioxide (MUYZER; STAMS, 2008).

As well as the toxicity by sulphate-reducing bacteria referred to above, other environmental factors can affect the convenient course of reactions in the AD, such as nutrient composition, temperature, pH and inhibitory substances (BATSTONE et al., 2002).

Nutrients supply the basic cellular building blocks for growth and ensure the cells are able to synthesize the enzymes and co-factors that drive the biochemical and metabolic reactions. While the lack of some nutrients have been identified to be the main reason behind poor process performance, excessive concentrations of some macro and micronutrient can lead to the inhibition of the reaction (ANDERSON; SALLIS; UYANIK, 2003; ROMERO-GÜIZA et al., 2016).

Figure 13 – Scheme of the anaerobic digestion of complex organic matter, depicting the steps and microbial populations involved.



Source: Muyzer and Stams (2008).

Temperature control is fundamental for maintaining optimal bacterial growth and conversion processes in anaerobic microbial systems. The optimum growth temperature of anaerobic microorganisms is 35°C or higher, and although anaerobic digesters have been reported to operate at substantially lower temperatures, such as 20°C, anaerobic growth under these conditions is protracted and difficulties in some reactors' start-ups have been reported (ANDERSON; SALLIS; UYANIK, 2003; STRONACH; RUDD; LESTER, 1986).

In the AD process, there is a syntrophic relationship among methanogens and acidogens in which the methanogens convert fermentation end products such as hydrogen, formate and acetate to methane and carbon dioxide. If the methanogenic organisms do not utilize the hydrogen produced fast enough, the propionate and butyrate fermentation will be slowed down with the accumulation of volatile fatty acids and a possible reduction in pH (METCALF; EDDY, 2003).

Ammonia (NH_3) and ammonium ion (NH_4^+) are the most significant inhibitors in the AD. Although some ammonium is beneficial for bacterial growth, undesirably high concentrations may be reached during the breakdown of proteins available in the substrate. Accumulation of substances such as ammonia, sulfide, heavy metals and organics may cause reactor upset, as indicated by reduced methane production and possible reactor failure (CHEN; CHENG; CREAMER, 2008; YENIGÜN; DEMIREL, 2013).

Despite the sensitivity associated with anaerobic reactor operations, the process can be sustained with a high biomass inventory and low enough loading. The presence of a toxic substance does not mean the process cannot function. Pretreatment steps may be used to remove components detrimental to the process. In some cases, a separation phase may prevent toxicity problems arising from the degradation of toxic components in the acid phase. Thus, the exposure of the sensitive *methanogenic archaea* to the possible toxic constituents is avoided (METCALF; EDDY, 2003).

2.4.2 Aspects of biogas conversion

Biogas can include many applications such as heating, combined heat and power (CHP) generation, transportation fuel (after being upgraded to bio-methane) or upgraded to natural gas quality for a wide range of uses. In developing countries mainly with household-scale digesters, however, the end use of biogas is primarily limited to cooking and lighting (SURENDRA et al., 2014).

Energy production from biogas depends on several factors. Among them, the characteristics of the by-product used in the AD, the composition of the gas formed and the need for cleaning, industrial production capacity, technologies for conversion into energy forms and economic feasibility. Besides methane, different components can be found in its composition, as shown in Table 5 (SALOMON; LORA, 2009).

Using biogas conversion technologies (such as internal combustion engines, turbines, and other equipment) requires pre-treatment. This cleaning is fundamental because biogas contains some impurities that may have significant adverse impacts on the utilization system, such as corrosion, increased emissions, and hazards for human health. In order to improve the calorific value and reduce unwanted components, e.g. CO_2 and H_2S, it is crucial to clean raw biogas and upgrade it to a higher fuel standard (KASIKAMPHAIBOON et al., 2013; KOUGIAS et al., 2017; RYCKEBOSCH; DROUILLON; VERVAEREN, 2011; SCHOLZ; MELIN; WESSLING, 2013; SUN et al., 2015; YANG et al., 2014).

Table 5 – Average composition of biogas.

Component	**Percentage (%)**
Methane (CH_4)	40 – 75
Carbon dioxide (CO_2)	25 – 40
Nitrogen (N)	0.5 – 2.5
Oxygen (O_2)	0.1 – 1
Hydrogen sulfide (H_2S)	0.1 – 0.5
Ammonia (NH_3)	0.1 – 0.5
Carbon monoxide (CO)	0 – 0.1
Hydrogen (H_2)	1 – 3

Source: Salomon and Lora (2009).

Therefore, the opportunity to use biogas from vinasse should consider the type of application, the need for cleaning and the impacts of implementing a system focusing on its production. As shown by Bernal et al. (2017), environmental and energy benefits can be obtained via power generation from biogas produced by the anaerobic digestion of vinasse and it is essential to include the use of such residue for energy in expansion plans for the Brazilian energy matrix (BERNAL et al., 2017; LEBRERO et al., 2016; LEME; SEABRA, 2017; MORAES et al., 2015; NOGUEIRA et al., 2015).

2.5 EXERGY ANALYSIS ON SYSTEMS EVALUATION

According to Kotas (1985), exergy is the useful work or quality of different forms of energy that can be obtained from a system when it is in a specified state different from the environment. If the system is in complete equilibrium with its environment, it does not have any exergy because there is no difference in temperature, pressure or chemical composition, and therefore it is in a dead state. For example, the natural atmosphere contains a tremendous amount of energy, but no exergy (ÇENGEL; BOLES, 2015; DINCER; ROSEN, 2013).

Any mass, heat, and work from a system in a state condition dissimilar to the environment is associated with an exergy content. Thus, the concept of exergy represents the quality index of energy and materials entering and leaving a system (CORNELISSEN, 1997; DINCER; ROSEN, 2013; OJEDA; EL-HALWAGI; KAFAROV, 2013; PARK et al., 2014; REMY et al., 2017).

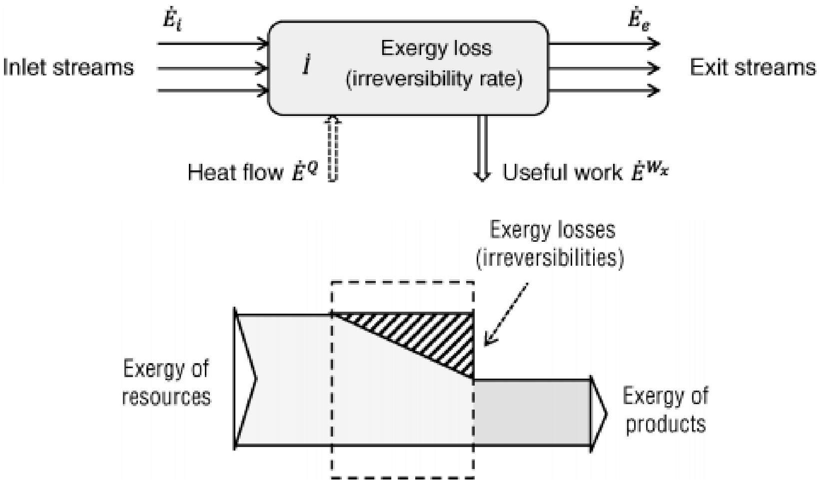
Exergy balance is similar to energy balance but has the fundamental difference that, while the latter is a statement of the law of energy conservation, exergy balance may be looked upon as a statement of the law of energy degradation. In fact, for real processes, while the quantities remain constant, the quality of energy and materials is progressively degraded (KOTAS, 1985; PTASINSKI, 2016).

Even so, in most cases, the efficiency of systems is evaluated by using mass and energy balances. However, this type of analysis does not consider the quality of the currents, only the quantity. Energy and mass balances treat all forms of energy as equivalent, without differentiating them between the different grades of energy crossing the system boundary. For example, it does not consider that heat has lower quality than mechanical work – it is because only a part of heat can be converted into mechanical work, while the conversion in the reverse direction holds that all mechanical work can be converted into heat (DINCER; ROSEN, 2013; KOTAS, 1985; PTASINSKI, 2016).

Exergy efficiency is based on the first and second laws of thermodynamics and constitutes a degree of approach to ideality (or reversibility). Considering the scheme in Figure 14, in irreversible processes, exergy input always exceeds exergy output due to irreversibilities or exergy destruction (CORNELISSEN, 1997; DINCER; ROSEN, 2013; PTASINSKI, 2016).

It is essential to distinguish beteween exergy destruction caused by irreversibilities and waste due to available exergy. Both represent exergy losses, but irreversibilities have, by definition, no exergy and no environmental effects. Internal exergy losses result from the irreversibility of the processes occurring inside the system. External exergy losses appear if the waste products of the processes are rejected into the environment (DINCER; ROSEN, 2013; REMY et al., 2017; SZARGUT, 1989).

Figure 14 – Schematic model of a system to develop the exergy balance.

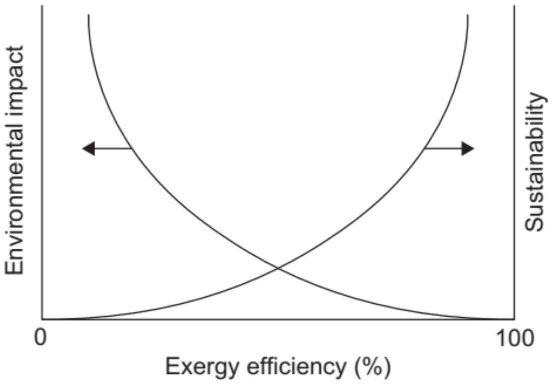


Source: adapted from Ptasinski (2016).

The sustainability character of the exergy analysis can be observed when a wastewater treatment plant is considered. When designing a system, avoiding an obvious problem in one place may lead to a bigger problem somewhere else. That is, although pollutants are no longer released into water bodies, problems such as inadequate treatment of sludge or generating greenhouse gases can arise. Thus, the total environmental performance should be examined by adopting a wider sustainability criteria such as the exergy analysis, which comprises all types of streams (DINCER; ROSEN, 2013; REMY et al., 2017).

Since exergy analysis represents a measure of sustainability, this method has been used to evaluate systems designed for recycling and resource reclamation, such as biorefineries. It is important to assess to what extent the implementation of recovery processes can bring benefits or if they could represent low conversion efficiencies and disadvantages (AMINI et al., 2007; CASTRO et al., 2007; IGNATENKO; VAN SCHAIK; REUTER, 2007; PARK et al., 2014; SHAO; CHEN, 2015).

Figure 15 – Relation between the environmental impact, sustainability and exergy efficiency of a process.



Source: Dincer and Rosen (2013).

Therefore, a description of the procedures of how to use exergy analysis is provided in the following subsection.

2.5.1 Procedures for exergy analysis

The earliest contributions to the theory of “energy availability” include considerations by Carnot, Thomson (who developed the Kelvin scale) and Gibbs. However, Gouy (1889) and Stodola (1898) are considered as responsible for the origin of the mathematic formulation of this concept. The term “exergy’ was devised by Rant (1956) and has now gained general acceptance (KOTAS, 1985; OLIVEIRA JUNIOR, 2013).

The procedures for exergy analysis presented below were described by more recent authors, guided by the concepts developed by the authors mentioned above.

Sciubba and Ulgiati (2005) defined the steps for exergy analysis of a system:

i. Define the control volume, including the immediate surroundings of the systems;
ii. Draw the flowchart of the system;

iii. Construct a library of the components chosen to represent the individual processes. Identify inputs and outputs, whether mass or energy flows, separating current types such as useful products or by-products.

iv. Identify the thermodynamic state of all fluxes, and quantify their relevant properties (temperature, pressure, enthalpy, entropy, composition and concentration, chemical potentials, etc.);

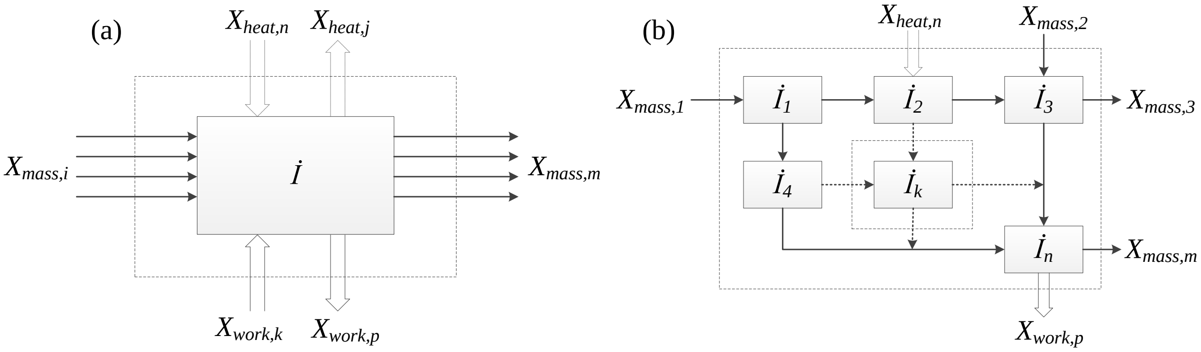
v. Perform mass and energy balances, first at the component level and then at the system level;

vi. Perform the exergy ‘balance’ of each component to compute the exergy destruction. Extend to system level;

vii. Compute the relative exergy efficiencies.

This procedure includes observing the inlet and outlet material currents, heat and work transfers, as shown in Figure 16 (PTASINSKI, 2016).

Figure 16 – (a) Overall exergy balance; (b) Exergy balance for the *kth* process component and overall exergy balance.



Source: adapted from Ptasinski (2016).

As can be seen, all kinds of streams must be included in the balance, as defined by the equation:

$$\sum_{i,in} X_{mass,i} + \sum_{j,in} X_{heat,j} - \sum_{k,in} X_{work,k} = \sum_{m,out} X_{mass,m} + \sum_{n,out} X_{heat,n} - \sum_{p,out} X_{work,p} + \dot{I} \tag{1}$$

Where:

$X_{mass,i}$ – Exergy of the mass of the input stream i (kW);
$X_{mass,m}$ – Exergy of the mass of the output stream m (kW);
$X_{heat,j}$ – Exergy of the heat of the input stream j (kW);
$X_{heat,n}$ – Exergy of the heat of the output stream n (kW);
$X_{work,k}$ – Exergy of the input work k (kW);
$X_{work,p}$ – Exergy of the output work p (kW);
$\dot{I}$ – Irreversibility or exergy destruction (kW).

The terms refer to the flow forms in an exergy analysis, as explained in the next section.

2.5.1.1 Exergy of a matter flow

Mass contains exergy as well as energy and entropy. The exergy of a flowing matter is the maximum work that can be obtained when the stream is brought from its initial state to the state of mechanical, thermal and chemical equilibrium with the environment. It can be expressed in terms of physical, chemical, kinetic and potential exergy (ÇENGEL; BOLES, 2015; KOTAS, 1985; PTASINSKI, 2016):

$$X_{mass} = X^{ph} + X^{ch} + X^{kin} + X^{pot} \tag{2}$$

According to Kotas (1985), the kinetic and potential energies of a stream of substance are ordered forms of energy and thus fully convertible to work. Therefore, when evaluated in relation to the environmental reference datum levels, they are equal to kinetic and potential exergy respectively, as shown in the next equations:

$$X^{kin} = m\frac{\upsilon^2}{2} \tag{3}$$

$$X^{pot} = m \cdot g \cdot z \tag{4}$$

where m designates the mass flow rate of the stream, g is the gravitational acceleration, υ is the velocity and z represents the altitude of the stream with reference to the sea level (PTASINSKI, 2016).

Physical exergy is correspondent to the maximum work that can be achieved when a system or a flow rate moves from a given thermodynamic state (pressure *P* and temperature *T*) to the environment state (pressure P_0 and temperature T_0). The physical exergy for a mass flowrate is given by (OLIVEIRA JUNIOR, 2013):

$$X^{ph} = (h - h_0) - T_0(s - s_0) \tag{5}$$

where h and h_0 are the specific enthalpies of the material in given thermodynamic and reference states, respectively, then s and s_0 refer to the entropies.

Understanding chemical exergy requires knowledge of the concept of the exergy reference environment, which is an idealized model of the real environment. This is characterized by the uniform environmental temperature T_0 and pressure P_0 (25°C and 1 bar, respectively) and the system of reference chemical species that are selected for each chemical element (PTASINSKI, 2016; SZARGUT; MORRIS; STEWARD, 1988).

Ptasinski (2016, p. 54) provides an elucidation about the reference chemical species:

> The reference species represent the lowest thermodynamic values for each chemical element. To illustrate this point, the reference species for carbon is CO_2 at the environmental temperature of 25°C and the mean environmental pressure of 0.0335 kPa. The exergy of CO_2 at these conditions is zero as this carbon species is commonly available and cannot deliver useful work with respect to the environment. On the other hand, other carbon-containing species, such as CO, CH_3OH, and CH_4 have positive exergy values, as useful work can be obtained from these species with respect to the environment. It is also assumed that the exergy reference environment is in a perfect state of equilibrium, which means an absence of any gradients or differences in temperature, pressure, and kinetic and potential energy as well as chemical composition (the latter condition refers to a component of the environment, such as atmosphere, sea water, and Earth's crust).

According to Szargut et al. (1988), the chemical exergy is a result of the deviation between the chemical composition of the material in the state under consideration and the composition of the components that form it in the natural environment. Chemical exergy is equal to the maximum amount of work that can be obtained when a substance is brought from the reference-environment state to the dead state by a process including heat transfer and exchange of substances only with the reference environment.

For the most common chemical compounds, the specific chemical exergy can be found in Szargut (1989) who presented values for inorganic and organic compounds. In addition, Zanchini and Terlizzese (2009) presented molar exergy and flow exergy of pure chemical fuels.

The chemical exergy of a mixture is expressed by the following equation (PTASINSKI, 2016):

$$X^{ch} = M_{sol}\left[\sum_{i=1}^{n} y_i \cdot x_i^{ch} + R \cdot T_0 \sum_{i=1}^{n} y_i \cdot \ln y_i\right] \tag{6}$$

where x_i^{ch} is the standard chemical exergy of a pure element; y_i is the molar fraction of this element; M_{sol} is the mass concentration of the solution in moles and R is the constant universal of the gases (PALACIOS-BERECHE et al., 2013; PTASINSKI, 2016).

Appendix F (page 149) comprises the standard chemical exergy of the components used in this work.

2.5.1.1.1 Exergy of organic components

Considering organic components, the chemical exergy of organic matter in wastewater can be calculated according to the equation proposed by Tai et al. (1986):

$$X_{org,mat} = 13.6 \cdot COD \tag{7}$$

Where $X_{org,mat}$ is the chemical exergy of organic matter in J/L and COD is the chemical oxygen demand in mg/L. The authors established this relation by analyzing 138 organic compounds and demonstrated the high correlation coefficient, between 95 and 100% of approximation. Thus, their equation is considered representative of organic matter streams.

2.5.1.2 Exergy of the heat stream

Heat is a form of disorganized energy, and thus only a portion of it can be converted to work, which is a form of organized energy. We can always produce work from heat at a temperature above the environment temperature by transferring it to a heat engine that rejects the waste heat to the environment (ÇENGEL; BOLES, 2015).

The exergy of thermal energy X_{heat} is associated with a heat transfer rate. It concerns the maximum work that could be performed by a Carnot engine operating between T and T_0, receiving Q at T, and rejecting heat to the environment at T_0 (OLIVEIRA JUNIOR, 2013):

$$X_{heat} = \left(1 - \frac{T_0}{T}\right) \cdot Q \quad \text{(exergy of thermal energy)} \tag{8}$$

The entropy generation is always accompanied by exergy destruction. It is worth observing that heat transfer Q at a location at temperature T is always accompanied by entropy transfer and exergy transfer (ÇENGEL; BOLES, 2015).

2.5.1.3 Exergy of work

Exergy is the useful work potential. The exergy transfer associated with work done by a system due to volume change is the net usable work due to the volume change, and is denoted by:

$$X_{work} = W - P_0 \frac{dV}{dt} \quad \text{(exergy of work)} \tag{9}$$

where W is the work done by the system due to volume change. The term $P_0(dV/dt)$ is the displacement work necessary to change the volume against the constant pressure P_0 exerted by the environment (ÇENGEL; BOLES, 2015; DINCER; ROSEN, 2013).

2.5.1.4 Irreversibilities or exergy destruction

Friction, mixing, chemical reactions, unrestrained expansion, compression, expansion, among other factors, always generate entropy in a system. Exergy destruction, also called irreversibility or lost work, is proportional to the entropy generated and represents the lost work

Exergy destruction or irreversibility I is given considering the environmental temperature T_0 and entropy generation S_{ger}:

$$I = T_0 \cdot S_{ger} \geq 0 \tag{10}$$

The exergy change of a system can be positive or negative during a process, but exergy destruction cannot be negative (ÇENGEL; BOLES, 2015).

2.5.1.5 Exergy efficiency

Once the terms of the equation have been defined, the efficiency calculation is carried out. The environmental exergy efficiency is the ratio of the final product exergy (or useful effect of a process) to the total exergy of natural and human resources consumed. All exergy inputs in a given energy conversion process must be included. The environmental exergy efficiency is calculated by (OLIVEIRA JUNIOR, 2013; PTASINSKI, 2016):

$$\eta_{env} = \frac{X_{product}}{X_{nat,res} + X_{processing} + X_{utilities} + X_{deactivation} + X_{dsiposal}} \tag{11}$$

Where:

- $X_{product}$ is the exergy rate of the useful effect of a process;
- $X_{nat,res}$ is the exergy rate of the natural resources consumed by the processes;
- $X_{processing}$ is the exergy rate or flow rate required for extraction and preparation of the natural resources;
- $X_{utilities}$ is the exergy rate or flow rate needed for the utilities of the process;
- $X_{disposal}$ is the exergy rate or flow rate related to waste disposal of the process;

- $X_{deactivation}$ is the exergy destruction rate of additional natural resources during waste deactivation.

In a general form, the exergy efficiency η is the ratio of the total outgoing exergy flow to the entire incoming exergy flow:

$$\eta = \frac{\sum \Delta X_{out}}{\sum \Delta X_{in}} \tag{12}$$

This is an unambiguous definition and can be used for all process plants and units. This ratio is also an indication of the theoretical potential of future improvements for a process (CORNELISSEN, 1997; OLIVEIRA JUNIOR, 2013).

2.5.2 Exergy analysis in sugarcane biorefineries

Evaporators, membrane processes, and anaerobic bioreactors have been increasingly considered as alternatives for handling vinasse. These approaches are proposed due in part to problems regarding fertigation, but also insights into opportunities offered in vinasse treatment. Considering this standpoint, the concept of the biorefinery offers the prospect of recovering valuable materials and making its management more attractive to industries. It can bring advantages both in economic terms by promoting reuse of materials and reducing the demand from external feedstocks, as well as environmental terms by providing alternative sources of material and energy.

In fact, there is a wide range of possible technologies to achieve resource recovery from vinasse. Choosing the best combination of technologies can be complicated, given the interactions between processes and characteristics of input. It can be stated that the design of any engineering system involves analysing the technical, economic, availability, reliability, sustainability, maintenance and environmental effects. Accordingly, exergy analysis is known as a useful tool that can be utilized to evaluate the performance of a system (BOROUMANDJAZI et al., 2012; FERNÁNDEZ-ARÉVALO et al., 2017).

Many studies have already used the exergy analysis method to study sugarcane biorefineries, mainly to evaluate different possibilities of biomass (AGHBASHLO et al., 2018; BECHARA et al., 2016; CLAUSEN; HOUBAK; ELMEGAARD, 2010; ENSINAS et al., 2009; GUERRA et al., 2018; PELLEGRINI; OLIVEIRA JUNIOR, 2007; SILVA ORTIZ; DE OLIVEIRA JR, 2014a, 2014b).

Biomass originating from sugarcane, mainly in the form of bagasse, is a byproduct that offers various energy opportunities in the sugar and alcohol industry. Many studies have sought to improve the two main routes of bagasse treatment: generating bioelectricity or second generation ethanol. The first one is currently achieved by using biomass boilers. The latter utilizes diverse types of lignocellulosic materials such as bagasse to produce ethanol, which is different from the first generation that utilizes sugars or starch as substrate (DIAS et al., 2011, 2012; KHATIWADA et al., 2016; LENNARTSSON; ERLANDSSON; TAHERZADEH, 2014).

