Modelamiento y simulación dinámica del proceso de digestión anaerobia

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April, 2021

Dynamic modeling and simulation of the anaerobic digestion process

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Thesis or degree project presented as a partial requirement to qualify for the title of:
Maestría en ingeniería - Ingeniería química

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Research area:
Bioprocess design and control
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Manizales, Colombia
April, 2021

“Focus your wit and will”
“Hope is the greatest ally”

Agradecimientos

Quiero agradecer a mi padre Hector y a mi madre Marleny por apoyarme, ser mi ejemplo y enseñarme que la nobleza, la honestidad y la humildad son los valores que hacen grande a una persona. A mis hermanos Mario y Laura, gracias por el cariño, los ánimos y por considerarme su modelo a seguir. Todo esto es por y para ustedes. Sepan que cada cosa que hago es para hacerlos sentir orgullosos. Igualmente quiero agradecer a mi Director de tesis, el profesor Oscar Andrés Prado, una persona a la que admiro y respeto demasiado. Gracias por su exigencia, su paciencia, confianza, y a las enseñanza académicas y humanas que me brindo en este proceso. A mi Co-directora de tesis, la profesora Beatriz Aristizabal. Una persona admirable que agradezco por el constante seguimiento, apoyo, motivación, confianza, comprensión en mi trabajo y por todas las enseñanzas inculcadas. A los dos, muchas gracias por hacerme un mejor profesional, y aún más, una mejor persona.

A mis dos amigos de toda la Universidad, Carlitos y Luna. Gracias por ser indispensables, por el apoyo académico y emocional, por ser de verdad mis parceros, por los consejos, regaños, paciencia y disposición. Me alegro saber que todos lo hemos conseguido. A Lau, una persona que se convirtió en mi parcera. Gracias por los consejos, ayuda académica y sobre todo por las risas y su comprensión. A Sophi, por enseñarme que la sinceridad siempre es la mejor elección, por los buenos momentos y en especial, por recordarme que todo lo puedo y nunca dudar de mí. A Xime, una de las personas más nobles, sensatas, cariñosas e incondicionales que he conocido. Gracias por todo el apoyo académico y moral en este proceso. A mis compañeros y amigos: Ebti, Jei, Luisito, viejo Julio, Miguelin, Jhonny, Laura M, Ana, Camilo Z, Santiago B. Gracias por el apoyo y los buenos momentos compartidos. A mis amigos S.P. por el apoyo, por ser indispensables y por todos estos años de amistad.

Agradezco a la Universidad Nacional de Colombia-sede Manizales. A la Fundación Ceiba con el programa Bécate Nariño por el apoyo financiero. A la colaboración de los laboratorios de Procesos Productivos a cargo de la profesora Maria Fanny, Laboratorio de Aprovechamiento de Residuos a cargo del profesor Andrés Felipe Rojas, al Laboratorio de Calidad del Aire, al grupo de Investigación en Aplicación de Nuevas Tecnologías, GIANT y Grupo de Trabajo Académico en Ingeniería Hidráulica y Ambiental, GTAIHA, así como también al apoyo de Wilmar, Juan, Jhon y Offir.

Resumen

Modelamiento y simulación dinámica del proceso de digestión anaerobia

El principal modelo productivo que tiene actualmente la sociedad se basa en producir-consumir-descartar. Este consiste en la extracción de materias primas que se suelen utilizar una sola vez, y cuando se desechan, no se vuelven a usar. Este sistema se conoce como economía lineal y funciona bajo el principio de que todo lo fabricado tiene un final y acaba saliendo del ciclo de producción. Sin embargo, existe otro modelo, la economía circular, y se basa en un proceso sostenible, donde los materiales y recursos se mantienen en el ciclo productivo y en la economía durante el mayor tiempo posible sin perder su valor y conservando su vida útil. Una de las tecnologías que implementa la filosofía de la economía circular es el proceso de digestión anaerobia. Es un proceso en el que microorganismos descomponen materia orgánica para producir energía renovable en forma de metano y productos plataforma de alto valor agregado. El desarrollo y estudio constante de esta tecnología une aspectos ambientales y energéticos, promoviendo la implementación de una economía circular, mitigando el impacto negativo en el medio ambiente, la preservación de los recursos y el desarrollo económico y social.

Esta tesis, a través de ensayos experimentales y modelado y simulación computacional, investiga escenarios de producción de metano y compuestos de valor agregado utilizando digestión anaerbia de residuos orgánicos locales. Desde una perspectiva experimental, se evaluó el Potencial Bioquímico de Metano (PBM) de residuos de alimentos del Departamento de Nariño, Colombia. El rendimiento de metano se determinó en condiciones mesófilas, monitoreando las variables del proceso como el pH, demanda química de oxigeno soluble (DQOs), la producción de biogás y la calidad del metano a través de un ensayo de medición de metano en línea y un ensayo con botellas destructivas. Los resultados de PBM de los residuos de alimentos con una relación C/N de 12.81, mostraron una producción de biogás de 306 mL gSV^{-1}, una concentración de metano del 73 % y un rendimiento específico de metano de 251 mL CH_4 gSV^{-1} en 31 días. Asi mismo, la remoción de DQOs fue del 62 % y el pH se mantuvo dentro del rango operativo óptimo para la digestión anaerobia (6.5-7.5).