Exergy analysis of sugarcane bagasse gasification was carried out by Pellegrini and Oliveira (2007). The objective was to evaluate irreversibilities associated with the process, and the influence of temperature, moisture, charcoal production and thermal losses on them. The first attempt to integrate a gasifier into a sugarcane mill was performed, which showed the potential benefits regarding the use of this technology.

Aghbashlo et al., (2018) analyzed a lignocellulosic biorefinery annexed to a sugar mill for simultaneous lactic acid and electricity production using sugarcane bagasse and brown leaves as feedstock. The primary goal was to reveal the reasons and sources of thermodynamic inefficiencies associated with the biorefinery under investigation. The results showed that the unit of steam generation contributed the most to the loss of exergy of the system, with 63.31%. In addition, the lactic acid production unit came next, accounting for 16.30% of exergy destruction in the biorefinery. The universal and functional exergy efficiencies of the system were determined as 52.71% and 44.73%, respectively.

Ometto and Roma (2010) made an assessment of the atmospheric emissions from the life cycle of ethanol coupled with the cogeneration of electricity from sugarcane in Brazil. The activity that most contributes to chemical exergy losses is sugarcane harvesting through greenhouse gases emitted in burning plantations. The authors suggested sugarcane harvesting without burning and use of renewable fuels in tractors, trucks, and buses instead of fossil fuel to improve environmental quality and higher efficiency of the ethanol life cycle.

In a novel way, considering a byproduct other than bagasse, Barrera et al. (2016) made a comparative assessment of anaerobic digestion power plants as an alternative to lagoons for vinasse treatment. The greatest environmental benefits found in the anaerobic digestion plant were related to biogas production from raw vinasse, sulfide removal by bio-oxidation with air oxygen addition and energy generation using spark ignition engines.

The referenced examples showed the applicability of this type of study in systems that take advantage of the potential of different residues. Exergy can help to better understand the benefits of utilizing recovery technologies, identifying efficiency improvements and reductions in thermodynamic losses (ROSEN; DINCER; KANOGLU, 2008).

2.6 CONSIDERATIONS ABOUT THE LITERATURE REVIEW

More emphatically in recent years, researchers have seen opportunities to obtain valuable products from materials generally depreciated in the environmental sphere. This paradigm represents the concept of biorefinery, which focuses on obtaining resources from waste and wastewater due to its valuable constituents and energy content.

Depending on the type of residue, a variety of elements can be reclaimed such as nitrogen, phosphorus, fibers, acids and heat. On the whole, energy, nutrients and water are the three significant resource recovery targets (GUEST et al., 2009; MO; ZHANG, 2013; VAN DER HOEK; DE FOOIJ; STRUKER, 2016).

Within this perspective, compensations include lowering the primary extraction requirement and obtaining cleaner energies linked to the proper disposal of waste in accordance with environmental standards. However, the challenge is to find or improve processes and technological routes in order to obtain resources efficiently, making the concept of biorefineries more and more concrete (BERTANZA; CANATO; LAERA, 2018; FERNÁNDEZ-ARÉVALO et al., 2017).

A clear example of biorefinery is the sugarcane industry, which produces energy from using bagasse, a by-product of the industrial process, such as fuel in cogeneration systems. This practice is a suitable destination for waste and profits for the sector.

Brazil's primary energy sources come from fossil fuels, hydroelectric plants and the sugarcane industry, the latter accounting for 9% of the electricity supply (UNICA, 2018b). Despite the importance of sugarcane biomass among energy sources in the country, the potential of sugar and alcohol industries is far from being realized. Therefore, researchers have been addressing ways to upgrade this sector by improving uses of its by-products, ensuring its importance in economical, energy and environmental contexts (CARPIO; SOUZA, 2017; DANTAS; LEGEY; MAZZONE, 2013; KHATIWADA et al., 2016; SOZINHO et al., 2018).

As can be seen in this chapter, there is a growing tendency to reallocate by-products of the sugarcane industry in order to realize their potential, such as bagasse gasification or second generation ethanol production. Within this context, vinasse management and fertigation have also gained attention, as discussed previously. The literature review has comprised anaerobic bioreactor, evaporator and membrane processes to manage effluent in the context of biorefineries. Therefore, some considerations should be mentioned:

- Although there are many types of membranes, forward and reverse osmosis processes were emphasized as being more selective membranes, causing fewer nutrient losses;
- Membrane distillation was described as a regeneration method, but there are other possibilities for that, including evaporation and reverse osmosis;
- Nutrients in vinasse could be reclaimed by crystallization, electrodialysis, among others, but these techniques need to be further investigated and are not within the scope of this study (MEHTA et al., 2015);
- Other ways to use vinasse could be attractive, such as recycling it in fermentation, yeast production and raw material to manufacture livestock and poultry feed. Thus, vinasse biorefineries could adopt various approaches (CHRISTOFOLETTI et al., 2013; LÓPEZ-CAMPOS et al., 2011; OLIVEIRA et al., 2013).
- Over the last years, a new perspective using vinasse nutrients has emerged: the generation of biofuels from microalgae cultures. In this case, the effluent from AD constitutes a nutrient-rich environment for microalgae growth. However, this thesis did not consider the study of this alternative as the aim of the research was to analyse different concentration methods of anaerobic digestion effluent (CHEW et al., 2017; COLLING KLEIN; BONOMI; MACIEL FILHO, 2018; GULDHE et al., 2017; JANKOWSKA; SAHU; OLESKOWICZ-POPIEL, 2017; MORENO-GARCIA et al., 2017).

Anaerobic digestion, evaporation and membrane processes have been emphasized in this literature review because they are well known and widely used techniques. Thus, it is valid that they are evaluated for use in biorefineries.

As can be observed, the concept of vinasse biorefineries considers different possibilities of technological configurations. In this case, the exergy analysis was used as a tool to compare the technological configurations in terms of their efficiency, not considering operational and installation costs or operation difficulties that may arise when a particular arrangement is adopted. The advantage of this procedure is that the whole comparison is based on a single unambiguous quantifiable indicator. Consequently, there is no need to establish equivalence factors or measures of weight. In this case, unlike Life Cycle Analysis, the answer can be acquired from the efficiency of processes within the immediate boundaries of the system, but not in environmental impacts on a global scale (BALKEMA et al., 2002).

Taking into account the above information in the literature review, this work was developed. The procedures adopted to carry out the present research are described in the next chapter.

3 METHODOLOGY

As seen in the previous chapter, the handling of the vinasse is generally thought of in two ways besides fertigation: anaerobic bioreactors and concentration, which can use different types of technology, such as evaporators and filtering membranes. Although these methods are well discussed in the literature, there are still no comparative studies that evaluate which technological combination would be more reasonable to be implemented in the sugarcane industry.

Therefore, the present work considered five different configurations for designing a vinasse biorefinery, aiming to recover water, nutrients and energy:

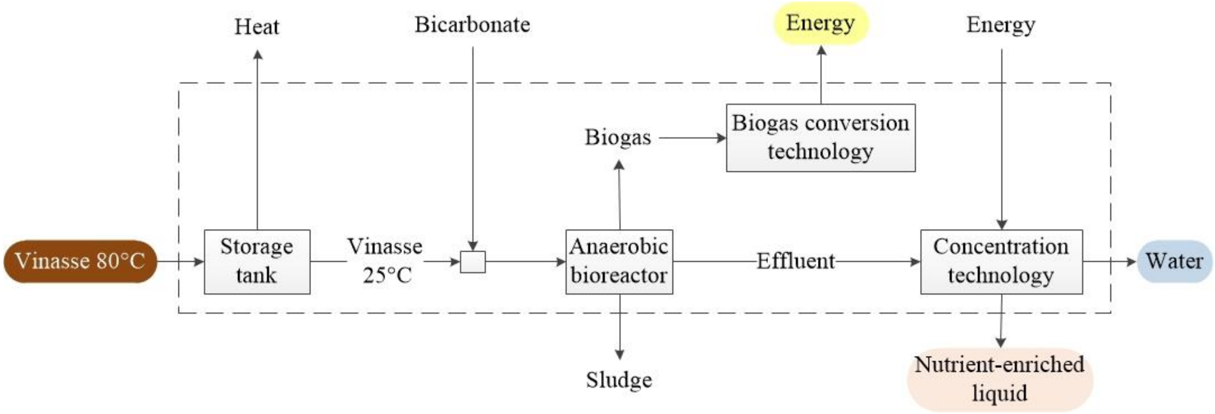
- Alternative 1: Anaerobic Digestion + Evaporation;
- Alternative 2: Anaerobic Digestion + Reverse Osmosis;
- Alternative 3: Anaerobic Digestion + Forward Osmosis + Evaporation;
- Alternative 4: Anaerobic Digestion + Forward Osmosis + Reverse Osmosis;
- Alternative 5: Anaerobic Digestion + Forward Osmosis + Membrane Distillation.

It can be observed that all alternatives include anaerobic digestion (AD) as an energy pathway, from the burning of methane present in biogas. The difference among them lies in the concentration stage for water recycling and production of a nutrient enriched liquid that would be redirected to fertigation (Figure 17).

For the concentration phase, evaporation was considered as equipment traditionally found in the sugarcane industry and membrane processes (reverse osmosis, forward osmosis and membrane distillation) as a novel approach.

Thus, material and energy balances were carried out for each alternative, firstly at the component level, and so on, for the global flowchart, as will be seen in Section 3.2. The balances for the anaerobic bioreactor and aspects in the conversion of biogas to energy forms will be discussed in Subsection 3.2.1. The balances for the concentration methods will be described from Subsections 3.2.2 to 3.2.4.4.

Figure 17 – Scheme of the vinasse biorefinery concept and its main inputs and outputs.



Source: Present author.

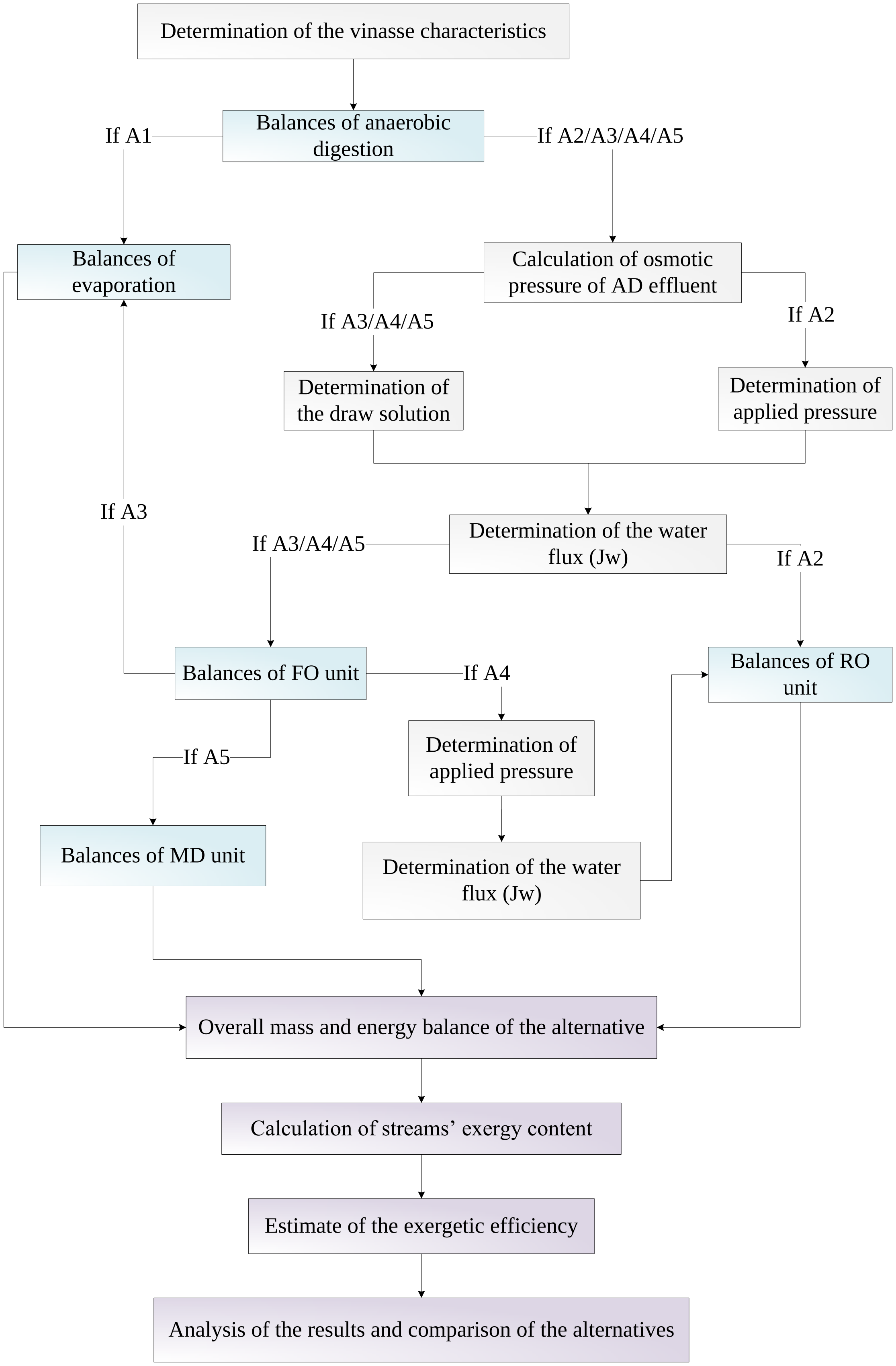
The exergy analysis, previously explained in Section 2.5.1, was used to determine the exergy content of the streams. From this method, which will be described in more detail in Section 3.3, the exergy efficiencies were observed that were the basis for the comparison of the different designs of biorefinery considered.

Thus, this chapter presents the outline of the methodology used. The study includes a description of the mass and energy balances for each alternative, the determination of the parameters used as input of the equations and the exergy calculation method, as can be seen in the next sections.

3.1 OUTLINE OF THE STUDY

In general, the flowcharts had vinasse as input of the anaerobic digestion unit and its effluent (AD effluent) was the feed for the concentration stage. Ultimately, other material and energy streams comprise the running of each process, which was analyzed by using local and global balances. It was essential to examine the overall boundary of the alternatives to supplement the exergy analysis. Figure 18 shows the outline of this study, which is explained in the following topics.

Figure 18 – Scheme of the methodology performed.



Source: Present author.

3.1.1 Characterization of vinasse

Firstly, it was necessary to determine the inorganic and organic content of the feed. The concentrations of the components in vinasse were obtained from a study carried out by Alves (2015) and from information provided by Valéria Del Nery (PhD), who operated a UASB vinasse bioreactor, as described in Section 1.2 (page 24). Thus, the reference values used as input data of the balance sheets are presented in Table 6.

Table 6 – Reference values used to characterize the vinasse.

Parameter	**Concentration**	**Parameter**	**Concentration**
COD raw (mg COD L^{-1})	19220	Nitrate (mg NO_3-N L^{-1})	441
Total solids (mg TS L^{-1})	14570	Total Kjeldahl Nitrogen (mgN L^{-1})	345
Total suspended solids (mg TSS L^{-1})	2210	Calcium (mg Ca L^{-1})	540
Total volatile solids (mg TVS L^{-1})	9340	Iron (mg Fe L^{-1})	39
Volatile suspended solids (mg VSS L^{-1})	1880	Magnesium (mg Mg L^{-1})	237
Ethanol (mg C_2H_6O L^{-1})	148	Sodium (mg Na L^{-1})	277
Phenol (mg C_6H_5OH L^{-1})	0.688	Potassium (mg K L^{-1})	1470
Acetic acid (mg $C_2H_4O_2$ L^{-1})	334	Zinc (mg Zn L^{-1})	1.291
Propionic acid (mg $C_3H_6O_2$ L^{-1})	46	Nickel (mg Ni L^{-1})	0.482
Butyric acid (mg $C_4H_8O_2$ L^{-1})	38	Chromium (mg Cr L^{-1})	0.052
Valeric acid (mg $C_5H_{10}O_2$ L^{-1})	15	Manganese (mg Mn L^{-1})	5.61
Sulfate (mg SO_4^{2-} L^{-1})	648	Lead (mg Pb L^{-1})	0.4
Sulfide (mg S^{2-} L^{-1})	3.04	Cadmium (mg Cd L^{-1})	0.032
Orthophosphate (mg PO_4^{3-} L^{-1})	102	Iron (mg Fe L^{-1})	59.8
Ammoniacal nitrogen (mg NH_3-N L^{-1})	45	Manganese (mg Mn L^{-1})	5.61
		Cooper (mg Cu L^{-1})	0.363

Font: Data from Del Nery (2017) and Alves (2015).

It was considered that the temperature for raw vinasse was 80°C. As the composition of vinasse can be highly inconstant, some parameters were varied in order to assess the sensibility analysis regarding different operating conditions of the following alternatives:

- Flowrate of vinasse: 30 – 100 kg s^{-1};
- COD: $15 \cdot 10^3 – 45 \cdot 10^3$ mg L^{-1};
- Total dissolved solids: $10 \cdot 10^3 – 45 \cdot 10^3$ mg L^{-1}.

Independent random variations for these parameters were considered. Total dissolved solids were varied in order to represent the brix of vinasse, a measure commonly used in the sugarcane industry (KIMBALL, 1991).

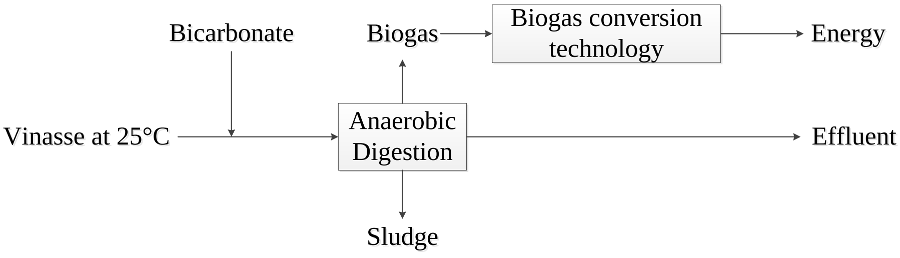
3.2 MASS AND ENERGY BALANCES

Knowing that it was first necessary to make a balance of the sub-units, each stage of the biorefinery has a sequence of calculations that include inputs and outputs within the boundaries and intrinsic transformations of the unit considered. The balances were done considering a continuous and steady-state regime.

3.2.1 Anaerobic digestion and biogas conversion

All the alternatives considered in this study included an anaerobic digestion unit. Thus, the balance of the anaerobic digestion unit is shown in Figure 19.

Figure 19 – Scheme of balance of anaerobic digestion unit.



Source: Present author.

Considering a mesophilic operation for anaerobic digestion, a storage tank to cool vinasse, initially at 80°C, until ambient temperature of 25°C was suggested. Although the mesophilic range can operate between 20 and 40°C (CHERNICHARO, 2007), this temperature was proposed to suit the ambient conditions established by Szargut (1989) of 25°C and atmospheric pressure of 1 atm. These conditions are essential for the exergy calculation involved in the currents of the system, as will be explained later.

It was considered that the inorganic content in vinasse is transformed by methanogenic nutritional requirements as presented by Chernicharo (2007) equations, shown in Appendix E (topic a). Besides that, it was assumed that sulfate was converted into hydrogen sulfide (H_2S) by sulfate reducing bacteria following the equation (BOYD, 2015):

$$SO_4^{2-} + 8e^- \rightarrow H_2S \tag{13}$$

In a study by Alves (2015), the use of sodium bicarbonate to adjust the pH in the reactor at a proportion of 0.3 g$NaHCO_3$ per gCOD was considered. Thus, this balance incorporated the presence of $NaHCO_3$ according to the following acid-base reaction:

$$\underset{\text{acetic acid}}{C_2H_4O_2} + \underset{\text{sodium bicarbonate}}{NaHCO_3} \rightarrow \underset{\text{sodium acetate}}{NaC_2H_3O_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} \tag{14}$$

Bearing in mind that most of the responses in the anaerobic system involve the presence of acetate, only this compound was weighed in the acid-base reaction.

For the organic material balance, phenol was considered as an inert element, and therefore the concentration of this component in the final effluent remains the same as the initial vinasse. For volatile acids and ethanol, it was assumed that the remaining value in the effluent would be the amount consumed for methane production. The efficiency of organic removal was varied in a range of 60-80%, based on results from the experiments performed by Barros et al. (2017), Barros, Duda and Oliveira (2016) and España-Gamboa et al. (2012).

The microorganisms formed within the process leave the system in the sludge stream, as explained in Appendix E (topic b).

3.2.1.1 Conversion of biogas into forms of energy.

Methane production was calculated from the equations shown in Appendix E (Topic c). The estimate made considered that 60% of the biogas consists of methane, 39% of CO_2 and 1% of H_2S, which are approximately the values presented by Salomon et al. (2011).

It is worth pointing out that biogas cleaning is a process intrinsically embedded in the conversion into energy step for any established configuration. As the objective of this work is to make a comparison among different forms of concentration, it was considered that the biogas cleaning technology would be the same for all alternatives. Thus, its analysis would not interfere in the final comparative study, and therefore, was not included in the balances.

However, it is possible to have an understanding about the performance of the different methods of biogas cleaning by analysing Barrera et al. (2013) and Barrera et al. (2016). These authors compared different ways of removing sulfate from the biogas generated from the anaerobic digestion of vinasse: absorption into ferric chelates of EDTA (ethylenediaminetetraacetic acid), absorption into ferric sulfate solutions and bio-oxidation with air oxygen addition. The authors concluded that the best alternative for biogas cleaning was bio-oxidation with added air oxygen, which represented an exergy efficiency of 98%.

Biogas conversion into energy requires implementing some kind of technology, such as internal combustion engines, combustion gas turbines or boiler steam turbines. The present work considers a spark-ignition engine, as cited in the research by Barrera et al. (2016), who analyzed different ways of converting biogas from vinasse. For this type of technology, electrical and thermal efficiencies of 41 and 46% (based on the lower heating value (LHV)), respectively, can be achieved (US EPA; CHP EPA, 2017).

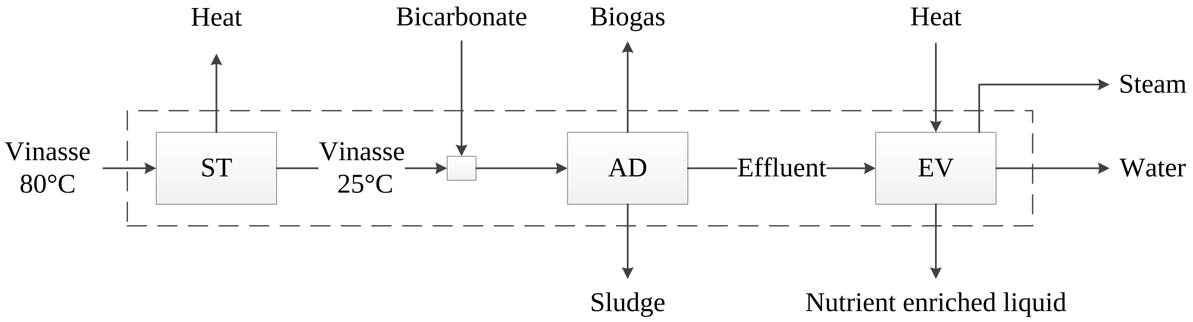
3.2.1.2 The osmotic pressure of AD effluent

The composition of anaerobic digestion effluent is meaningful for the quantification of its osmotic pressure, an essential parameter for membrane system balances. After balances in the AD, calculating the consumption of nutrients and organic matter, the number of moles of each component in the effluent was obtained. By using the van’t Hoff equation presented in Appendix D (Table 17), the osmotic pressure of the AD effluent was estimated.

3.2.2 Alternative 1: Evaporation

The concentration method used in Alternative 1 was the multi-effect evaporation as shown in Figure 20.

Figure 20 – Balances of Alternative 1.



ST – storage tank; AD – anaerobic digestion; EV – evaporation.

Source: Present author.

The traditional design of the multi-effect evaporator used in sugarcane mills was considered with 5 effects, temperature and pressure of the first effect of 115°C and 1.69 bar, respectively. The balances at this stage included analysing the vapor and liquid streams. In order to simplify this analysis, it was considered that the vinasse has the same thermodynamic properties as the water. The detailed calculation method of the multi-effect evaporator is presented in Appendix B.

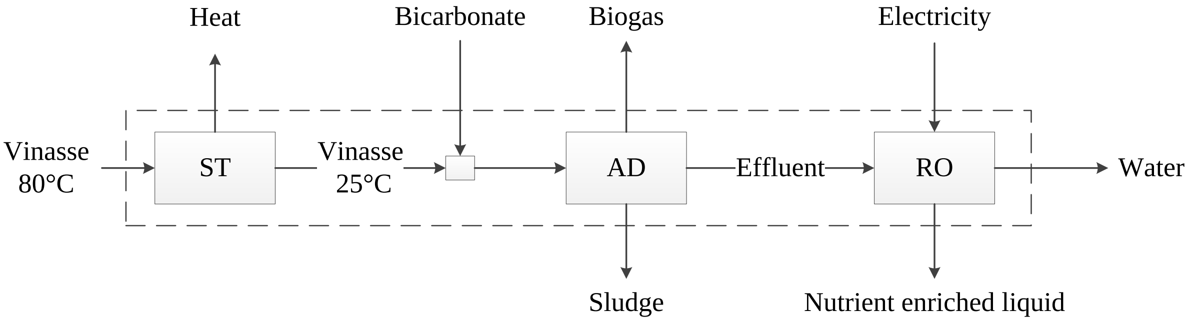
Usually, evaporator balances in the sugarcane industry involve the Brix indicator as a parameter to determine the concentration of solids contained in the solution. Thus, the index Brix (1g of solute for 100g of solution) can be used to express the total solids concentration in the liquid.

It is important to highlight that the sugarcane industrial plant has many flow streams of vapor, for example, from juice evaporation, distillation and sugar boiling units (ENSINAS et al., 2007). This excess vapor can be reused as a heat source for the anaerobic digestion effluent (AD effluent) evaporators. Thus, the amount of energy required for the evaporation system was determined to achieve water recovery in the range of 20-80%.

3.2.3 Alternative 2: Reverse Osmosis

Reverse Osmosis was the concentration technology adopted in Alternative 2 (Figure 21).

Figure 21 – Balances of Alternative 2.

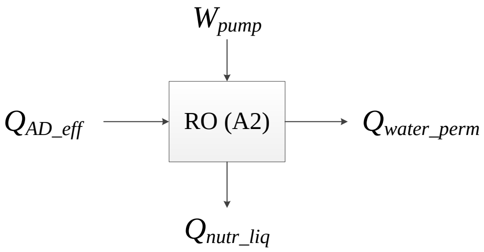


ST – storage tank; AD – anaerobic digestion; RO – reverse osmosis.

Source: Present author.

Firstly, the water flux and concentration were calculated considering the concentration polarization effect, using the equation presented in Appendix D (Table 18). The balance for the reverse osmosis unit considered the scheme shown in Figure 22.

Figure 22 – Balance of reverse osmosis unit of Alternative 2.



RO (A2) – Reverse Osmosis unit in Alternative 2.

Source: Present author.

Thus, the equations used were:

$$Q_{AD\_eff} = Q_{vinasse} - Q_{sludge} \tag{15}$$

$$Q_{water\_perm} = Jw \cdot S_{membrane} \tag{16}$$

$$Q_{nutr\_liq} = Q_{AD\_eff} - Q_{water\_perm\_RO} \tag{17}$$

$$W_{pump} = \Delta P \cdot Q_{AD\_eff} / (3.6 \cdot 10^{6}) \tag{18}$$

Where:

Q_{AD_eff} = AD effluent flowrate (m^3 h^{-1});
$Q_{vinasse}$ = Vinasse flowrate (m^3 h^{-1});
Q_{sludge} = Volumetric sludge production (m^3 h^{-1});
Q_{water_perm} = Flowrate of water that permeates the membrane (m^3 h^{-1});
Jw = Transmembrane water flux (m h^{-1});
Js = Transmembrane solute flux (m h^{-1});
$S_{membrane}$ = Membrane area (m^2);
Q_{nutr_liq} = Nutrient enriched liquid flowrate (m^3 h^{-1});
W_{pump} = Work done by the pump (kW);
ΔP = pressure applied (Pa).

The energetic balance refers to the power entering the unit to promote the separation. As was done for evaporation, the input energy quantification was determined by the trial and error method in order to achieve 20-80% of water recovery.

3.2.4 Alternatives 3, 4 and 5: Forward Osmosis + draw solution regeneration method

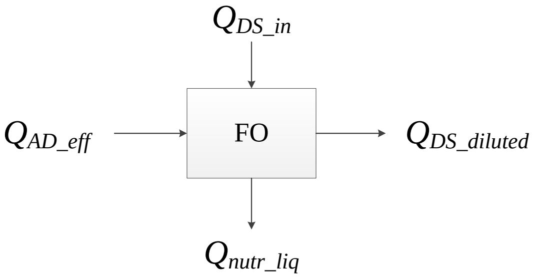
3.2.4.1 Forward Osmosis

Alternatives 3, 4 and 5 were designed using a forward osmosis process coupled with a regeneration method of the draw solution. Therefore, an essential factor that must be considered in this process is the determination of the draw solution.

At first, NaCl was regarded as a draw solution in the calculation phase because it is a well-studied solution widely used to develop transmembrane flux models for forward osmosis. However, a more in-depth discussion on the draw solution to be applied in the sugarcane industry will be presented in the results and observations in Chapter 4.

Initially, water and reverse fluxes in the forward osmosis process were calculated by using equations presented in Appendix D (Table 19). In this case, there is no external energy consumption. The flow is governed by the potential chemical difference between the solution and the feed. The balance for this unit followed the scheme in Figure 23.

Figure 23 – Balance for forward osmosis unit of Alternatives 3, 4 and 5.



FO – Forward Osmosis.

Source: Present author.

Then,

$$Q_{DS\_in} = Q_{water\_perm} \tag{19}$$

$$Q_{DS\_\text{diluted}} = Q_{DS\_in} + Q_{water\_perm} \tag{20}$$

Q_{AD_eff} = AD effluent flowrate (m³ h^{-1}) – equation (15);
Q_{nutr_liq} = Nutrient enriched liquid flowrate (m³ h^{-1}) – equation (17).
Q_{DS_in} = Flowrate of the draw solution flowrate entering in FO unit (m³ h^{-1});
$Q_{DS\_diluted}$ = Flowrate of diluted draw solution leaving the unit (m³ h^{-1}).

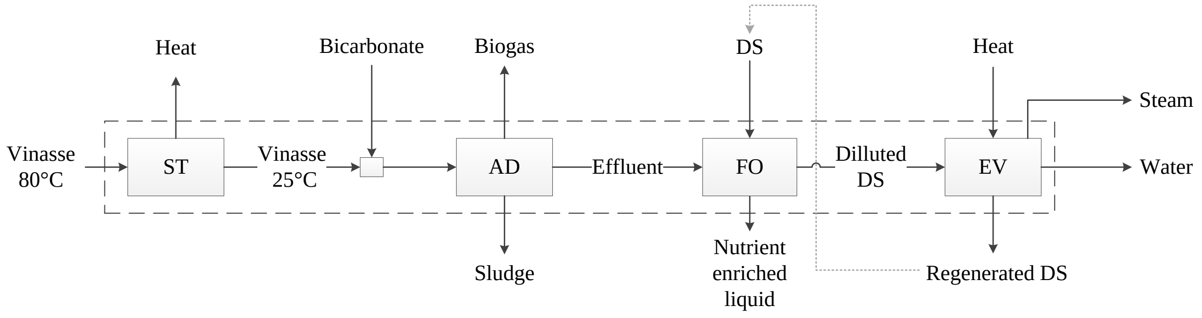
As can be observed, the draw solution is mixed with water that permeates the forward osmosis membrane, thus it generates a diluted draw solution stream that should be regenerated if a recycle is desired.

The regeneration methods analysed were evaporation (Alternative 3), reverse osmosis (Alternative 4) and membrane distillation (Alternative 5). These technologies after FO also require forms of energy as input, which were determined to ensure the total regenerate of the draw solution, representing 50% of recovery rate in relation to the diluted draw solution flowrate.

3.2.4.2 Alternative 3: Evaporation

Evaporation was the regeneration method of Alternative 3 (Figure 24).

Figure 24 – Balance of Alternative 3.



ST – storage tank; AD – anaerobic digestion; FO – forward osmosis; EV – evaporation; DS – draw solution.

Source: Present author.

The balances for this evaporation system followed the same principles applied in Alternative 1 (A1), using the calculation method described in Appendix B (page 133). The difference of evaporation in A1 and A3 are the feed and the concentrate so that:

- A1 evaporator unit: feed = effluent of anaerobic digestion (AD effluent); concentrated = nutrient enriched liquid (Figure 20);
- A3 evaporator unit: feed = diluted draw solution (DS diluted); concentrated = regenerated draw solution (Figure 24).

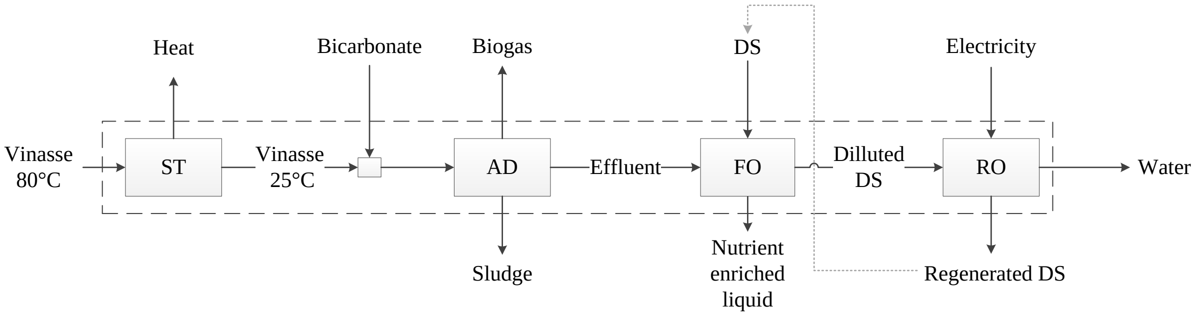
3.2.4.3 Alternative 4: Reverse Osmosis

In Alternative 4, the regeneration method was the reverse osmosis (Figure 25).

As for Alternative 2 (A2), the equations presented in Appendix D (Table 18) and section 3.2.3 (equations (15) to (18)) were applied in the balances of Alternative 4 (A4). The difference between RO in A2 and A4 lies in the feed and the concentrated streams:

- A2 RO unit: feed = effluent of anaerobic digestion (AD effluent); concentrated = nutrient enriched liquid (Figure 21);
- A3 evaporator unit: feed = diluted draw solution (DS diluted); concentrated = regenerated draw solution (Figure 25).

Figure 25 – Balance for Alternative 4.



ST – storage tank; AD – anaerobic digestion; FO – forward osmosis; RO – reverse osmosis; DS – draw solution.

Source: Present author.

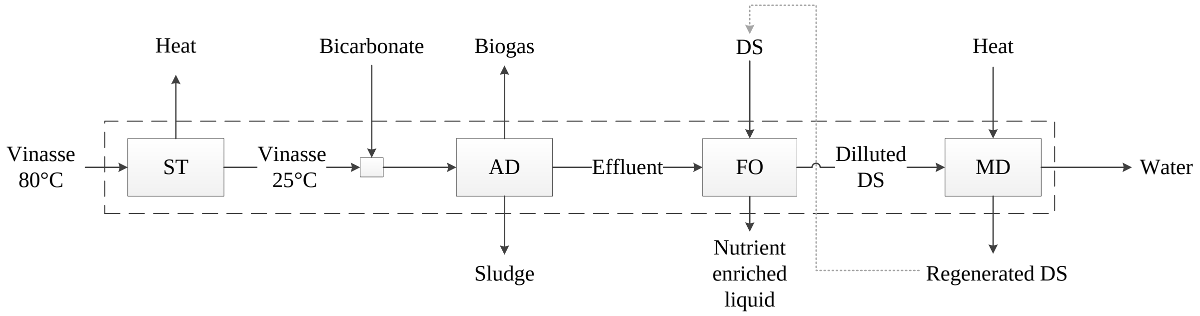
3.2.4.4 Alternative 5: Membrane Distillation

Alternative 5 shows a membrane distillation system as a regeneration method, which requires low grade energy in the form of heat to promote the separation between water and the draw solution (Figure 26).

Unlike evaporation and reverse osmosis, which was used as the main concentration methods, membrane distillation was considered only as a regeneration method of the draw solution. The set of equations used to evaluate the MD process is presented in Appendix D

(Table 20), including the calculation method to determine the energy consumption in the system.

Figure 26 – Balance for Alternative 5.



ST – storage tank; AD – anaerobic digestion; FO – forward osmosis; MD – membrane distillation; DS – draw solution.

Source: Present author.

3.3 EXERGY CALCULATION

The exergy of streams was calculated bearing in mind the environmental reference established by Szargut (1989), with a temperature of 25°C and pressure of 1 bar. The equations used in this step can be found in Section 2.5.1.

As pointed out by Veziroğlu et al. (1990), since the streams are close to the ground, the potential energy (which is the same as the potential exergy) is small. Similarly, kinetic exergy can be neglected. Therefore, for the material flows, the kinect and gravitational exergies were neglected as these exergies are orders of magnitude lower than the exergies due to heat and chemical energies. This means that only the thermomechanical and chemical plots were considered in determining the exergy of the mass currents. For energy streams, the heat and work exergy were weighed.

Table 7 presents the classification of the streams. For matter flows, the exergy was calculated by using equations (5), (6) and (7). Exergies of heat and work streams were determined by equations (8) and (9), respectively. Details of the exergy calculation of the streams are presented in Appendix G.

Table 7 – Classification of the streams.

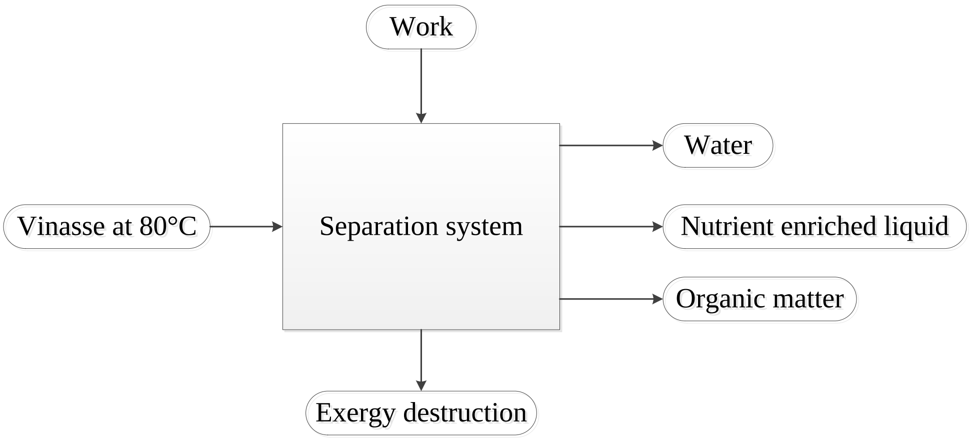
Classification	Stream
Matter	Vinasse at 80°C
	Vinasse at 25°C
	Bicarbonate
	Anaerobic digestion effluent
	Sludge
	Biogas
	Draw solution
	Diluted draw solution
	Regenerated draw solution
	Nutrient-enriched liquid
	Recovered water
Heat	Input heat of evaporation
	Input heat of membrane distillation
	Output heat from biogas conversion
Work	Input power of reverse osmosis
	Output power from biogas conversion

After calculating the exergies of the streams, the exergy efficiency of each unit was performed, followed by the overall alternative, as described in Subsection 2.5.1.5. The variables and parameters used in the calculation methods can be found in Appendix H.

3.3.1 Partial exergy of separation

The exergy of separation is the least amount of useful mechanical energy needed to separate all the components of a mixture. Partial exergy is the amount of useful work demanded to promote the separation of a portion of the components (KOTAS, 1985). Accordingly, the work required to separate water and organic matter (which would be equivalent to organic matter removal by the anaerobic bioreactor) from vinasse was calculated (Figure 27).

Figure 27 – Hypothetical separation system of the components.



Source: Present author.

The exergy of partial separation was determined as a measure of comparison among the different processes chosen in this study so that it follows the condition:

$$\text{Exergy efficiency of separation} > \text{Exergy efficiency of the process} \tag{21}$$

3.4 CONSIDERATIONS ABOUT THE METHODOLOGY

The presented models were adopted in order to represent the processes considered in this study in a more general perspective, since the objective was to promote an overall analysis of the system. This type of approach is convenient in studies involving decision-making as it uses more direct mathematical methods, but sufficiently representative.

The application of more detailed models, which require considering a large number of variables and computational resources, is usually used in more specific analyses, for example, to design and control the unit of interest. In this case, it is essential to specify, for example, the hydrodynamic and biological characteristics of the reactor or the type of material used in the membrane.

4 RESULTS AND DISCUSSIONS

This chapter presents the correlation among the observed parameters, local and global balances, and the exergy efficiencies of the configurations studied. The alternatives were compared in order to analyze the best opportunities in the resource recovery concept. In addition, study scenarios presented in the literature to evaluate the interference of implementing the vinasse biorefinery in the scope of the sugarcane industry were considered.

4.1 ANALYSIS OF THE METHANE PRODUCTION PATHWAY

Initially, some parameters were compared with the values found in the literature in order to verify the representativeness of the balances used assuming that:

- the osmotic pressure was analyzed using the characterization of anaerobic digestion effluent presented in Appendix I (page 163);
- the biogas production estimated was compared with values found by Bernal et al. (2017). The validation considered 59.20 10^3 $m^3_{vinasse}$ year^{-1}, 60% of methane in biogas, 21 kg COD m^{-3}, and 74% of removal efficiency of COD in a UASB reactor;
- the exergy efficiency of anaerobic digestion to treat vinasse was presented by Barrera et al. (2016), in which the initial COD was 48 kg COD m^{-3};
- the specific exergy of vinasse found by Palacios-Bereche et al. (2013) was calculated for a vinasse at a temperature of 75°C of and 136.6 kg/s of flowrate.

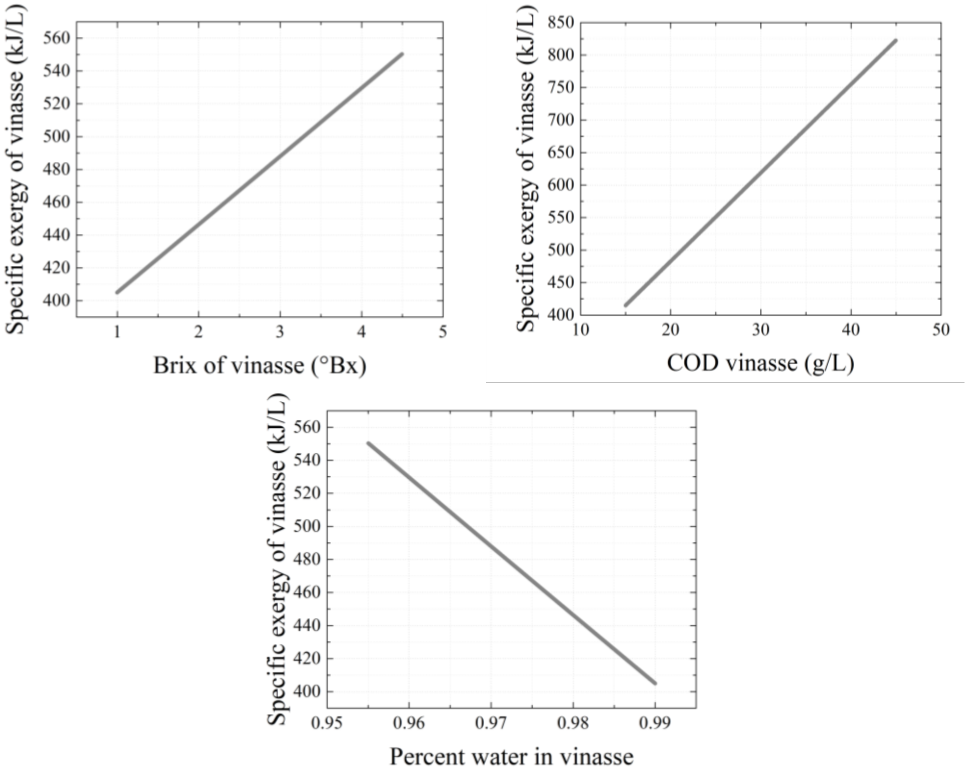
Thus, the comparisons among the references and implemented model values are shown in Table 8. The calculated results approached 98%, 94%, 96% and 99% of the reference values for osmotic pressure of AD effluent, biogas production, exergy efficiency of AD and specific exergy of vinasse, respectively. It indicates the representativeness of the models in this type of analysis.

Table 8 – Validation of balances for energy pathway.

Parameter	**Present work**	**Reference value**	**Relative error**	**Reference**
Osmotic pressure of the AD effluent (MPa)	0.42	0.41	0.02	Calculated using data presented in Appendix I.
Biogas production (10^3 m^3 $year^{-1}$)	287	304	0.06	Bernal et al. (2017)
Exergy efficiency of AD (%)	82	85	0.035	Barrera et al. (2016)
Specific exergy of the vinasse (kJ/kg)	443	443	0	Palacios-Bereche et al. (2013)

From the characterization of the vinasse, the relationship between its composition and its exergy content was observed (Figure 28). As expected, specific exergy of vinasse increases with the concentration of solids, represented by brix and COD, emphasizing that the pollutant load reflects the deviation from the environment. In contrast, exergy content of vinasse diminishes as the percentage of water increases.

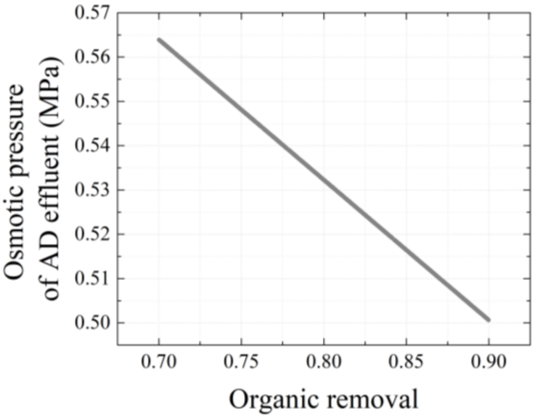
Figure 28 – Correlation among the characteristics of vinasse at 80°C.



Source: Present author.

After balances involving organic matter and nutrient consumption by microorganisms in an anaerobic bioreactor, the osmotic pressure (OP) of the anaerobic digestion effluent (AD effluent) was estimated. Figure 29 shows that the osmotic pressure of AD effluent diminishes with the increase in the organic removal as it refers to a decrease in the concentration of solids in the liquid.

Figure 29 – Relationship between organic removal and osmotic pressure of AD effluent.



Considerations: 70 $kg_{vinasse}$ s^{-1}; 1.2°Bx raw vinasse.

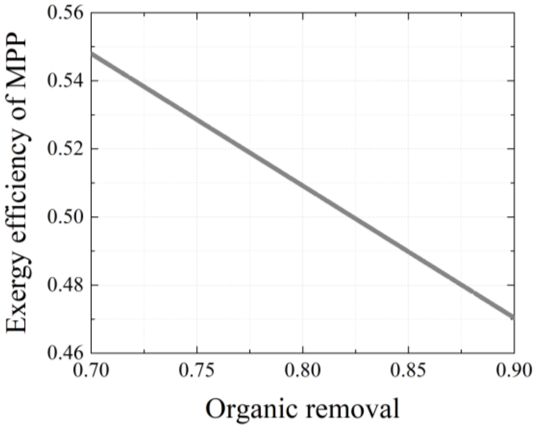
Source: Present author.

Analyzing the osmotic pressure of the AD effluent is important because this parameter is essential for the design and behavior of the membrane processes. It is understood that the lower the osmotic pressure of the AD effluent, the lower its solids concentration. Therefore, this would facilitate the transmembrane flux of water, requiring less potential of driving forces or even smaller areas of the membrane. Thus, it can be observed that the efficiency of the anaerobic bioreactor can directly interfere in the posterior membrane process.

Therefore, the methane production pathway (MPP) was analyzed, including a storage tank (ST), anaerobic digestion (AD), and a technology which converts biogas into energy (BC). By performing the exergy analysis for this stage, it was observed that exergy efficiency diminishes with the variation in organic removal (Figure 30).

This behavior can be explained considering that the degradation by microorganisms increase the entropy of the system, making it an irreversible process. Appendix J (page 165), which comprises the main reactions of anaerobic digestion phases showing the free energy for each stoichiometric equation, explains this statement.

Figure 30 – Exergy efficiency of methane production pathway varying COD and organic removal.

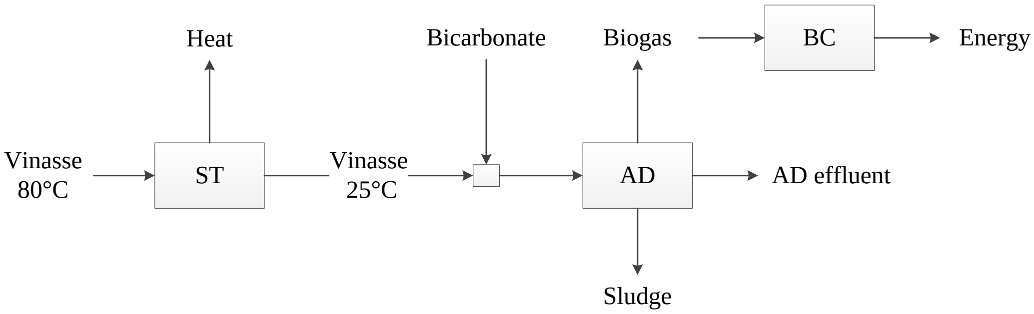


MPP: methane production pathway.

Source: Present author.

In order to evaluate a specific scenario, the case was considered where the operational conditions of the biorefinery would be: vinasse with 1.2°Bx, 70 $kg_{vinasse}$ s^{-1} and 70% of organic removal. The currents shown in Figure 31 were considered in the balances of the methane production pathway, which were carried out following the methodology explained in Section 3.2.1 (page 73) and Appendix E.

Figure 31 – Balance for methane production pathway.



ST – storage tank; AD – anaerobic digestion; BC – biogas conversion.

Source: Present author.

The specific exergies of the streams were calculated according to the steps explained in Section 3.3 (page 82) and Appendix G. Therefore, the estimated streams for this scenario are presented in Table 9.

Table 9 – Streams of the balance of methane production pathway.

Stream	**Flowrate**	**Specific exergy (kJ/L)**
Vinasse at 80°C	252 m³/h	472.14
Vinasse at 25°C	252 m³/h	363.62
Bicarbonate	0.65 m³/h	1.48
Sludge	17.46 m³/h	60.41
AD effluent	234.54 m³/h	224.87
Biogas	1067.3 Nm³/h	23.64

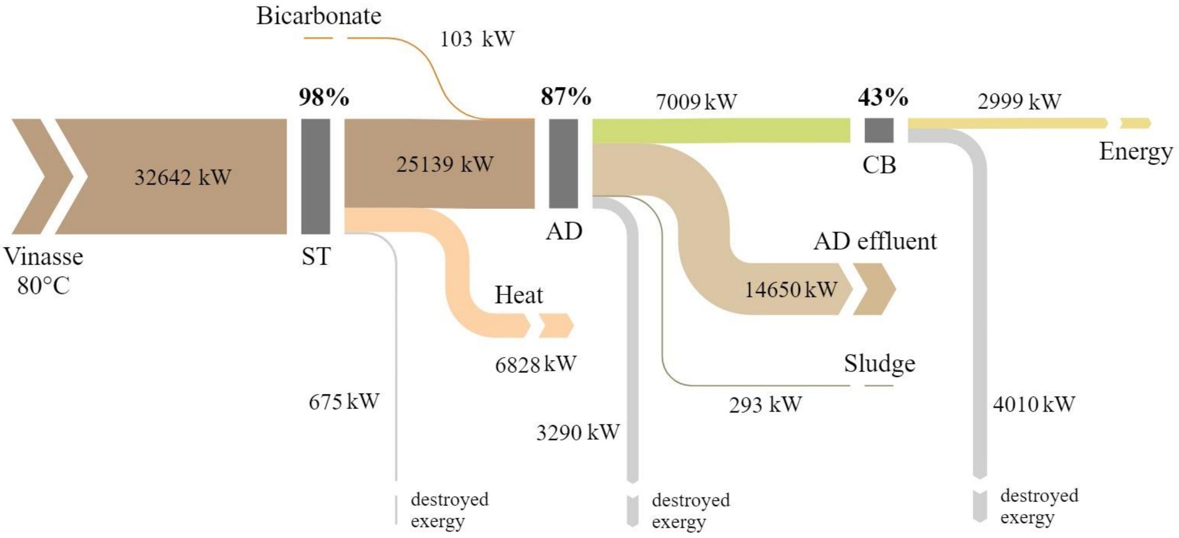
The results showed that the exergy of vinasse at 25°C corresponds to 77% of exergy content of vinasse at 80°C. This difference in the exergy content concerns the variation in temperature, where heat leaves the stream. In this case, there is exergy destruction of 7503kW in the storage tank, which accounts for 77% of exergy efficiency (Figure 32).

The AD effluent comprises higher specific exergy content amongst the outputs (AD effluent, sludge and biogas) since it contains significant concentrations of remaining nutrient and organic matter, important to be used in fertigation. It is worth mentioning that sludge is also a rich stream in water and biomass, resulting in the substantial 60 kJ/L of exergy content. Biogas comprises 23.64 kJ/L or 31,520 kJ/kg of specific exergy, which was close to the value found by Palacios-Bereche et al. (2013) of 30,233 kJ/kg.

The importance of this specific exergy content of streams is emphasized when the flowrates are observed, representing the total exergy entering and leaving the system. Figure 32 and Figure 33 show the schematic diagrams for the methane production pathway considering the last scenario (vinasse at 1.2°Bx, 70 $kg_{vinasse}\ s^{-1}$ and 70% of organic removal).

As pointed out previously, in the storage tank, commonly used in sugarcane industries to stock the effluent before fertigation, vinasse loses a low grade heat that accounts for 21%.

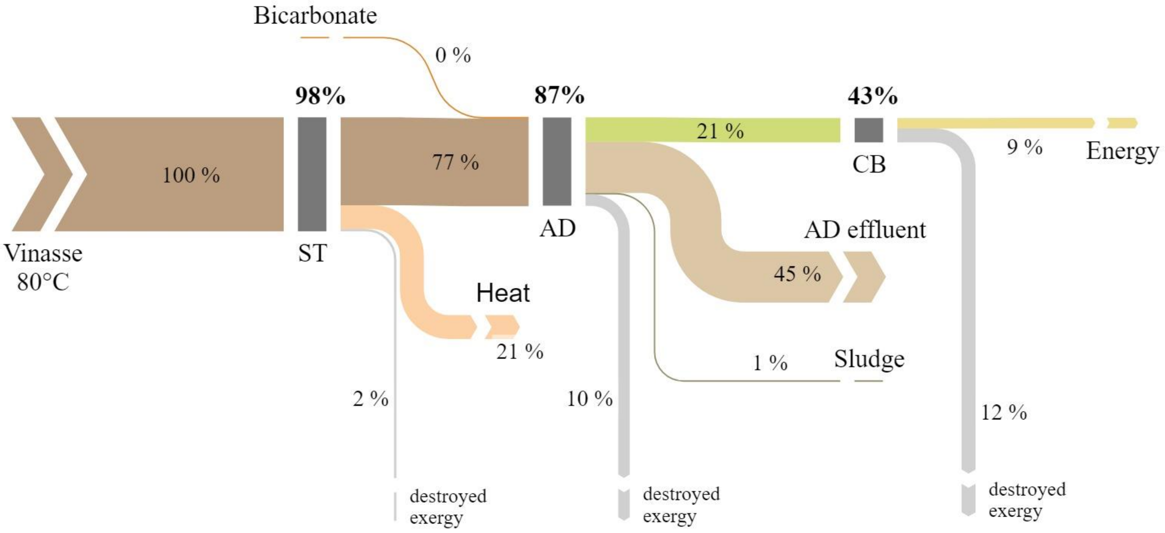
Figure 32 – Sankey diagram of energy pathway in kW.



ST: storage tank; AD: anaerobic digestion; BC: biogas conversion.

Source: Present author.

Figure 33 – Sankey schematic diagram in percentage.



ST: storage tank; AD: anaerobic digestion; BC: biogas conversion.

Source: Present author.

Bicarbonate accounts for merely 0.31% of the total exergy input in the methane production pathway. The AD effluent represented the stream with higher exergy content, 45% regarding inputs. The exergy efficiency of anaerobic digestion was 87%. The 10% of exergy destruction can be related to the irreversibilities associated with that process.

A unit of biogas conversion to heat and power was considered by using a spark-ignition engine. In this case, the electrical and thermal conversion efficiencies were 41 and 46%. As a result, the estimate in the methodology used in this study accounted for 43% of exergy efficiency for the biogas conversion to energy technology. This result is equivalent to the value presented in the research by Barrera et al. (2016), which also analyzed a spark-ignition engine to convert biogas from vinasse.

Thus, in the scenario studied in this research (see Figure 32 and Figure 33), 9% of exergy leaves the system as energy, in which 53% is in the form of heat (1585.8 kW) and 47% is electricity (1413.4 kW).

Therefore, the estimated exergy efficiency of the overall methane production pathway, including the storage tank, anaerobic bioreactor and biogas conversion technology was 76%. The improvement in the efficiency of this stage could be achieved by using heat from the storage tank and by enhancing biogas conversion technologies.

4.2 EVALUATION OF THE CONCENTRATION METHODS

4.2.1 Evaporation

The calculation method for the evaporators were validated considering the 5 multiple-effect evaporator of vinasse studied by Carvalho and Silva (2011). Considering 105 m³/h of vinasse and an initial solid content of 4.5°Bx, the authors achieved a final brix of 21.44 recovering 78% of the water. For the same conditions, the equations used to simulate the evaporators in this study reached the final brix of 20.5, which represents a suitable approximation of 95% of the reference value.

A study conducted by Costa et al. (2016) was also used as reference. The authors studied a 4 multi-effect evaporator of vinasse with 86.65 kg/s and 1.69°Bx; the results showed that for 90% of water recovery, the final brix was 6.9 for a concentrated flowrate of 21.09 kg/s. Using the same characteristics, the models used here provided a value of 6.9°Bx with a flowrate of 21.22 kg/s, representing an acceptable relative error of 0.006. It is important to emphasize that the low value of final brix in the study by Costa et al. (2016) was related to the small availability of steam to the evaporation process in the industrial scenario evaluated by these authors.

Therefore, this study analyzed the variation of parameters such as COD, heat consumption by the evaporator, biogas production and exergy efficiency of the evaporator. Establishing a scenario in that brix of vinasse was 1.2°Bx, flowrate of 70 kg/s and 70% of water recovery. The results can be seen in Table 10.

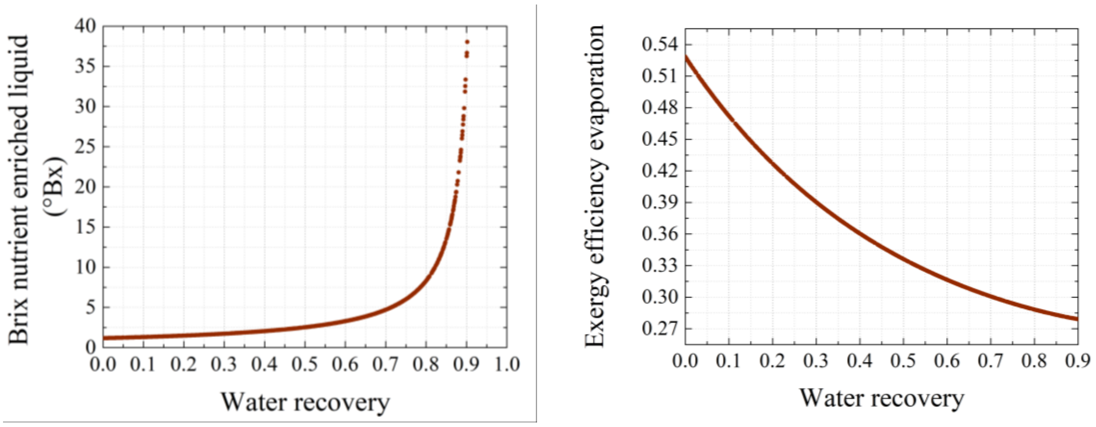
Table 10 – Variation of some parameters of the system with evaporation (Alternative 1).

Vinasse COD g/L	**Biogas flowrate** Nm^3/h	**Brix of the AD effluent** g solids/100g effluent	**Heat consumption** kW	**Exergy efficiency of Alternative 1**
10	555.32	0.90	42628	0.24
15	832.97	1.05	42276	0.26
20	1110.6	1.19	41923	0.27
25	1371.1	1.33	41570	0.28
30	1665.9	1.47	41216	0.28
35	1943.6	1.61	40864	0.29
40	2221.3	1.75	40509	0.30
45	2498.9	1.90	40158	0.30

It was observed that the higher the vinasse COD, the greater the exergy efficiency of Alternative 1 (methane production pathway + evaporation). This is because biogas production rises due to the greater amount of organic matter in the vinasse. In addition, it can be seen that less heat is required as AD brix effluent increases due to lower water availability. It is important to emphasize that the brix of anaerobic digestion effluent can be greater than that of the vinasse because of the presence of the sodium acetate formed in the acid-base reaction of the bicarbonate.

Another significant parameter when analyzing the vinasse biorefinery is the brix of nutrient enriched liquid presented in Figure 34, which is the concentrated stream that will be used for fertigation. It is important to note that the water recovery value of the reclaimed water is from the vinasse and not the percentage found in the anaerobic digestion effluent.

Figure 34 – Water recovery, final solids and exergy efficiency of evaporation system.



(a) (b)

Variation of the water recovery with (a) brix of the nutrient enriched liquid; (b) exergy efficiency of the evaporator.

Source: Present author.

As can be observed, the 100°Bx in the nutrient enriched liquid is related to the total removal of water from vinasse. As water recovery increases, more heat is required by the system to promote the separation, and therefore the exergy efficiency decreases.

Considering the same scenario adopted in the methane production pathway (1.23°Bx of vinasse, 70 $kg_{vinasse}$ s^{-1}, 70% of organic removal and 70% of recovered water) the streams obtained in the balance of evaporator are exposed in Table 11.

As can be observed, nutrient enriched liquid has specific exergy content (521.45 kJ/L) higher than vinasse at 80°C (472.14 kJ/L). This is because concentration of inorganic and organic matter in the concentrated stream (4.7°Bx) is higher than in vinasse (1.2°Bx). In this case, the nutrient enriched liquid has 4.7°Bx and 58.14 m³/h flowrate, while the flowrate of vinasse was 252 m³/h. This observation is important because the objective of the concentration phase is to reduce the volume of the liquid to be transported to the sugarcane plantation. Thus, a reduction of 77% of the initial volume of vinasse was achieved.

Table 11 – Streams of the multi-effect evaporator balance.

Stream	Flowrate	Specific exergy (kJ/L)
AD effluent	234.54 m³/h	224.87
Heat	41976 kW	-
Steam	10.72 kg/s	318.5
Water	176.4 m³/h	50
Nutrient enriched liquid	58.14 m³/h	521.45

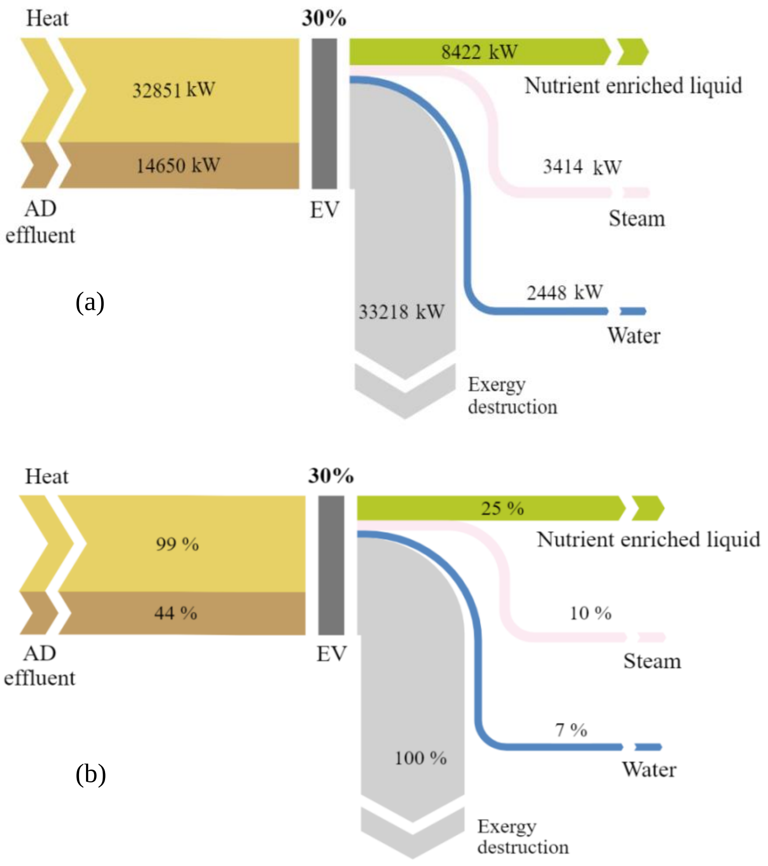
Therefore, the exergy efficiency of the multi-effect evaporator in this scenario was 30%, as presented in Figure 35. The input exergy of heat accounted for 78% of this low grade energy stream (i.e., 41976 kW_{heat} = 32851 kW_{exergy}). The exergy of the AD effluent is 44% smaller than the exergy content of the heat, approximately.

The vapor leaving the evaporator system is an important source of heat that can be recycled back into the industry, with a 3414 kW of exergy content. Nutrient enriched liquid has 8422 kW of exergy and water for recycling 2448 kW.

It must be pointed out that the exergy destruction of 100% shown in the last figure is considered for 143% of inputs. It is equal to 70% of irreversibilities in the multi-effect evaporator. The 33218 kW of loss exergy is higher than the exergy that enters in the system in the form of heat (32851 kW). It indicates that this system presents a low efficiency in the conversion of resources.

Nevertheless, to achieve a suitable higher dry solid concentration of 21°Bx, the system would require 48052 kW of heat (~37606 kW of exergy) to remove 88% of the initial water content, resulting in a concentrated stream of 3.62 kg/s or 13 m³/h, approximately.

Figure 35 – Sankey diagrams for evaporation unit of Alternative 1.



EV: evaporation; (a) balance in kW; (b) balance in percentage.

Source: Present author.

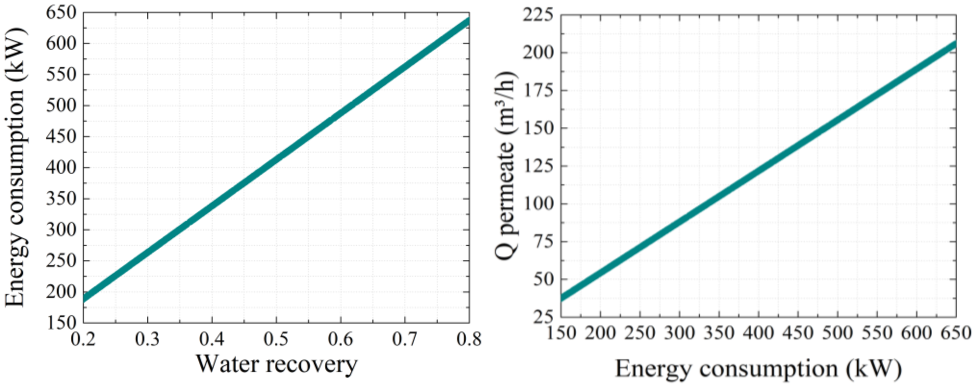
4.2.2 Reverse Osmosis

The reverse osmosis model was validated observing the specific energy consumption. In the research carried out by Ryan et al. (2009), the specific power requirement for a reverse osmosis process, calculated based on an effluent osmotic pressure of 30 bar, was 3.37 kWh/m³ for 70% of water recovery. In this study, the specific energy consumption (SEC) was 3.65 $kWh{\cdot}m^{-3}$ for the same condition, representing 0.08 of relative error or 92% of approximation.

Considering 50% of recovery of water from the anaerobic digestion effluent studied here, the SEC in the RO system was 2.44 $kWh{\cdot}m^{-3}$. This value is coherent with the amount found by Veerapaneni et al. (2011) of 2.5 kWh·m^{-3}. The membrane characteristics considered in this study are presented in Appendix H (page 161).

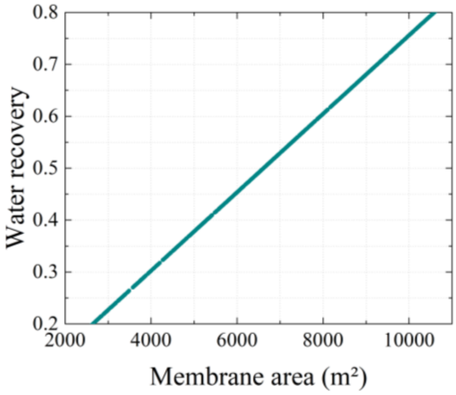
Initially, it is noteworthy that the higher the water recovery, the higher the energy requirement, as can be seen in Figure 36. In this case, 5000 m² of membrane area was considered. However, establishing the constant pump input of 5·10^6 Pa, the variation of the water recovery depends on the increase of the membrane area, as presented in Figure 37.

Figure 36 – Relation among water recovery, permeate flowrate and energy consumption in RO (A2).



Source: Present author.

Figure 37 – Correlation between the area of RO and water recovery.

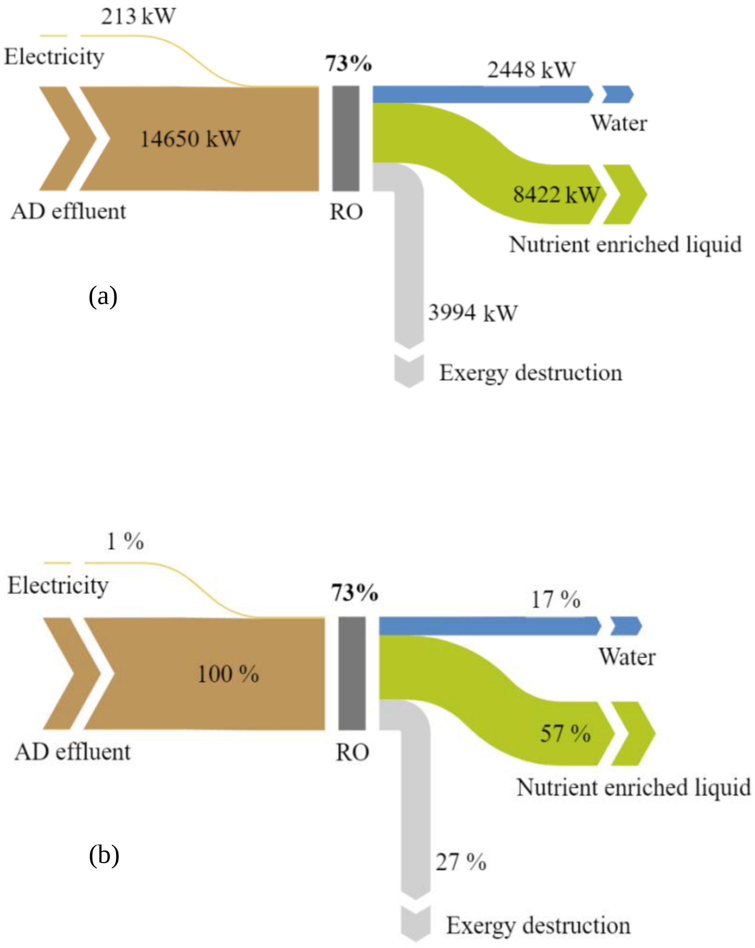


Source: Present author.

To reclaim 70% of water in the same scenario pointed out previously, the reverse osmosis concentration method had 73% of exergy efficiency. In this case, the power requirement of 213 kW represents 1% of the exergy of the input resources (Figure 38). The exergy demand of reverse osmosis corresponds to 0.64% of the one required in Alternative 1 (evaporator) showing that this membrane process tends to be more efficient.

Exergy destruction of 27% in reverse osmosis system could be related to concentration polarization, fouling formation and irreversibilities intrinsic to the process. In the scenario considered in Figure 38, a larger membrane area of 14823 m² was considered aiming to represent the same conditions used in the forward osmosis analysis, as discussed next.

Figure 38 – Sankey diagram of RO (A2).



RO: Reverse Osmosis; (a) balance in kW; (b) balance in percentage.

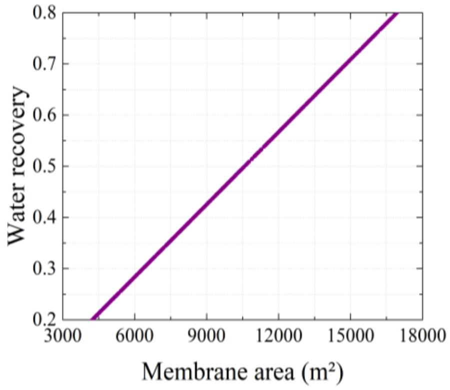
Source: Present author.

4.2.3 Forward Osmosis + Evaporation

Initially, the forward osmosis process was analyzed considering the same membrane characteristics applied to reverse osmosis – water permeability *A*, solute permeability *B*, hydraulic diameter, crossflow and channel length (Appendix H, page 161).

Bearing in mind 2 $mol \cdot L^{-1}$ of concentration of the draw solution, the water flux was of 11.9 $L \cdot m^{-2} \cdot h^{-1}$ and the reverse draw solute flux was 0.14 $mol \cdot m^{-2} \cdot h^{-1}$. In this case, the water recovery depended on the variation in the membrane area, as shown in Figure 39.

Figure 39 – Relationship between membrane area and water recovery in FO process.



Source: Present author.

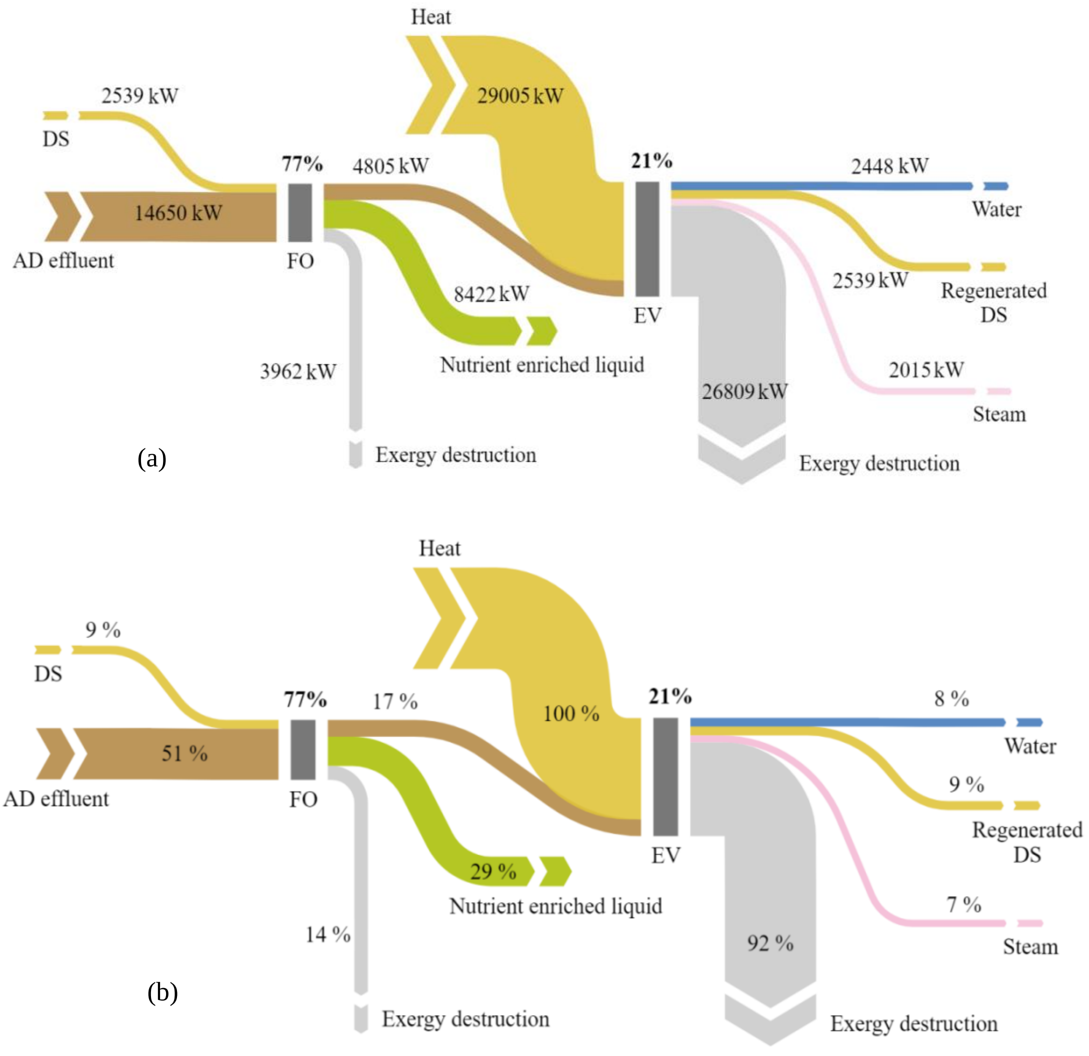
Some operational conditions for forward osmosis membrane processes were summarized by Kim et al. (2017), as can be seen in Appendix K (page 167). It should be mentioned that water flux depends on the membrane characteristics used; even using the same draw solution. Thus, in this study, the parameters (Appendix H) established by Suh and Lee (2013) were used, who developed the model applied in this study.

Therefore, as can be observed, to recover 70% of water, the area required in the forward osmosis system was 14823 m^2. In this scenario, the draw solution input had 51.81 kJ/L of specific exergy content and 176.39 $m^3 \cdot h^{-1}$ of flowrate.

The Sankey diagrams in Figure 40 present the exergy of the flowrates of Alternative 3 (methane production pathway + forward osmosis + evaporation). It is important to emphasize that the heat that enters the system refers to the energy required for the regeneration of the draw solution, in order to promote its recirculation.

Therefore, forward osmosis and evaporators account for 77% and 21% of exergy efficiency, respectively. The exergy destruction in this concentration phase (FO + EV) was 67%, where most of the lost exergy comes from evaporation (26809 kW) while osmosis had 3962 kW of losses. The exergy efficiency of the combination of forward osmosis and evaporation was 33%.

Figure 40 – Sankey diagrams of Alternative 3.



FO: Forward Osmosis; EV: Evaporator; DS: draw solution; (a) balance in kW; (b) balance in percentage.

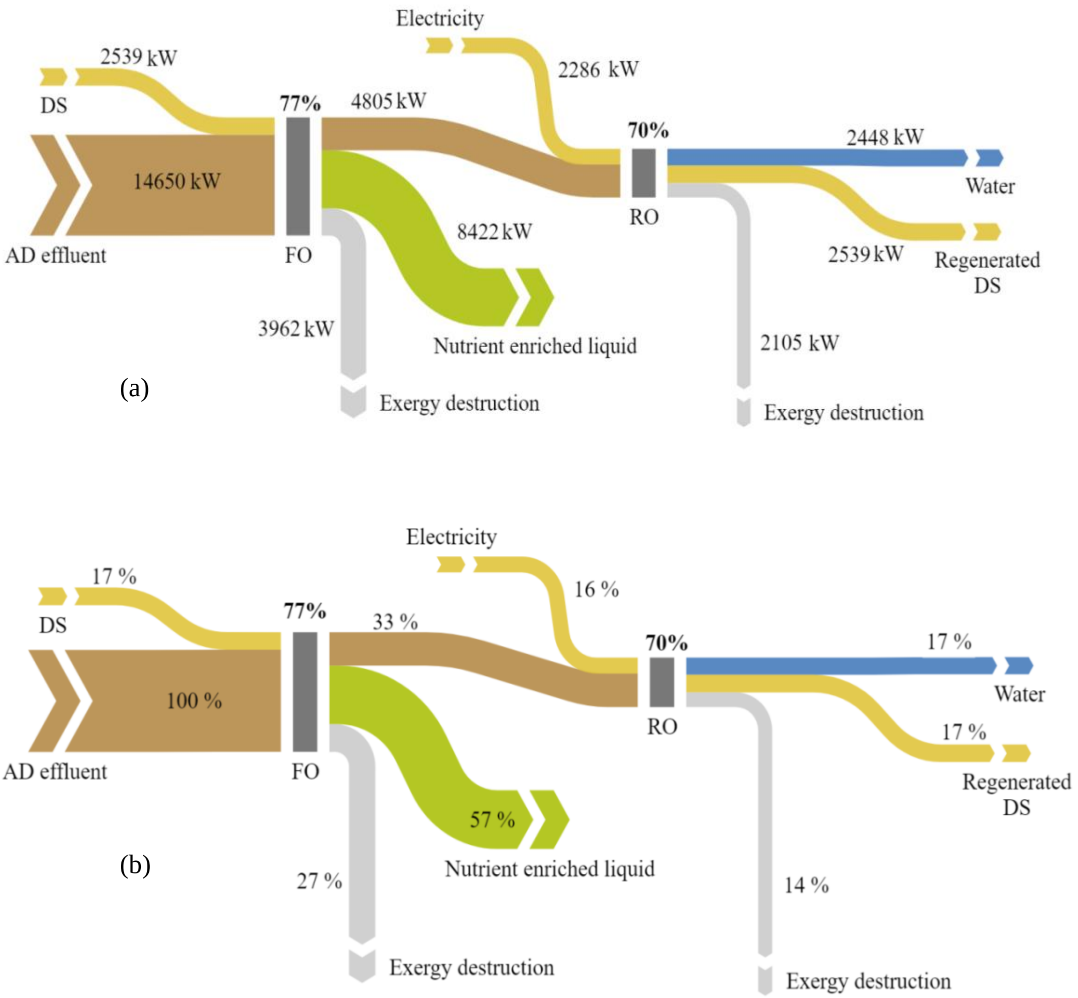
Source: Present author.

4.2.4 Forward Osmosis + Reverse Osmosis

Forward Osmosis was analyzed in the previous subsection.

Reverse Osmosis in Alternative 4 had 70% of exergy efficiency. This efficiency was 3% lower than the RO at Alternative 2 (A2) because the draw solution regeneration required more energy (2286 kW of power) than direct water reclaim from the anaerobic digestion effluent (Figure 41). This can be explained since the flowrate of diluted draw solution (352.79 $m^3 \cdot h^{-1}$) was higher than the AD effluent (176.39 $m^3 \cdot h^{-1}$).

Figure 41 – Sankey diagrams of Alternative 4.



FO: Forward Osmosis; RO: Reverse Osmosis; DS: draw solution; (a) balance in kW; (b) balance in percentage.

Source: Present author.

The exergy efficiency of the forward osmosis unit (77%) is higher than the reverse osmosis unit (70%). The 27% of exergy destruction in FO accounts for 133% of all inputs in the system, but accounts for 23% if only the draw solution and AD effluent are the inputs. Similarly, 14% of exergy loss of RO refers to all inputs, however this percentage is 30% if only diluted draw solution and electricity are considered as the input. The concentration method of Alternative 4 (FO + RO) had 69% of exergy efficiency. It means that the process accounted for 31% of exergy destruction.

4.2.5 Forward Osmosis + Membrane Distillation

The forward osmosis unit is similar to Alternatives 3 and 4.

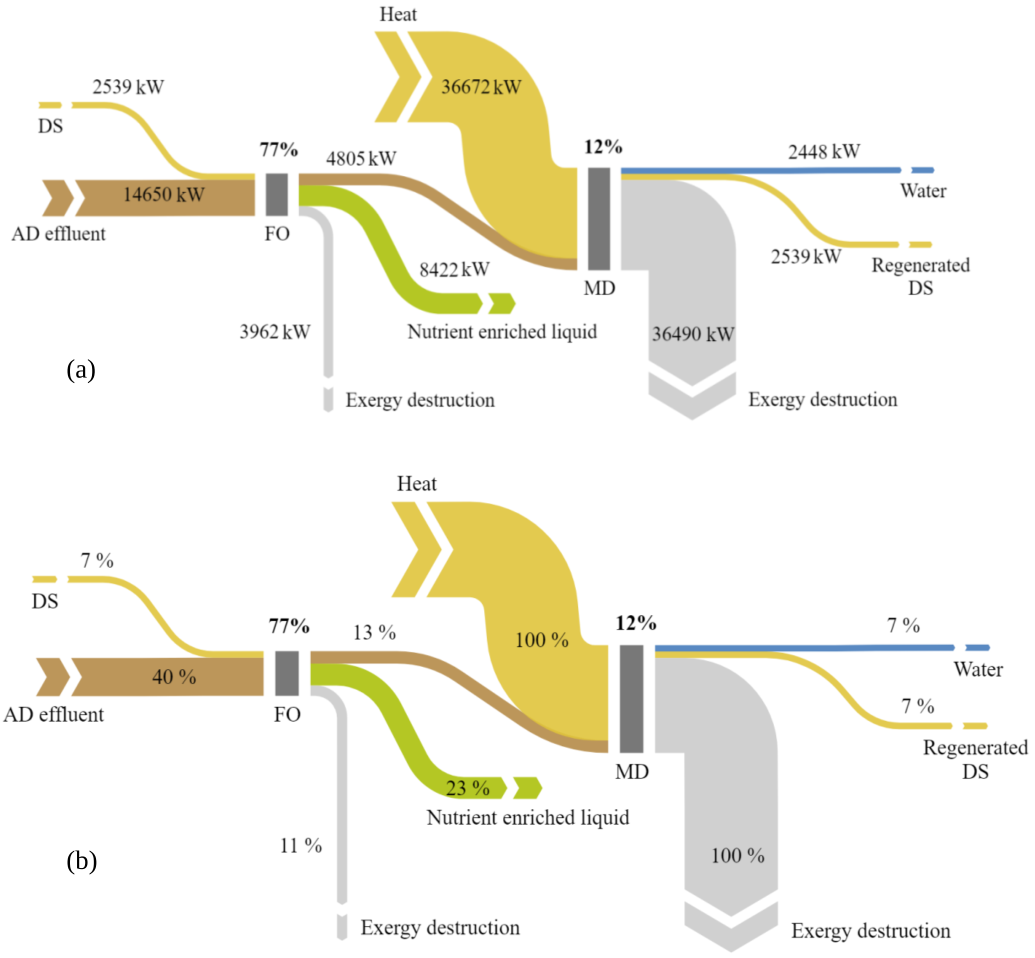
In Alternative 5, a Direct Contact Membrane Distillation (DCMD) module was considered, which needs to be heated in order to compensate the heat loss by conduction and evaporation and to keep a preset average feed temperature. Besides that, some preheating energy has to be supplied to the feed in order to reach the desired temperature at the module inlet, in this case, a diluted draw solution that ranges from 25°C to 100°C (JANTAPORN; ALI; AIMAR, 2017).

According to some authors such as González et al. (2017), Jantaporn et al. (2017) and Lokare et al. (2018), specific energy consumption in the MD module can achieve values higher than 1000 kWh·m^{-3}. It depends on the evaporation efficiency, which in turn depends on the factors as membrane characteristics, hydrodynamic conditions and vapor pressures. Thus, Figure 42 shows the input and output of Alternative 5, considering the scenario described in the previous alternatives.

For the same scenario considered in the previous alternatives (vinasse with 1.2°Bx and 70kg/s of flowrate, 70% of organic removal and 70% of water recovery), the specific energy consumption was 277 kWh·m^{-3}. This value was compatible with that presented in the literature, validating the balances used.

Thus, the input heat was 48896 kW, equivalent to 36672 kW of exergy. Thus, membrane distillation unit had an exergy efficiency of 12%. The exergy efficiency of the concentration system of Alternative 5 (FO + MD) was 25%, with 75% of exergy destruction.

Figure 42 – Sankey diagrams of Alternative 5.



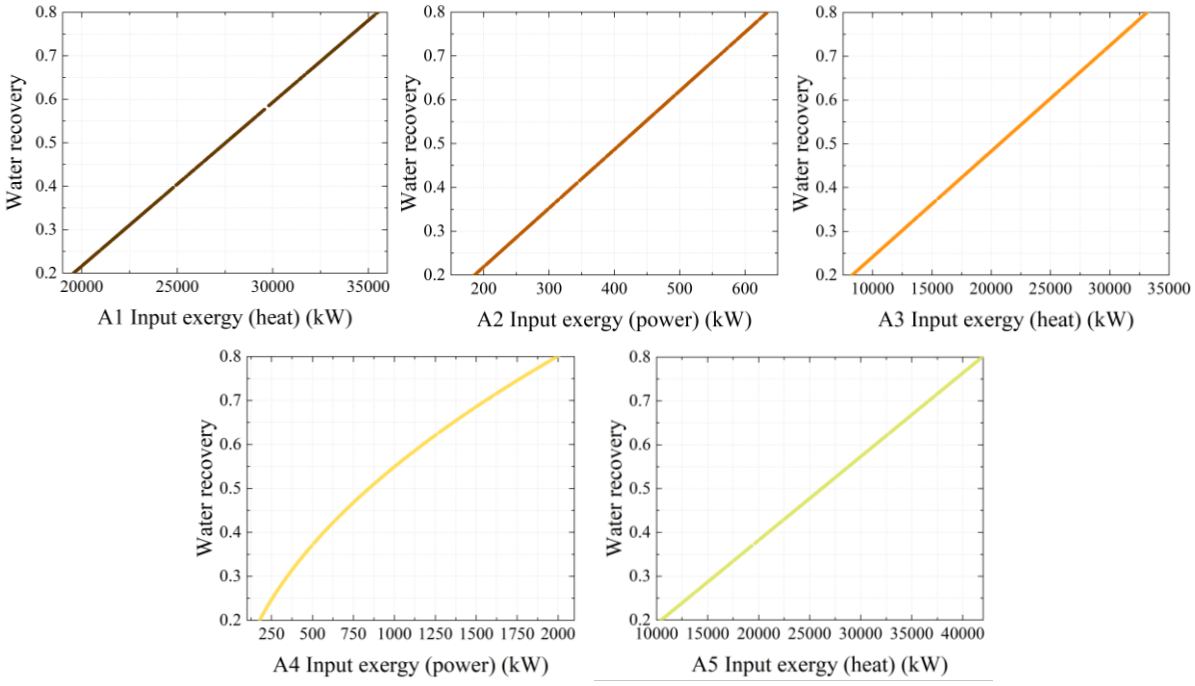
FO: forward osmosis; MD: membrane distillation; DS: draw solution; (a) balance in kW; (b) balance in percentage.

Source: Present author.

4.3 COMPARISON OF THE ALTERNATIVES

The principal aspect that differentiates the concentration methods studied is the energy requirement for separating the water contained in the feed stream. As can be observed in Figure 43, in general, the alternatives that use heat as input energy resources had greater exergy requirements. This means that alternatives that used reverse osmosis processes (A2 and A4) tended to demand less exergy of energy.

Figure 43 – Input exergy of energy in each alternative.



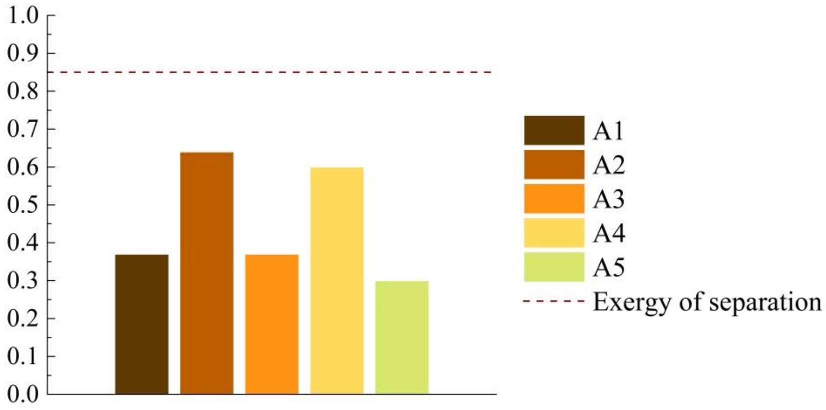
A1: Alternative 1 (EV); A2: Alternative 2 (RO); A3: Alternative 3 (FO+EV); A4: Alternative 4 (FO+RO); A5: Alternative 5(FO+MD).

Source: Present author.

As observed previously, the membrane distillation regeneration method is the system that requires more energy, while reverse osmosis needs less power. It reflects in the exergy efficiency of the systems, as can be seen in Figure 44. Alternative 2 (RO) followed by Alternative 4 (FO + RO) presented higher exergy efficiencies (64% and 60%, respectively). Alternative 5 (FO + MD) had smaller efficiency (30%). It is interesting to note that the exergy of separation to achieve 70% of water recovery was 85%. This means that a minimum of 11557 kW of work is required to promote the partial separation of the components found in the vinasse.

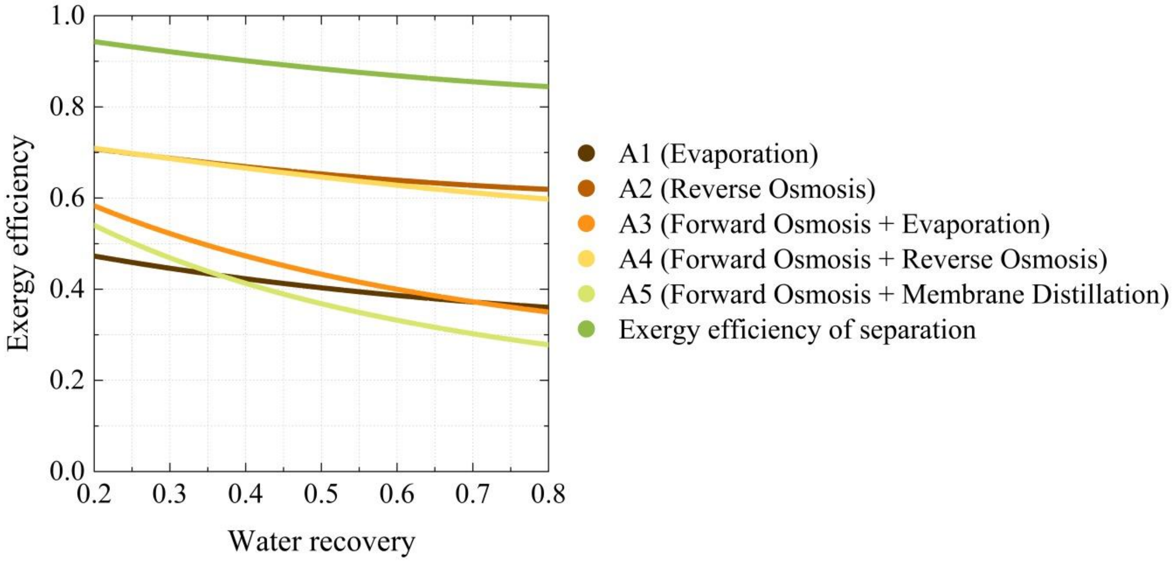
The total exergy efficiency of the alternatives (including the methane production pathway and concentration method) is presented in Figure 45, considering 70kg·s^{-1} of vinasse and 70% of organic removal. It was observed that Alternative 2 (Reverse Osmosis) and Alternative 4 (Forward Osmosis + Reverse Osmosis) had similar exergy efficiencies. The other alternatives were less efficient, indicating that even requiring low grade energy, the amount of exergy in the form of heat tended to be significantly higher than the electricity required for pumping.

Figure 44 – Comparison among the exergy efficiencies of the alternatives.



Source: Present author.

Figure 45 – Exergy efficiency of the alternatives.



Source: Present author.

Thus, it can be observed that although the FO unit is thermodynamically more favorable, the regeneration process of the draw solution makes the system less efficient. This statement is emphasized in the study conducted by McGovern and Lienhard (2014), who affirmed that reverse osmosis is significantly more energy efficient than forward osmosis due to the theoretical and actual energy requirements for draw solution regeneration.

In addition to the energy requirement, the implementation of a forward osmosis system may have a drawback in terms of choosing the draw solution to be used. For the estimates made in this work, NaCl was considered because it is widely applied as a draw solution in this type of process, presenting a low cost and high osmotic pressure. However, it would not be advantageous to transport seawater to sugarcane industries as one of the reasons for vinasse concentration is to decrease transport costs.

In addition to NaCl, sucrose was considered as a draw solution as it is an abundant organic substance in the sugar cane industry. However, it was taken into account that this simple organic has lower osmotic pressure than inorganic salts, where NaCl has 4.8MPa/1.0M and sucrose 2.4MPa/1.0M. Thus, the application of sucrose as a solution requires further investigation (JOHNSON et al., 2018).

Therefore, it is appropriate to point out that reverse osmosis could be the most suitable method of concentration among the analyzed alternatives. RO is a well-known technology that can be coupled with a biological step, providing an interesting design for the biorefinery. If applied in the sugarcane industry, it would use the surplus electricity generated from burning bagasse or that produced from burning methane from the anaerobic digestion.

Thus, the next section presents some examples of studies that covered the sugarcane industry. Associations were made to verify the influence of implementing a biorefinery based on Alternative 2 (methane production pathway coupled with reverse osmosis concentration method) in the scope of the industry.

4.4 BRIEF STUDY OF SCENARIOS

As explained earlier, the concept of biorefineries for resource recovery from waste originally has an environmental bias. This premise consists of promoting these systems as alternative sources of material and energy associated with the proper disposal of their waste or by-products. However, it is important to verify to what extent the annexation of a vinasse resource recovery unit can bring benefits, making the idea of biorefinery attractive to the industrial context. Thus, a brief analysis was made of two examples from the sugarcane industry found in the literature. The first one focuses solely on ethanol production and the second on sugar and alcohol.

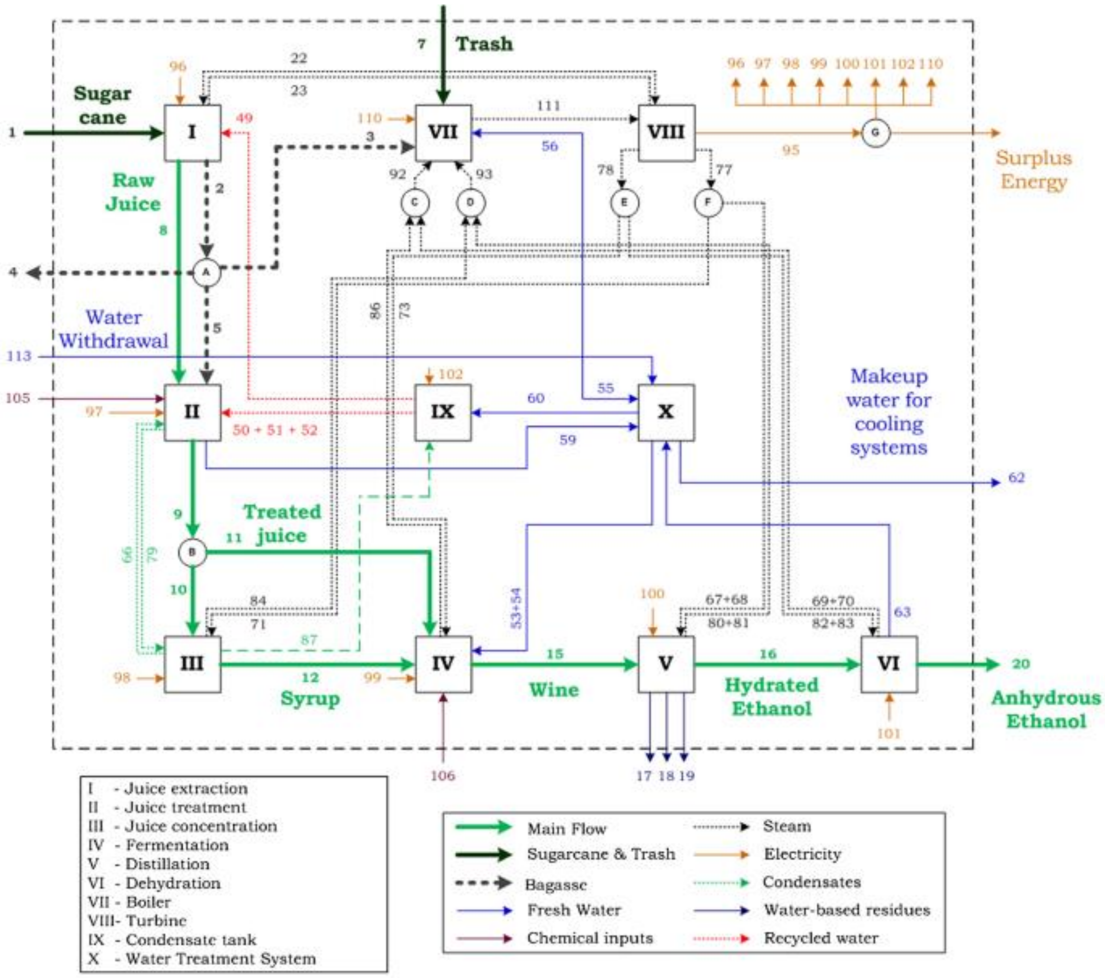
It is important to emphasize that in the study of the scenarios presented below, the data from the research used as a reference were used (ENSINAS et al., 2009; PALACIOS-BERECHE et al., 2013). Thus, the exergy balances for the industrial configurations were initially presented by these authors. The present work carried out an extension of these presented balance sheets when including the vinasse biorefinery within the industrial scope. Thus, from the vinasse flow given in these reference works, hypothetical biorefineries were designated as an annex to the sugar and alcohol industries used as examples.

4.4.1 Scenario 1: Ethanol Industry

Scenario 1 comprises an ethanol industry studied by Palacios-Bereche et al. (2013). The base case studied by these authors constitutes a conventional anhydrous ethanol and electricity production process. Thus, the distillery evaluated has the following industrial stages: cane cleaning, preparation and extraction, cogeneration system, juice treatment, juice concentration, fermentation, distillation and dehydration (Figure 46). The flowrates entering and leaving the system are presented in Table 12.

Thus, the present research provided a balance for a hypothetic biorefinery of vinasse using the information about a vinasse stream (136.6 $kg \cdot s^{-1}$ and 443 kJ/kg) presented by Palacios-Bereche et al. (2013). The calculated biorefinery flowrates are shown in Table 13.

Figure 46 – Flow diagram of a conventional ethanol production process.



Source: Palacios-Bereche et al. (2013).

Table 12 – Flow rates in the ethanol industry.

Flow	Exergy content	Flow	Exergy content
Inputs		*Outputs*	
1 – Sugarcane	800341.8 kW	4 – Bagasse for hydrolysis	152678.7 kW
7 – Sugarcane trash	171504 kW	17 – Second-grade alcohol	8074.8 kW
105 – Calcium oxide	196.5 kW	19 – Phlegmasse	1228.5 kW
106 – Sulphuric acid	0 kW	20 – Anhydrous ethanol	279632.5 kW
107 – Sulphur dioxide	1467.6 kW	62 – Make-up water for general uses	5175 kW
113 – Water withdrawal	7165 kW	95 – Surplus energy	21151.692 kW
121 – Enzyme	14238 kW	18 – Vinasse	60513.8 kW

Source: data from Palacios-Bereche et al. (2013).

Table 13 – Flow rates of the vinasse biorefinery in Scenario 1.

Flow		**Exergy content**
Inputs	Vinasse	60513.8 kW
	Bicarbonate	189.05 kW
	Energy	1331.5 kW
Outputs	Sludge	533.95 kW
	Energy biogas	5518.80 kW
	Water	5461.10 kW
	Concentrated	13651.00 kW

Source: Values calculated in the present research.

Therefore, according to the estimate carried out, considering 80% of water recovered (393.54 $m^3 \cdot h^{-1}$), the industry would reduce 67% of the water demand from external sources. In addition, the electricity generated from biogas conversion (2601 kW) would be equivalent to 13% of the energy from the bagasse and 2918 kW of heat could be reused in the industry.

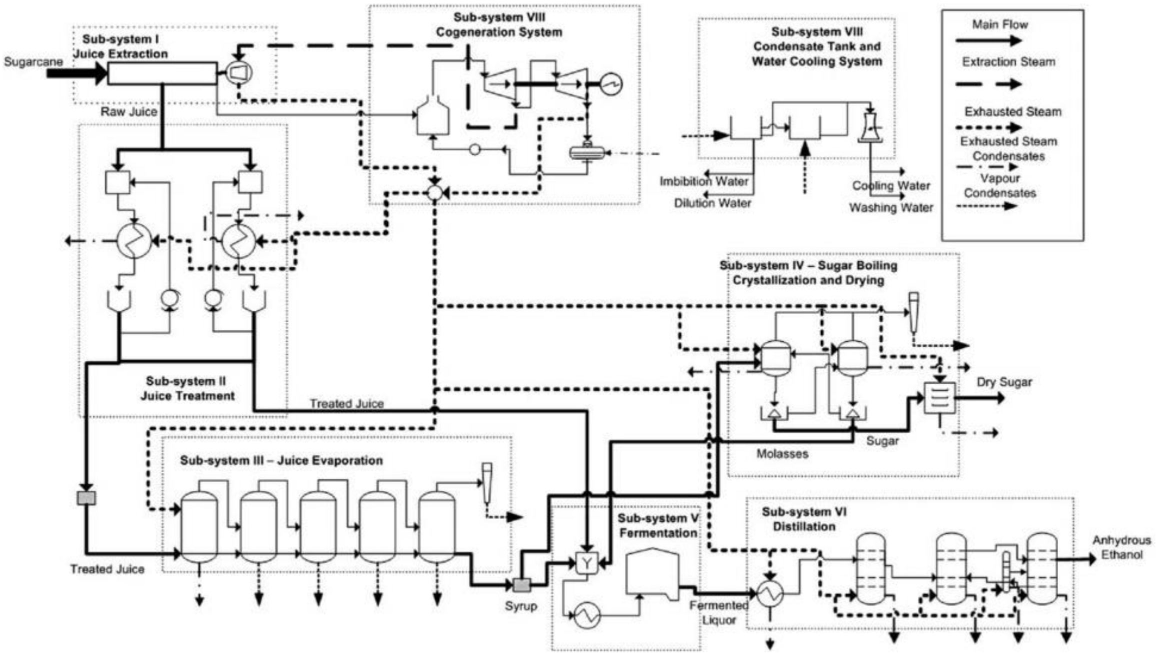
The electricity demanded for reverse osmosis accounted for 6% of the surplus energy of the industry, which is less if considering the amount of water recovered. In this case, the exergy efficiency of the vinasse biorefinery was 52%.

4.4.2 Scenario 2: Sugar and Alcohol Industry

Ensinas et al. (2009) analysed the exergy efficiency of a whole plant from a typical sugar and ethanol industry presented in Figure 47.

The authors calculated the exergy for each subsystem (Table 14) and found that the cogeneration system is responsible for 63% of the irreversibility generated. The total exergy efficiency of the ethanol and sugar industry was 35%.

Figure 47 – Sugar and ethanol production processes.



Source: Ensinas et al. (2009).

Table 14 – Exergy analysis of the ethanol and sugar industry.

Subsystem	**Exergy efficiency**	**Fraction of the total irreversibility generation of the plant**
I – Juice extraction	91%	14%
II – Juice treatment	97%	2%
III – Juice evaporation	97%	2%
IV – Sugar boiling, crystallization and drying	95%	2%
V – Fermentation	70%	12%
VI – Distillation	90%	3%
VII – Cogeneration system	18%	63%
VIII – Condensate tank and water-cooling system	85%	2%
Industry (total)	35%	100%

Source: values presented by Ensinas et al. (2009).

In the industry analyzed by Ensinas et al. (2009), 4.54 kg/s of anhydrous ethanol were produced, which would be equivalent to 45.4 kg/s of vinasse. Therefore, considering this flowrate of vinasse, this study calculated the streams of the hypothetical biorefinery (Table 15).

Table 15 – Flowrates of the vinasse biorefinery in Scenario 2.

Flow		**Exergy content**
Inputs	Vinasse	20112 kW
	Bicarbonate	62.83 kW
	Energy	336.22 kW
Outputs	Sludge	177.46 kW
	Energy biogas	1834.20 kW
	Water	1816.3 kW
	Concentrate	4535.10 kW

Source: Values calculated in the present research.

The exergy efficiency of the vinasse biorefinery in this case would be 40%. The electricity generated by the methane conversion would represent 11% of the surplus energy in the industry from burning bagasse. Moreover, 969 kW of heat would be available to reuse in the industry. The energy requirement by reverse osmosis would be 4% of the surplus energy from the burning bagasse.

Compared to the ethanol industry, less alcohol is produced as part of the sugarcane juice is designated for sugar production. Consequently, less vinasse is generated and a smaller amount of water is available for recovery. Therefore, 130.89 m^3/h of water would be reclaimed, representing 26% of reduction in water withdrawals or 80% of water removal from vinasse.

4.5 FINAL CONSIDERATIONS

This study was conducted with the purpose of promoting an analysis of design possibilities for a biorefinery aimed at the recovery of water, energy and nutrients from vinasse. Anaerobic digestion was considered to be a well-established process as an energy pathway (from the production and burning of biogas). However, five concentration methods of anaerobic digestion effluent were analysed, since no comparative studies have been carried out on this topic.

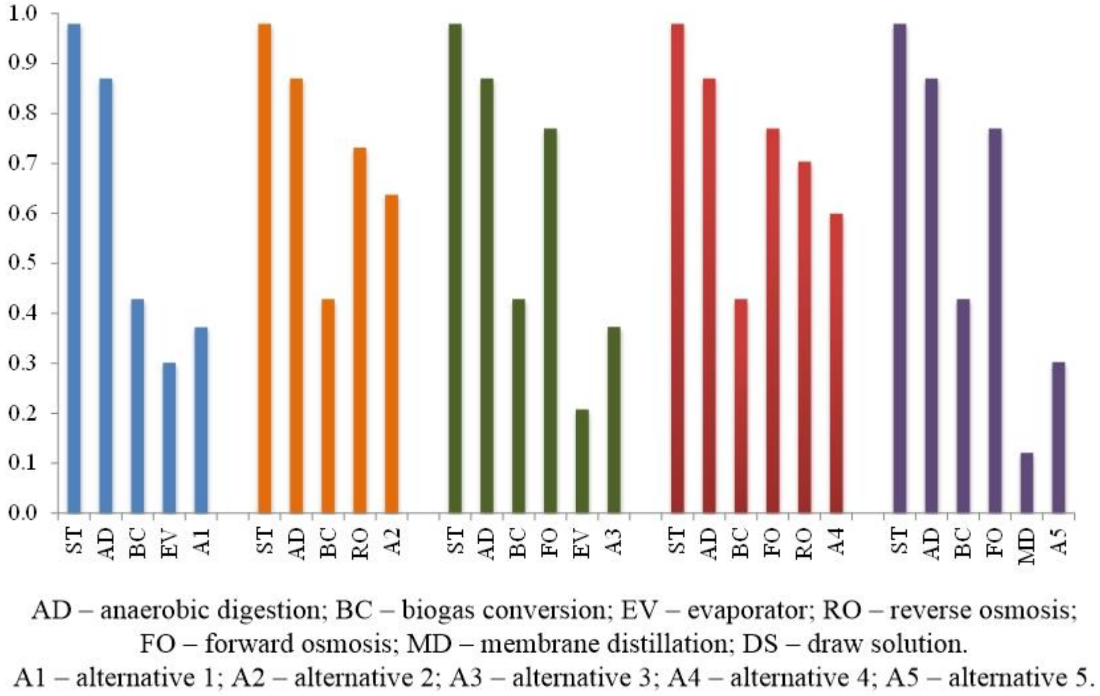
Using the exergy analysis tool, it was found that it would be interesting to take advantage of the heat from the vinasse lost in the storage tank. In general, the exergy efficiency of the systems presented would be improved from the best use of the energies involved in the process, for example, from recycling the heat streams.

The results showed that implementing vinasse treatment units tends to bring benefits to the industrial scope by promoting water recycling, reducing the extraction of water from the environment. In addition, the electricity generated within the industry itself would be sufficient for the vinasse biorefinery to function. In other words, the addition of a vinasse biorefinery would not cause losses in terms of energy use, as it could still bring an additional one referring to biogas conversion.

Considering the complexity of a large-scale sugar and alcohol industry, implementing a vinasse treatment system would not have significant effects in terms of exergy efficiency. This can be explained by verifying that in the above examples the exergy efficiency has remained virtually the same by including this vinasse resource recovery unit. For example, in Scenario 1 (alcohol industry), the exergy efficiency was 53% to 52%. In scenario 2 (sugar and alcohol industry), the total exergy efficiency remained at 35%.

An overview of exergy efficiency in each subunit is presented in Figure 48. Within the methane production pathway, the biogas conversion unit into energy has the lowest efficiency (43%), while anaerobic digestion presented 87%. Amongst the concentration technologies, membrane distillation presented the higher exergy destruction, while forward osmosis was the most efficient. However, a general analysis indicates that alternatives 2 and 4 (A2 and A4) were the most interesting in this context.

Figure 48 – Overview of the exergy efficiency of the biorefinery units.



Source: Present author.

It is important to emphasize that other concentration options could be adopted, such as different configurations for evaporators or for membranes, such as hybrid systems involving ultrafiltration and nanofiltration. In addition, other biorefinery arrangements can be devised, including, for example, biofuel generation by microalgae cultivation.

Thus, it is emphasized that the alternatives considered in this study are feasible options to be applied in the industry. However, the potential of biorefineries in the sugarcane industry can be further explored.

5 CONCLUSIONS

Five vinasse biorefinery designs were analyzed for water, nutrient and energy recovery. The alternatives contained a methane production pathway, which incorporated a storage tank, an anaerobic bioreactor and a biogas conversion technology into energy. However, each option included different concentration methods: (1) evaporation; (2) reverse osmosis; (3) forward osmosis + evaporation; (4) forward osmosis + reverse osmosis; (5) forward osmosis + membrane distillation.

It was observed that the processes involving heat as the driving force for water recovery were less efficient because they require significant amounts of energy. They are represented in Alternatives 1, 3 and 5, which include evaporation and membrane distillation processes.

Despite the potential of forward osmosis as a more economical energy method, two main factors prevent it from being implemented efficiently in the sugarcane industry: the choice of an efficient draw solution and the regeneration method. If the regeneration step can be neglected, the forward osmosis process would represent 77% exergy efficiency as the concentration method.

However, among the options evaluated, it was observed that processes involving reverse osmosis, where the motivating energy for water separation is in the form of electricity, are more efficient in terms of exergy. This means that resources are better utilized in these systems, with less exergy destruction.

It is important to emphasize that the exergy analysis is a measure of the conversion efficiency of materials and energy in the system. Sustainability is related to effectively using resources within the system, making use of these resources in a better way, and reducing the need for extraction from natural resources.

In the case of systems such as biorefineries, this type of analysis is valid to verify to what extent the recovery of materials and energy can be advantageous or costly. For example, it was found that by promoting the recycling of vinasse water, energy and nutrients, the alcohol industry would reduce 67% of external water demand and add 13% more electricity than that generated by using bagasse.

Thus, it can be concluded that vinasse treatment, as well as fertigation can be beneficial to reduce the pollutant load of the material disposed in the soil, to recycle water and to produce biogas, increasingly taking advantage of the energy potential of the sugar-alcohol sector.

5.1 SUGGESTIONS FOR FUTURE RESEARCH

The following is suggested for future work:

- Promote exergy analysis of different biogas cleaning and conversion technologies;
- Evaluate the availability of substances in the industry that could act as a draw solution, avoiding the need to seek external solutions;
- Conduct experimental analyses of the reverse osmosis process, using anaerobically treated vinasse;
- Promote the analysis of possible excess currents within industries that could be redirected to vinasse biorefineries;
- Consider the treatment of sludge on the analysis;
- Study sugarcane interaction with anaerobically treated and concentrated vinasse;
- Perform an exergy analysis of different sludge treatment options;
- Carry out an economic analysis of the options studied.

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APPENDIX A – General characteristics of vinasse presented in the literature.

Table 16 – Vinasse characteristics: inorganic content.

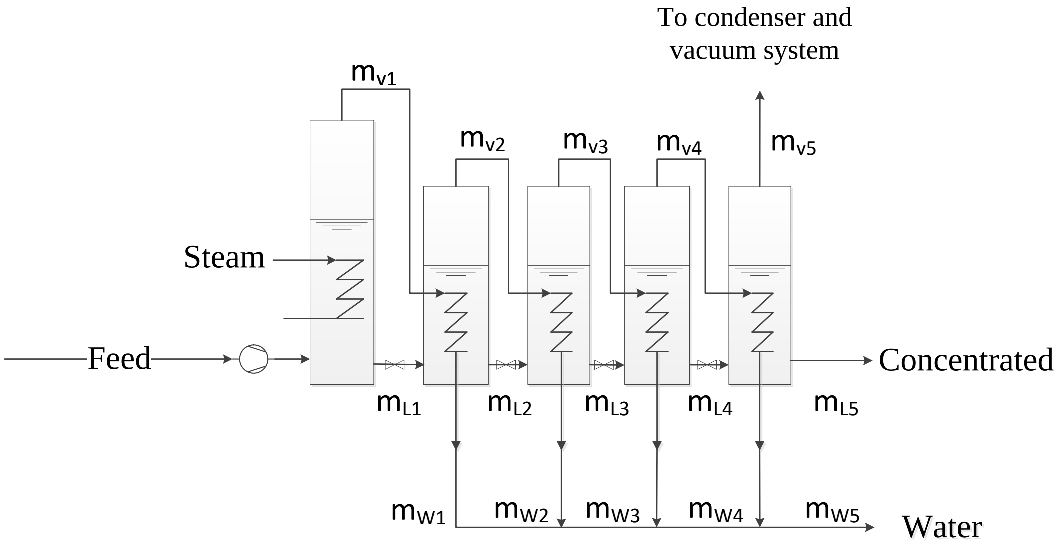
Parameter	**Unit**	**Molasses**	**Juice**	**Molasses and juice mix**
Organic matter	mg C L^{-1}	63400	19500	3800
Calcium	mg CaO L^{-1}	450-5180	130-1540	1330-4570
Magnesium	mg MgO L^{-1}	420-1520	200-490	580-700
Sulfate	mg SO_4^{2-} L^{-1}	6400	600-760	3700-3730
Carbon	mg C L^{-1}	11200-22900	5700-13400	8700-12100
Cupper	mg Cu L^{-1}	0.27-1.71	4	-
Cadmium	mg Cd L^{-1}	0.04-1.36	-	-
Lead	mg Pb L^{-1}	0.02-0.48	-	-
Iron	mg Fe L^{-1}	12.8-157.5	16	-
Zinc	mg Zn L^{-1}	1.66	19.7-21.07	16.4-16.43
Nickel	mg Ni L^{-1}	0.03		
Molybdenum	mg Mb L^{-1}	0.008		
Mercury	mg Hg L^{-1}	0.0019		
Barium	mg Ba L^{-1}	0.41		
Chromium	mg Cr L^{-1}	0.04		
Sodium	mg Na L^{-1}	52.2		
Manganese	mg Mn kg^{-1}	167		

Source: Carrilho et al. (2016)

APPENDIX B – Calculation methods for evaporation.

The balances were made based on Figure 49[1]

Figure 49 – Analysis of multi-effect evaporator.



Source: Present author.

Parameters

$Q_0 \rightarrow$ heat from input steam (kW)

$Ti \rightarrow$ temperature of i effect (°C)

$\mathrm{m}_{Vi} \rightarrow$ vapor output from i effect (kg s^{-1})

$\mathrm{m}_{Li} \rightarrow$ liquor output from i effect (kg s^{-1})

$\mathrm{m}_{Wi} \rightarrow$ condensed water output from i effect (kg s^{-1})

$\mathrm{h}_{Liq\_i} \rightarrow$ enthapy of i liquid stream (kJ kg^{-1})

$\mathrm{h}_{Vap\_i} \rightarrow$ enthalpy of i vapor stream (kJ kg^{-1})

$\mathrm{h}_{Lat\_i} \rightarrow$ enthalpy of vaporization of i effect (kJ kg^{-1})

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[1] The calculation methods were based on class material from Professor Paulo Seleghim Júnior from the Department of Mechanical Engineering, São Carlos School of Engineering, University of São Paulo. More explanations on balance in multi-effect evaporators are presented by Foust et al., (1960) and McCabe et al. (1985).

First effect

$$h_{Liq\_1} = 4.209 \cdot T1 - 0.97$$

$$h_{Vap\_1} = -0.0021269 \cdot T1^2 + 1.9789 \cdot T1 + 2498.4$$

$$h_{Lat\_1} = h_{Vap\_1} - h_{Liq\_1}$$

$$m_{V1} = \frac{Q_0}{h_{V1} - h_{L1}} + \left(\frac{h_{feed} - h_{L1}}{h_{V1} - h_{L1}} \right) \cdot m_{feed}$$

$$m_{L1} = m_{feed} - m_{V1}$$

Second effect

$$h_{Liq\_2} = 4.209 \cdot T2 - 0.97$$

$$h_{Vap\_2} = -0.0021269 \cdot T2^2 + 1.9789 \cdot T2 + 2498.4$$

$$h_{Lat\_2} = h_{Vap\_2} - h_{Liq\_2}$$

$$m_{V2} = \left(\frac{h_{L1} - h_{L2}}{h_{V2} - h_{L2}} \right) \cdot m_{L1} + \left(\frac{h_{Lat\_1}}{h_{Lat\_2}} \right) \cdot m_{V1}$$

$$m_{L2} = m_{L1} - m_{V2}$$

Third effect

$$h_{Liq\_3} = 4.209 \cdot T3 - 0.97$$

$$h_{Vap\_3} = -0.0021269 \cdot T3^2 + 1.9789 \cdot T3 + 2498.4$$

$$h_{Lat\_3} = h_{Vap\_3} - h_{Liq\_3}$$

$$m_{V3} = \left(\frac{h_{L2} - h_{L3}}{h_{V3} - h_{L3}} \right) \cdot m_{L2} + \left(\frac{h_{Lat\_2}}{h_{Lat\_3}} \right) \cdot m_{V2}$$

$$m_{L3} = m_{L2} - m_{V3}$$

Fourth effect

$$h_{Liq\_4} = 4.209 \cdot T4 - 0.97$$

$$h_{Vap\_4} = -0.0021269 \cdot T4^2 + 1.9789 \cdot T4 + 2498.4$$

$$h_{Lat\_4} = h_{Vap\_4} - h_{Liq\_4}$$

$$m_{V4} = \left(\frac{h_{L3} - h_{L4}}{h_{V4} - h_{L4}} \right) \cdot m_{L3} + \left(\frac{h_{Lat\_3}}{h_{Lat\_4}} \right) \cdot m_{V3}$$

$$m_{L4} = m_{L3} - m_{V4}$$

Fifth effect

$$h_{Liq\_5} = 4.209 \cdot T5 - 0.97$$

$$h_{Vap\_5} = -0.0021269 \cdot T5^2 + 1.9789 \cdot T5 + 2498.4$$

$$h_{Lat\_5} = h_{Vap\_5} - h_{Liq\_5}$$

$$m_{V5} = \left(\frac{h_{L4} - h_{L5}}{h_{V5} - h_{L5}} \right) \cdot m_{L4} + \left(\frac{h_{Lat\_4}}{h_{Lat\_5}} \right) \cdot m_{V4}$$

$$m_{L5} = m_{L4} - m_{V5}$$

Water recovered from the feed

$$m_{water\_recovered} = m_{feed} - m_{L5}$$

APPENDIX C – Research on membranes to treat effluents in distilleries.

Reference	**Configuration used**	**Objective**	**Results**
Nataraj et al. (2006)	Nanofiltration and Reverse Osmosis.	Remove the color and contaminants from the distillery spent wash.	Rejections achieved: 99.80% of total dissolved solids; 99.90% of chemical oxygen demand; 99.99% of potassium.
Magalhães et al. (2012)	Ultrafiltration combined with aerated membrane bioreactor and post-treatment using nanofiltration.	Concentration of vinasse as pretreatment; Investigate a new module submerged; Evaluate the use of membrane bioreactor and final polish using nanofiltration aimed at reuse.	Reduction of 98.8 – 100% of organic matter, allowing the reuse of remaining water.
Gomes and Viotto (2012)	Single nanofiltration; Sequential filtration of microfiltration and nanofiltration.	Concentration of vinasse.	A single NF resulted in a retentate concentration that was almost twice as high as the hybrid MF and NF process.
Amaral et al. (2016)	Microfiltration	Concentration of vinasse aiming to improve the use of its nutritive potential.	Critical flux varied from 13 $L.h^{-1}.m^{-2}$ to 8 $L.h^{-1}.m^{-2}$, and this reduction may be related to changes in the vinasse characteristics, such as the concentration of solids and substances with higher fouling potential, for example, melanoidins and phenolic compounds.
Morin Couallier et al.(2006)	Reverse osmosis	Treatment and exploitation of condensates from the concentration of vinasses	10% inhibition at pH 6. In order to eliminate all traces of inhibition, it would be necessary to envisage double RO or coupling with another process.
Murthy and Chaudhari (2009)	Ultrafiltration followed by reverse osmosis	Treatment of distillery spent wash.	Rejections achieved: 97.9% of total dissolved solids; 96.8% of chemical oxygen demand; 97.9% of biochemical oxygen demand; 99.7% of sulfate; 94.65% of potassium.
Thirugnanasambandham et al. (2016)	Reverse osmosis	Treatment process to reuse the distillery wastewater	Permeate flux was achieved with 91% of salinity removal and 85% of COD removal.
Sagne et al. (2010)	Reverse osmosis	Purification of condensate arising from distillery vinasse concentration plant	Treating 100 m3 h^{-1} of the condensate, 3280 m^2 membrane area would be required.
Basu et al. (2015)	Microfiltration	Treatment of molasses distillery wastewater	Electrocoagulation followed by separation by MF is better than chemical coagulation followed by biological treatment in MBR

APPENDIX D – Calculation methods for membrane processes.

This Appendix describes the equations used for balances in membrane processes.

Initially, the osmotic pressure of solutions and hydrodynamics on the membrane surfaces need to be determined as shown in Table 17. After that, fluxes are determined according to the process adopted (ATKINS; PAULA, 2010; ÇENGEL, 2007; SANDLER, 1989).

Table 17 – Osmotic pressure and hydrodynamics on membrane surfaces.

Equation		**Variables**
Osmotic pressure of solutions		
van't Hoff equation $\Pi = \frac{n}{V} RT$	(22)	n: number of moles of solute (mol L^{-1}) V: volume of the mixture (L) R: constant of the gases (T: temperature of the solution.
Hydrodynamics on the membrane surface		
Schmidt number $Sc = \frac{\mu}{\rho D}$	(23)	D: the bulk diffusion coefficient μ: the viscosity ρ: the density of water.
Sherwood number $Sh = 1.85\left(\mathrm{Re}\, Sc \frac{d_h}{L}\right) \rightarrow (\text{laminar flow})$	(24)	Re: Reynolds number L: length of the channel d_h: hydraulic diameter
$Sh = 0.04\, \mathrm{Re}^{0.75}\, Sc^{0.33} \rightarrow (\text{turbulent flow})$	(25)	
Mass transfer coefficient $k = \frac{ShD}{d_h}$	(26)	

For reverse osmosis, the model proposed by Foley (2013) was considered. For forward osmosis, Suh and Lee (2013) presented a model based on reverse draw solute flux. Both deliberated the interference of concentration polarization in transmembrane fluxes (Table 18 and Table 19).

Table 18 – Reverse osmosis equations.

Equation		**Variables**
Reverse Osmosis		
Water flux		
$Jw = A\cdot\left(\Delta P - \Delta\Pi\right)$	(27)	
Concentration in membrane surface		
$C_w = \dfrac{A\cdot k_{osm}\cdot C_p^2 + \left(A\cdot\Delta P + B\right)\cdot C_p}{B + A\cdot k_{osm}\cdot C_p}$	(28)	A: water permeability constant B: solute permeability ΔP: pressure gradient $\Delta\Pi$: osmotic pressure gradient C_0: concentration in the feed C_r: concentration in the retentate $k_{osm} = \Delta\Pi/c_0$
Concentration in the permeate		
$C_p = \ln\left(\dfrac{C_w - C_p}{C_0 - C_p}\right) - \dfrac{A}{k}\cdot\left(\Delta P - \Delta\Pi\right)$	(29)	
Solute rejection		$\dot{W}_{pump}$ is the rate of work done by the pump Q_p is the permeate flow rate Q_F is the volumetric feed flow rate
$R_{solute} = 1 - \dfrac{C_p}{C_r}$	(30)	
Specific energy consumption in RO		
$SEC = \dfrac{W_{pump}}{Q_p} = \dfrac{\Delta P\cdot Q_F}{Q_p}$	(31)	

Table 19 – Forward osmosis equations.

Equation	**Variables**
Forward osmosis	
Ratio of the reverse draw solute flux to the water flux	Js: reverse solute flux C_p: concentration of draw solution C_0: concentration in the feed S: membrane area
$\frac{Jw}{Js} = \frac{A}{B} nRT$ (32)	
$Jsw = \frac{Js}{Jw}$ (33)	
Solute resistivity for diffusion within the support layer	
$K = {}^{S}\!/_{D}$ (34)	
Reverse draw solute flux	
$Js = B\left(\frac{C_p + Jsw}{\exp\left(Js\left(K/Jsw\right)\right)\exp\left(Js/Jsw \cdot k\right)} - \left(C_0 + Jsw\right)\exp\left(\frac{Js}{Jsw}\right)\right)$ (35)	

Membrane distillation process modelling was explained by Jantaporn et al. (2017). In this case, authors deliberated equations to characterize the flux in hollow fiber membranes, which represent less area requirement. The equation used in the balance for membrane distillation unit is presented in Table 20.

Table 20 – Membrane distillation equations.

Equation		Variables
Membrane distillation		
Water flux $Jw = B_{MD}\left(P_{Fm} - P_{Dm}\right)$	(36)	P_{Fm}: vapor pressure at the membrane surface on the feed side P_{Dm}: vapor pressure at the membrane surface on the permeate side
Free path of water vapors $\lambda = \frac{k_B T}{\sqrt{2}\pi P_{avg}\sigma^2}$	(37)	k_B: Boltzmann constant P_{avg}: pressure inside the membrane pore
if nominal pore size r<0.5λ $B_{MD} = \frac{2}{3RT}\frac{\varepsilon r}{\tau\delta}\left(\frac{8RT}{\pi M}\right)^{1/2}$	(38)	σ: collision diameter ε: porosity τ: tortuosity δ_m: membrane thickness
in the range, 0.5λ<r<50λ $B_{MD} = \left[\frac{3\tau\delta_m}{2\varepsilon r}\left(\frac{\pi RT}{8M}\right)^{1/2} + \frac{\tau\delta_m}{\varepsilon}\frac{Pa}{PD}\frac{RT}{M}\right]^{-1}$	(39)	$PD = 1.895 \times 10^{-5} \times (T)^{2.072}$ Pa: atmospheric pressure M: concentration in moles
Antoine equation $P_{Fm/Dm} = \exp\left(23.2 - \frac{3816.44}{\left(T_{Fm/Dm} + 273.15\right) - 46.13}\right)$	(40)	T_{Fm} (°C) and T_{Dm} (°C) are the feed and permeate temperatures at the membrane surface
Required membrane area $S_{MD} = \frac{Q_F \cdot \varphi \cdot 1000}{Jw}$	(41)	φ: recovery rate Q_F: feed flowrate
Total heat flux through the membrane $P_{tot} = P_{ctot} + P_v$	(42)	ρ_F: feed density
Latent heat flux for dilute solutions $P_v = \varphi \cdot Q_F \cdot \rho_F \cdot H_v$	(43)	
Water latent heat of vaporization $H_v\{T\} = 1.7535 \cdot T_{Fm} + 2024.3$	(44)	

Evaporative heat flux

$$W_v = \frac{P_v}{\varphi \cdot Q_F} \tag{45}$$

Conductive heat flux of one hollow fiber

$$P_{cfiber} = \frac{2\pi \cdot \gamma \cdot \Delta T \cdot L \cdot (\mathrm{r}_2 - \mathrm{r}_1)}{\delta_m \cdot \ln\left(\frac{r_2}{r_1}\right)} \tag{46}$$

L: length

r_1: internal radius

r_2: external radius

γ: membrane thermal conductivity

Membrane surface area

$$S_{fiber} = 2\pi \cdot r_1 \cdot L \tag{47}$$

Number of hollow fibers required

$$N_{fiber} = \frac{S_{MD}}{S_{fiber}} \tag{48}$$

Total conductive heat flux of hollow fibers

$$P_{ctot} = P_{cfiber} \cdot N_{fiber} \tag{49}$$

Total conductive heat flux transferred through membrane pores

$$W_{ctot} = \frac{P_{ctot}}{\varphi \cdot Q_F} \tag{50}$$

Internal energy consumption

$$W_{\mathrm{int}ernal} = \frac{(1-\varphi) \cdot Q_F \cdot \rho_r \cdot C_{pr} \cdot T_{Fa} + P_{ctot} + P_v - Q_F \cdot \rho_F \cdot C_{pF} \cdot T_{Fa}}{\varphi \cdot Q_F} \tag{51}$$

External energy consumption

$$W_{external} = \frac{Q_F \cdot \rho_F \cdot C_{pF} \cdot (T_{Fa} - T_{co})}{\varphi \cdot Q_F} \tag{52}$$

ρ_r: retentate density

T_{Fa}: feed temperature

Tc_0: the cold fluid temperature at the outlet

Specific energy consumption in MD

$$E_p = W_{external} + W_{\mathrm{int}ernal} \tag{53}$$

C_{pr}: retentate specific heat

C_{pF}: feed specific heat

APPENDIX E – Calculation methods for anaerobic digestion.

a) Methanogenic archaea nutritional requirement

The consumption of nutrients in an AD can be estimated by evaluating the microorganisms' nutritional requirement that is usually established from the chemical composition of the microbial cell. As the precise composition is rarely known, the nutrient requirements are determined based on the empirical composition, as presented for methanogenic archaea in Table 21. Such deliberation is based on the fact that almost all living cells are formed by related types of compounds, and that such cells present similar chemical composition, consequently requiring the same elements in the same relative proportions (CHERNICHARO, 2007).

Table 21 – Chemical composition of methanogenic microorganisms.

Macronutrients		**Micronutrients**	
Element	**Concentration (g/kgTSS)**	**Element**	**Concentration (g/kgTSS)**
Nitrogen	65	Iron	1800
Phosphorus	15	Nickel	100
Potassium	10	Cobalt	75
Sulphur	10	Molybdenum	60
Calcium	4	Zinc	60
Magnesium	3	Manganese	20
		Copper	10

Source: Chernicharo (2007).

The minimum nutrient requirements can be calculated by the following expression:

$$Nr = C_{S0} Y N_{bac} \frac{TSS}{VSS} \qquad (54)$$

Where Nr is the nutrient requirement (kg m^{-3}), C_{S0} is the concentration of influent COD (kg COD m^{-3}), Y is the yield coefficient (g SSV g^{-1} COD), N_{bac} is the concentration of nutrient in the bacterial cell (g g^{-1} VSS) and *TSS/VSS* is the total solids/volatile solids ratio for the bacterial cell (CHERNICHARO, 2007).

b) Estimate of sludge production

Sludge is one of the constituents removed in wastewater treatment plants in the form of a liquid or semisolid liquid formed by solids and biosolids. The sludge resultant of anaerobic digesters range contains between 2 – 5 % of dry solids concentration. The production of sludge can be estimated by (CHERNICHARO, 2007; METCALF; EDDY, 2003):

$$P_S = Y \times COD \tag{55}$$

$$Q_S = \frac{P_S}{\gamma_{sludge} \times \left(C_S / 100\right)} \tag{56}$$

Where P_S is the production of solids in the system (kgTSS/d), Y is the yield coefficient (kgSST/kgCOD), Q_S is the volumetric sludge production (m^3/d), γ_{sludge} is the sludge density (usually in the order of 1,020 to 1,040 kg/m^3), and C_S is the solids concentration in the sludge (%). The determination of sludge production is important in the mass balances for anaerobic digestion processes (CHERNICHARO, 2007; METCALF; EDDY, 2003).

c) Estimate of methane production

Although the mechanism of methane production involves a complex set of microorganism interactions and reactions, the amount of gas produced can be estimated, as presented by Chernicharo (2007). The following equations can be used to simulate an approximation of the methane production in anaerobic digestion. Initially, the simple stoichiometry for the degraded COD is considered:

$$\begin{gathered} CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \\ \text{(16g)+(64g)} \Rightarrow \text{(44g)+(36g)} \end{gathered} \tag{57}$$

The general expressions that determine the theoretical production of methane per gram of COD removed from the waste are:

$$Q_{CH_4} = \frac{COD_{CH_4}}{K(t)} \tag{58}$$

$$COD_{CH4} = (COD_{in} \times Eff_{rem}) - COD_{met} - COD_{acid} \tag{59}$$

$$COD_{acid} = Y_{acid} \times COD_{in} \times Eff_{rem} \tag{60}$$

$$COD_{met} = Y_{met} \times (COD_{in} \times Eff_{rem} - COD_{acid}) \tag{61}$$

Where Q_{CH_4} is the flowrate of methane produced (m^3 d^{-1}), COD_{CH_4} is a load of COD removed from the reactor and converted into methane (g COD), COD_{in} is the initial chemical oxygen demand; Eff_{rem} is the removal efficiency of organic matter. COD_{acid} and COD_{met} represent the COD converted into acidogenic and methanogenic biomass, respectively, and Y_{acid} and Y_{met} are yield coefficients for acidogenic and methanogenic microorganisms. *K(t)* is the correction factor for the operational temperature of the reactor (kg COD m^{-3}), calculated using the following equation:

$$K(t) = \frac{P \times K_{COD}}{R \times (273 + T)} \tag{62}$$

Where *P* is the atmospheric pressure (1 atm), K_{COD} is the COD corresponding to one mole of CH_4 (64 g COD mol^{-1}), *R* is the gas constant (0.08206 atm L mol^{-1} K^{-1}), and *T* is the operational temperature of the reactor (°C). Considering that the production of methane can be easily determined in an anaerobic reactor, this is a fast, direct measurement of the conversion degree of the waste and of the efficiency of the treatment system (CHERNICHARO, 2007).

APPENDIX F – Standard chemical exergy of the components used in this study.

Substance	**State**	**Molecular mass (g·mol^{-1})**	**Standard chemical exergy (kJ·mol^{-1})**
Ba	s.II	137.34	775.1
CH_4	g.methane	16.04	831.2
CO_2	g	44.0095	19.48
Cd	s.α	112.40	293.8
Cr	s	51.996	584.7
Cu	s	63.54	134.2
Fe	s.α	55.847	374.3
H_2O	g	18.015	9.5
H_2O	l	18.015	0.9
H_2S	g	34.080	812.0
K	s	39.102	366.6
Mg	s	24.312	626.1
Mn	s.α	54.9381	487.7
N_2	g	28.0134	0.72
Na	s	22.9898	336.6
NaCl	s	58.443	14.3
$NaC_2H_3O_2$	s	82.034	873.6
$NaHCO_3$	s	84.0071	21.6
P	s. α, white	30.9738	861.4
Pb	s	207.2	232.8
S	s. rhombic	32.064	609.6
SO_3	g	80.0622	249.1
Zn	s	5.37	339.2

Source: values from Szargut (1989).

APPENDIX G – Details of exergy content calculation of the streams.

This appendix shows details of the calculation method to determine the exergy of the streams. In general, the calculus followed the type of current, as presented in Table 7 (page 83), so that:

Exergy of matter stream

$$X_i = x_i \cdot m_i = \left(x_{ch\_i} + x_{ph\_i} + x_{org,mat\_i}\right) \cdot m_i \tag{63}$$

Where:

X_i = Exergy of the mass stream i (kW)
x_i = specific exergy of the stream i (kJ/L)
x_{ch_i} = chemical exergy of the stream i (kJ/L)
x_{ph_i} = physical exergy of the stream i (kJ/L)
x_{org,mat_i} = exergy of the organic content in stream i (kJ/L)
m_i = flowrate of the stream i (L/s)

Exergy of heat stream

$$X_{Q\_j} = \left(1 - \frac{T_0}{T}\right) \cdot Q_j \tag{64}$$

Where:

X_{Q_j} = Exergy content of the heat stream j (kW)
T_0 = environment temperature (°C)
T = temperature of the stream j (°C)
Q_j = heat (kW)

Exergy of the work

$$X_{W\_k} = W_k \tag{65}$$

Where X_{W_k} is the exergy in the work form (kW) and W_k is work (kW).

Therefore, the exergy of the streams were determined following:

Exergy of the vinasse at 80°C and 25°C

- Chemical exergy of vinasse

$$x_{ch\_vinasse} = \left[\left(y_{component} \cdot x_{component} \right) + R \cdot T \cdot (y_{component} \cdot \ln y_{component}) \right] \cdot n_{vinasse} \qquad (66)$$

Where $y_{component}$ refers to the molar fraction of the components present in vinasse (mol/mol), $x_{component}$ is the specific exergy (kJ/mol) of the component (see Appendix F), R is the constant of the gases, T is the environment temperature and $n_{vinasse}$ is the concentration of the vinasse in mols (mol/L). The components in vinasse were determined by the characterization presented in Section 3.1.1 (page 72).

- Physical exergy of vinasse

Physical exergy of vinasse was determined following the equation established by Kotas (1985) for solids and liquid streams. In this case, the specific heat of pure water (1 cal/g·°C) was considered:

$$x_{ph\_vinasse} = c_P \left[\left(T - T_0 \right) - T_0 \ln \frac{T}{T_0} \right] \qquad (67)$$

Where c_P is the specific heat of vinasse and T is the temperature of vinasse (80°C). Thus, this part was used to calculate only the exergy of vinasse at 80°C since vinasse at 25°C is at the environmental temperature.

- Exergy of organic matter in vinasse

For organic matter exergy, equation (7) on page 60 was considered, based on the COD (g/L) of vinasse:

$$x_{org,mat\_vinasse} = 13.6 \cdot COD \tag{68}$$

- Exergy of the vinasse streams

$$X_{vinasse\_80} = \left(x_{ch\_vinasse} + x_{ph\_vinasse} + x_{org,mat\_vinasse} \right) \cdot m_{vinasse} \tag{69}$$

$$X_{vinasse\_25} = \left(x_{ch\_vinasse} + x_{org,mat\_vinasse} \right) \cdot m_{vinasse} \tag{70}$$

Where:

$X_{vinasse\_80}$ = exergy of vinasse stream at 80°C (kW);

$X_{vinasse\_25}$ = exergy of vinasse stream at 25°C (kW);

$m_{vinasse}$ = flowrate of vinasse (L/s).

Exergy of the bicarbonate stream

The exergy of the bicarbonate stream is determined by:

$$X_{bicarbonate} = x_{NaHCO_3} \cdot M_{NaHCO_3} \cdot m_{bicarbonate} \tag{71}$$

Where x_{NaHCO3} is the specific exergy of the bicarbonate, M_{NaHCO3} is the concentration in mol/L and $m_{bicarbonate}$ is the bicarbonate flowrate in L/s.

Exergy of the sludge stream

It was considered that sludge is formed by water and organic solids.

- Exergy of organic matter in sludge

$$x_{org,mat\_sludge} = 13.6 \cdot COD \cdot P_{solids\_sludge} \tag{72}$$

Where P_{solids_sludge} is the percentage of organic matter presented in the sludge stream.

- Exergy of water in sludge

$$x_{H_2O\_sludge} = x_{H_2O} \cdot M_{H_2O\_sludge} \tag{73}$$

Where x_{H2O} is the specific exergy of the water (kJ/mol) and M_{H2O_sludge} is the amount of water in the sludge in mol/L.

- Exergy of sludge stream

$$X_{sludge} = \left(x_{org,mat\_sludge} + x_{H_2O\_sludge} \right) \cdot m_{sludge} \tag{74}$$

Where m_{sludge} is the flowrate of sludge (L/s) defined in Appendix E.

Exergy of the biogas

- Chemical exergy of the biogas

$$x_{ch\_biogas} = \left(\left(y_{gas} \cdot x_{gas} \right) + R \cdot T \cdot \left(y_{gas} \cdot \ln y_{gas} \right) \right) \cdot n_{biogas} \tag{75}$$

Where y_{gas} refers to the molar fraction of the gas component present in biogas (mol/mol), x_{gas} is the specific exergy (kJ/mol) of the gas component (see Appendix F), R is the constant of the gases, T is the environment temperature and n_{biogas} is the concentration of the biogas in mols (mol/L). The following was considered: 60% of CH_4, 39% of CO_2 and 1% of H_2S in the biogas.

- Exergy of the biogas stream

$$X_{biogas} = x_{ch\_biogas} \cdot m_{biogas} \tag{76}$$

Where m_{biogas} is the flowrate of biogas (L/s) defined in Appendix E.

Exergy of the heat and work from biogas conversion

The exergy of heat and electricity generated from biogas conversion are:

$$X_{Q\_biogas} = Q_{biogas} \cdot 0.6 \cdot LHV_{biogas} \cdot 0.46 / 86400 \tag{77}$$

$$X_{W\_biogas} = Q_{biogas} \cdot 0.6 \cdot LHV_{biogas} \cdot 0.41 / 86400 \tag{78}$$

Where Q_{biogas} is the biogas flowrate (Nm³/d), LHV_{biogas} is the calorific value of the biogas (kJ/Nm³) and the efficiencies of conversion are 0.46 for heat and 0.41 for electricity.

Exergy of anaerobic digestion effluent

- Chemical exergy of the AD effluent

$$x_{ch\_ADeff} = \left[\left(y_{comp,ADeff} \cdot x_{comp,ADeff}\right) + R \cdot T \cdot (y_{comp,ADeff} \cdot \ln y_{comp,ADeff})\right] \cdot n_{ADeff} \tag{79}$$

Where $y_{comp,ADeff}$ refers to the molar fraction of the components present in AD effluent (mol/mol), $x_{comp,ADeff}$ is the specific exergy (kJ/mol) of the component (see Appendix F), R is the constant of the gases, T is the environment temperature and n_{ADeff} is the concentration of the vinasse in mols (mol/L). The components in AD effluent were calculated as presented in Section 3.2.1 (page 75) and Appendix E.

- Exergy of organic matter in AD effluent

$$x_{org,mat\_ADeff} = 13.6 \cdot COD \cdot (1 - organic\_removal) \tag{80}$$

Where *organic_removal* is the percentage of organic matter removed in anaerobic bioreactor.

- Exergy of AD effluent stream

$$X_{ADeff} = \left(x_{ch\_ADeff} + x_{org,mat\_ADeff}\right) \cdot m_{ADeff} \tag{81}$$

Where m_{ADeff} is the flowrate of AD effluent (L/s).

Exergy of draw solution streams

- Chemical exergy of the draw solution

$$x_{DS} = \left[\left(y_{comp,DS} \cdot x_{comp,DS}\right) + R \cdot T \cdot (y_{comp,DS} \cdot \ln y_{comp,DS})\right] \cdot n_{DS} \tag{82}$$

Where $y_{comp,DS}$ refers to the molar fraction of the components present in the draw solution (mol/mol), $x_{comp,DS}$ is the specific exergy (kJ/mol) of the component (see Appendix F), R is the constant of the gases, T is the environment temperature and n_{DS} is the concentration of the draw solution in mols (mol/L).

In this case, the components present in the draw solution are NaCl and water. Therefore, the calculation of the exergy of the draw solution, diluted draw solution and regenerated draw solution follows equation (82). The difference among them lies in the concentrations of NaCl and water in the solution.

- Exergy of draw solution streams

$$X_{DS} = x_{DS} \cdot m_{DS} \tag{83}$$

$$X_{DS\_diluted} = x_{DS\_diluted} \cdot m_{DS\_diluted} \tag{84}$$

$$X_{DS\_regenerated} = x_{DS\_regenerated} \cdot m_{DS\_regenerated} \tag{85}$$

Where:

X_{DS} = exergy of draw solution (kW);

m_{DS} = flowrate of draw solution (L/s);

$X_{DS\_diluted}$ = exergy of diluted draw solution – after forward osmosis (kW);

$m_{DS\_diluted}$ = flowrate of diluted draw solution (L/s);

$X_{DS\_regenerated}$ = exergy of the regenerated draw solution (after regeneration method), which equals X_{DS} in case of total regeneration.

$m_{DS\_regenerated}$ = flowrate of regenerated draw solution (L/s);

Exergy of nutrient enriched liquid

- Chemical exergy of nutrient enriched liquid

$$x_{ch\_nut\_liq} = \left[\left(y_{comp,\text{nut\_liq}} \cdot x_{comp,\text{nut\_liq}}\right) + R \cdot T \cdot (y_{comp,\text{nut\_liq}} \cdot \ln y_{comp,\text{nut\_liq}})\right] \cdot n_{nut\_liq} \tag{86}$$

Where y_{comp,nut_liq} refers to the molar fraction of the components present in nutrient enriched liquid (mol/mol), x_{comp,nut_liq} is the specific exergy (kJ/mol) of the component (see Appendix F), R is the constant of the gases, T is the environment temperature and n_{nut_liq} is the concentration of the nutrient enriched liquid in mols (mol/L).

The components present in nutrient enriched liquid are the same in the anaerobic digestion effluent. The difference lies in the concentration as nutrient enriched liquid contains less water due to the concentration phase.

- Exergy of organic matter in nutrient enriched liquid

The same organic matter in AD effluent was considered as:

$$x_{org,mat\_nut\_liq} = 13.6 \cdot COD \cdot (1 - organic\_removal) \tag{87}$$

- Exergy of nutrient enriched liquid

$$X_{nut\_liq} = (x_{ch\_nut\_liq} + x_{org,mat\_nut\_liq}) \cdot m_{nut\_liq} \tag{88}$$

Where m_{nut_liq} is the flowrate of the nutrient enriched liquid (L/s).

Exergy of recovered water

The exergy of the recovered water is merely the product of specific exergy of water by the flowrate of reclaimed H_2O:

$$X_{water\_recovered} = x_{H_2O} \cdot m_{water\_recovered} \tag{89}$$

Where x_{H_2O} is the specific exergy of the water (kJ/L) and $m_{water\_recovered}$ is the flowrate of water recovered (L/s).

Exergy of the vapor leaving the evaporator

- Physical exergy of the vapor

$$x_{ph\_\text{steam}} = (h - h_0) - T_0(s - s_0) \tag{90}$$

Where *h* and h_0 are the specific enthalpies of the saturated vapor at 62°C and 25°C, respectively, as *s* and s_0 refers to the entropies.

- Exergy of the vapor

$$X_{steam} = \left(x_{ph\_steam} + x_{H_2O} \right) \cdot m_{steam} \tag{91}$$

Where x_{H_2O} is the specific exergy of the water (kJ/L) and m_{steam} is the flowrate of the vapor leaving the system (L/s).

Exergy of input heat and work

The exergies of the energy required for each concentration technology were calculated, which may be in the form of heat or electricity.

Therefore, for evaporators and membrane distillation, the exergy of heat is:

$$X_{Q\_EV} = \left(1 - \frac{T_0}{T_{EV}} \right) \cdot Q_{EV} \tag{92}$$

$$X_{Q\_MD} = \left(1 - \frac{T_0}{T_{MD}} \right) \cdot Q_{MD} \tag{93}$$

Where X_{Q_EV} and X_{Q_MD} are the exergies in kW demanded for evaporators and the membrane distillation unit, respectively. T_0 is the environment temperature and T_{MD} (100°C) is the operational temperature of membrane distillation. T_{EV} (115°C) is the temperature of the first effect in the evaporator. Q_{EV} and Q_{MD} are the heat in kW provided to those technologies.

For reverse osmosis, the drive energy is the electricity, thus the exergy is given by:

$$X_{W\_RO} = W_{RO} \tag{94}$$

Where W_{RO} is the power required in the reverse osmosis unit (kW).

APPENDIX H – Variables and parameters used in the balances.

Parameter	**Symbol**	**Unit**	**Value**	**Reference**
Yield coefficient	Y	g SSV g^{-1} COD	0.15	Chernicharo (2007)
Concentration of influent COD	COD	kg COD m^{-3}	10 – 45	-
Total solids/volatile solids ratio for the bacterial cell	TSS/VSS		1.14	Chernicharo (2007)
Sludge density	γ_{sludge}	kg/m³	1040	Chernicharo (2007)
Removal efficiency of organic matter	Eff_{rem}	%	70 – 90	-
Yield coefficient for acidogenic microorganism	Y_{acid}	gSSV/gDQO	0.15	Chernicharo (2007)
Yield coefficient for methanogenic microorganism	Y_{met}	gSSV/gDQO	0.03	Chernicharo (2007)
Constant of the gases	R	L.atm/mol.K	0.082	
Ambient temperature	T	°C	25	-
Calorific value of the methane	LHV_{biogas}	MJ/Nm³	21.32	Salomon et al. (2011)
Bulk diffusion coefficient	D	m²/s	$1.74\cdot10^{-9}$	Suh and Lee (2013)
Viscosity of the water	μ	$g\cdot m^{-1}\cdot s^{-1}$	1	Suh and Lee (2013)
Density of the water	ρ	$g\cdot m^{-3}$	$1\cdot10^{6}$	Suh and Lee (2013)
Length of the channel	L	m	1	Cardew and Le (1998)
Hydraulic diameter	d_h	mm	1	Cardew and Le (1998)
Water permeability constant	A	$m^2\cdot s\cdot g^{-1}$	$1.22\cdot10^{-15}$	Suh and Lee (2013)
Solute permeability	B	$m\cdot s^{-1}$	$7.22\cdot10^{-8}$	Suh and Lee (2013)
Pressure gradient	ΔP	MPa	1.5 – 14	-
Vinasse flowrate	$Q_{vinasse}$	kg/s	50 – 100	-
Brix of vinasse	$Bx_{vinasse}$	°Bx	1.0 – 4.5	-
Membrane area	S	m²	500 – 15000	-
Concentration of the draw solution	Cp	mol/L	2	Kim et al. (2017)
Boltzmann constant	k_B	J/K	$1.38\cdot10^{-23}$	Jantaporn et al. (2017)

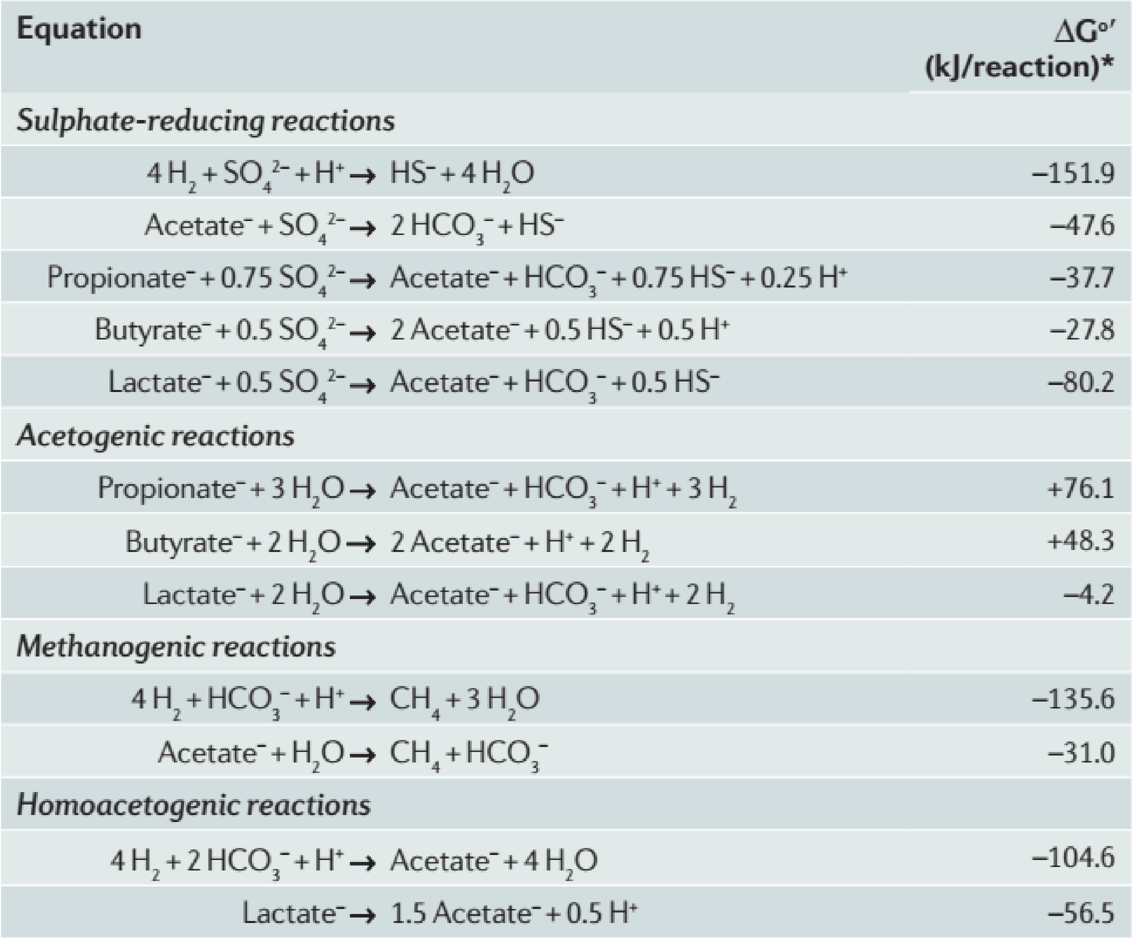
Pressure inside the membrane pore	P_{avg}	kPa	140	Jantaporn et al. (2017)
Collision diameter	σ	Å	2.641	Jantaporn et al. (2017)
Porosity	ε	-	0.73	Jantaporn et al. (2017)
Tortuosity	τ	-	2	Jantaporn et al. (2017)
Membrane thickness	δ_m	m	$0.6\cdot10^{-3}$	Jantaporn et al. (2017)
Atmospheric pressure	Pa	Pa	101325	Jantaporn et al. (2017)
Feed temperature at the membrane surface	T_{Fm}	K	368.15	Jantaporn et al. (2017)
Permeate temperature at the membrane surface	T_{Dm}	K	363.15	Jantaporn et al. (2017)
Internal radius	r_1	m	$0.8\cdot10^{-3}$	Jantaporn et al. (2017)
External radius	r_2	m	$1.4\cdot10^{-3}$	Jantaporn et al. (2017)
Membrane thermal conductivity	γ	W/K·m	0.08	Jantaporn et al. (2017)
Feed temperature	T_{Fa}	K	373.15	Jantaporn et al. (2017)
Cold fluid temperature at outlet	Tc_0	K	298.15	Jantaporn et al. (2017)

APPENDIX I – Characterization of AD effluent used as reference.

Parameter	**Concentration**
COD raw (mg COD L^{-1})	2270
Total solids (mg TS L^{-1})	8830
Total suspended solids (mg TSS L^{-1})	990
Total volatile solids (mg TVS L^{-1})	2140
Volatile suspended solids (mg VSS L^{-1})	710
Ethanol (mg C_2H_6O L^{-1})	0.3
Acetic acid (mg $C_2H_4O_2$ L^{-1})	32.20
Propionic acid (mg $C_3H_6O_2$ L^{-1})	4.85
Butyric acid (mg $C_4H_8O_2$ L^{-1})	12.77
Valeric acid (mg $C_5H_{10}O_2$ L^{-1})	13.45
Sulfate (mg SO_4^{2-} L^{-1})	46.17
Sulfide (mg S^{2-} L^{-1})	38.36
Orthophosphate (mg PO_4^{3-} L^{-1})	48
Ammoniacal nitrogen (mg NH_3-N L^{-1})	43
Nitrate (mg NO_3-N L^{-1})	86
Total Kjeldahl Nitrogen (mgN L^{-1})	219
Calcium (mg Ca L^{-1})	424
Iron (mg Fe L^{-1})	10
Magnesium (mg Mg L^{-1})	192
Sodium (mg Na L^{-1})	1170
Potassium (mg K L^{-1})	1220

Source: information provided by Valéria Del Nery (PhD) (2018).

APPENDIX J – Sulphate-reducing, methanogenic and acetogenic reactions.



Equation	**$\Delta G^{o\prime}$ (kJ/reaction)***
Sulphate-reducing reactions	
$4\,H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\,H_2O$	−151.9
$Acetate^- + SO_4^{2-} \rightarrow 2\,HCO_3^- + HS^-$	−47.6
$Propionate^- + 0.75\,SO_4^{2-} \rightarrow Acetate^- + HCO_3^- + 0.75\,HS^- + 0.25\,H^+$	−37.7
$Butyrate^- + 0.5\,SO_4^{2-} \rightarrow 2\,Acetate^- + 0.5\,HS^- + 0.5\,H^+$	−27.8
$Lactate^- + 0.5\,SO_4^{2-} \rightarrow Acetate^- + HCO_3^- + 0.5\,HS^-$	−80.2
Acetogenic reactions	
$Propionate^- + 3\,H_2O \rightarrow Acetate^- + HCO_3^- + H^+ + 3\,H_2$	+76.1
$Butyrate^- + 2\,H_2O \rightarrow 2\,Acetate^- + H^+ + 2\,H_2$	+48.3
$Lactate^- + 2\,H_2O \rightarrow Acetate^- + HCO_3^- + H^+ + 2\,H_2$	−4.2
Methanogenic reactions	
$4\,H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\,H_2O$	−135.6
$Acetate^- + H_2O \rightarrow CH_4 + HCO_3^-$	−31.0
Homoacetogenic reactions	
$4\,H_2 + 2\,HCO_3^- + H^+ \rightarrow Acetate^- + 4\,H_2O$	−104.6
$Lactate^- \rightarrow 1.5\,Acetate^- + 0.5\,H^+$	−56.5

Source: adapted from Muyzer and Stams (2008); Thauer et al. (1977).

APPENDIX K – Operating conditions of Forward Osmosis membrane by recent research.

Summary of test results and operating conditions reported in recent research on FO membrane development.

Draw solution	Feed solution	Membrane	Water flux, LMH	Solute flux, gMH	Membrane orientation	Water permeability (A) LMH bar^{-1}	Solute permeability (B) LMH	Structure parameter (S) µm	Method for determining FO membrane characteristics
1.0 M NaCl	DI water	TFC	31.1	8.5	AL-FS	1.685	0.26	205.8	RO-FO method
1.0 M NaCl	DI water	TFC	17.1	6.0	AL-FS	0.91	0.25	314	Single FO method
1.5 M NaCl	DI water	TFC with lignin additive	27.6	0.38 g/s	AL-FS	1.88	6.26	439	RO-FO method
0.5 M NaCl	DI water	HH-IPN-CNF	47.2	9.5	AL-FS	–	–	–	–
2.0 M NaCl	DI water	PVA/clay nanocomposite (LbL)	25.5	0.051	AL-FS	–	–	–	–
2.0 M NaCl	DI water	TFC	11.8	2.5	AL-FS	1.51	0.44	110	RO-FO method
1.0 M NaCl	DI water	TFC	22.9	6.4	AL-FS	2.5	1.75	620	RO-FO method
1.0 M NaCl	DI water	TFC	10	3.6	AL-FS	–	–	–	–
1.0 M NaCl	DI water	TFC-nano fiber	15	0.5	AL-FS	0.56	0.05	190	RO-FO method
0.5 M $MgCl_2$	DI water	SG-PAN	28.6	5.8 g/L	AL-FS	3.79	6.084	250	RO-FO method
0.5 M NaCl	DI water	Nano TFC	27.24	–	AL-FS	1.69	0.24	66	RO-FO method
2.0 M NaCl	DI water	TFC	27.6	37.5	AL-FS	–	–	–	–
2.0 M NaCl	DI water	PVA/MMt (LbL)	25.5	0.051	AL-FS	–	–	–	–
0.5 M NaCl	DI water	TiO_2 TFN	18.81	7.35	AL-FS	2.63	0.446	390	RO-FO method
2.0 M NaCl	0.01 M NaCl	MWCNT-PES	12	–	AL-FS	2.31	0.792	2042	RO-FO method
0.5 M NaCl	0.01 M NaCl	TFN	17.1	3.974	AL-FS	1.96	0.384	–	
2.0 M NaCl	DI water	TFI	60.3	11.4	AL-FS	1.152	0.648	38	RO-FO method
0.5 M NaCl	DI water	PSf N-TFC	21	12.6	AL-FS	3.3		340	
0.5 M $MgCl_2$	DI water	3-bilayer LbL	28	1.97	AL-DS	1.15	3.161	445	RO-FO method
0.5 M NaCl	DI water	TFC-sPPSU	22.51	5.49	AL-FS	1.99	0.0399	163	RO-FO method
1.5 M NaCl	DI water	Nylon-TFC	6	1	AL-FS	0.917	0.3	1940	RO-FO method
0.5 M NaCl	10 mM NaCl	LbL AgNPs	17.9	2.8	AL-FS	3.924	–	–	–
2.0 M NaCl	10 mM NaCl	TFN	25	3	AL-FS	3.6	0.103	380	RO-FO method
1.0 M NaCl	DI water	CTA/CA	10.39	4.909	AL-FS	–	–	–	–
2.0 M NaCl	DI water	TFC-sPPSU	48	7.6	AL-FS	3.23	1.05	65.2	RO-FO method
0.5 M $MgCl_2$	DI water	PAI-PES/PEI	20.8	6.448	AL-FS	4.1	0.08	63.3	RO-FO method
1.5 M NaCl	DI water	TFC with nano fiber	35.0	8.0	AL-FS	2.04	1.57	109.1	RO-FO method
1.5 M NaCl	DI water	PA/ACE-TFC	12.5	1.4	AL-FS	–	–	–	–
0.3 M NaCl	DI water	LbL	11	8	AL-DS	–	–	–	–
0.1 M $MgCl_2$	DI water	LbL	20.66	0.138 g/L	AL-FS	6.1	–	–	–
2.0 M NaCl	DI water	TFC	35	7	AL-FS	–	–	–	–
1.0 M NaCl	DI water	CAB	9.4	3.9	AL-FS	0.51	0.4	–	–
0.5 M $MgCl_2$	DI water	PAI/PES	27.5	5.5	AL-FS	15.9	–	–	–
2.0 M NaCl	DI water	PDA@Psf TFC	24	–	AL-DS	0.6	0.19	151	RO-FO method
2.0 M NaCl	DI water	CAP-TFC	31.8	1.6	AL-DS	1.42	0.132	695	RO-FO method
2.0 M NaCl	DI water	TFC-PES	32.1	6.15	AL-FS	1.18	0.135	219	RO-FO method
0.5 M $MgCl_2$	DI water	LbL	42.3	19.516	AL-FS	3.204	0.508	–	–
0.5 M $MgCl_2$	DI water	LbL	8	16.8	AL-DS	–	–	–	–
0.5 M NaCl	DI water	TFC	13	3.6	AL-FS	0.77	0.11	238	RO-FO method
2.0 M NaCl	DI water	TFC	21	2.2	AL-FS	0.73	0.25	324	RO-FO method
0.5 M NaCl	DI water	TFC	18.7	1.6	AL-FS	–	–	–	–
1.0 M $MgCl_2$	DI water	LbL	28.7	17.136	AL-FS	10.224	3.456	–	–
3.0 M NaCl	DI water	PES	30	8.766	AL-FS	–	–	–	–
2.0 M NaCl	DI water	CA	10	3	AL-FS	0.2	–	–	–
0.5 M NaCl	10 mM NaCl	TFC	12	4.9	AL-FS	1.78	0.338	–	–
1.5 M $MgCl_2$	DI water	TFC	11.7	3.861	AL-FS	–	–	–	–
1.0 M NaCl	DI water	TFC	25	–	AL-FS	1.9	0.33	312	RO-FO method

DI water: deionized water, AL-FS: active layer facing feed solution, AL-DS: active layer facing draw solution

Source: Kim et al. (2017).