Después, se implementó un estudio tecnoeconómico para comparar la producción de biometano y la producción de Ácidos Grasos Volátiles (AGV) a partir de la digestión de residuos de alimentos en un contexto Colombiano. Para evaluar la viabilidad económica se utilizó el índice de Valor Presente Neto (VPN) con un modelo económico riguroso, utilizando variables de entrada como: costos de construcción, costos de logística y servicios, cantidad de sustrato disponible, tasa de inflación, precios de venta del producto, calidad de metano encontrada en ensayos los de PBM, entre otros. Esta evaluación económica permitió encontrar que el proceso de digestión anaerobia orientado a la producción de AGV puede ser 11 veces más lucrativo que la generación de biometano. A su vez, el biometano podría reemplazar y satisfacer hasta el 15 % (545455 m^3 biometano año^{-1}) del consumo de gas natural en el sector de transporte y el 5 % (378 ton de AGV año^{-1}) de las exportaciones de AGV de Colombia.

Finalmente, se propuso un caso de estudio para investigar la bioproducción óptima de AGV bajo perturbaciones de entrada. Anaerobic Digestion Model 1 (ADM1) se utilizó para diseñar e implementar la optimización de la estructura de control basada en una estrategia "override", donde el pH fue la variable controlada. Un algoritmo de optimización en tiempo real encontró los mejores escenarios de producción bajo perturbaciones de entrada. La implementación de la optimización en tiempo real en un control de lazo cerrado de digestión anaerobia permitió mejorar la producción y los ingresos por ventas de AGV, lo que se evidenció en un aumento de 8771 USD día^{-1} respecto al proceso nominal, y un aumento del 7 % cuando el sistema fue perturbado en condiciones desfavorables, con respecto al punto de operación.

Los resultados obtenidos de los ensayos experimentales y de la simulación y control del modelo matemático propuesto, mostraron el potencial de producción de metano a partir de residuos de alimentos en Colombia, así como la rentabilidad económica de la producción de AGV como una nueva perspectiva de la digestión anaerobia. Este estudio contribuye a la transferencia de conocimiento del proceso, se promueven prácticas para la economía sustentable y se presentan oportunidades de obtener productos de valor agregado y a su vez, demostrar el potencial económico de productos no convencionales en digestión anaerobia.

Palabras clave: Digestión anaerobia; Residuos de alimentos; ADM1; Modelamiento y simulación; Análisis tecnoeconómico.

Dynamic modeling and simulation of the anaerobic digestion process

Abstract

The main productive system that society has is to produce-consume-discard. It consists of extracting raw materials, which are usually used only once and when discarded, they are not used again. This approach is known as linear economy and works under the principle that everything manufactured has an end and ends up leaving the production cycle. However, there is another approach, the circular economy it is based on a sustainable process, where materials and resources are to be maintained in the production cycle and in the economy, for as long as possible, without losing its value and conserving its lifespan. One of the technologies that implements the philosophy of the circular economy is the anaerobic digestion process. A process by which microorganisms break down organic material to produce renewable energy in the form of methane and high value-added platform products. The development and constant study of this technology unites environmental and energy aspects, promoting the implementation of a circular economy, mitigating negative impact on the environment, resource preservation and economic and social development.

This thesis, through experimental work and computational modeling and simulation, investigates methane and value-added compounds production scenarios using anaerobic digestion from local organic waste. From experimental perspective, Biochemical Methane Potential (BMP) of domestic food waste, Colombia was evaluated. Methane yield was determined under mesophilic conditions, monitoring process variables such as pH, soluble chemical oxygen demand (CODs), biogas production, and methane quality through a on-line methane measurement assay and destructive bottle assay. The BMP results of the anaerobic digestion of food waste with a C/N ratio of 12.81, showed a biogas production of 306 mL gVS^{-1}, a methane concentration of 73 %, and a specific methane yield of 251 mL CH_4 gVS^{-1} in 31 days. Likewise, CODs removal was 62 % and the pH remained within the optimal operating range for the anaerobic digestion (6.5-7.5).

Next, a techno-economic study was implemented to compare the biomethane production and Volatile Fatty Acids (VFAs) production from the digestion of food waste in a Colombian context. To evaluate the economic viability, the Net Present Value (NPV) index with a rigorous economic model was used, using as inputs: construction costs, logistics and services costs, the amount of substrate available, inflation rate and product selling prices, methane quality found in BMP assays, among others. This economic evaluation allowed to find that the anaerobic digestion process oriented towards VFAs production can be 11 times more lucrative than biomethane generation. In turn, biomethane could replace and satisfy as much as 15 % (545455 m^3 biomethane $year^{-1}$) of natural gas consumption in the transport sector and 5 % (378 Ton VFAs $year^{-1}$) of VFAs exports in Colombia.

Finally, case study was proposed to investigate optimal bio-production of VFAs under input disturbances. The Anaerobic Digestion Model 1 (ADM1) was used to design and implement a optimizing control structure based on an override strategy where pH is the controlled variable. A real-time optimization algorithm found the best production scenarios under inlet disturbances. The implementation of a real-time optimization layer in a closed-loop control of anaerobic digestion allowed to enhance the production and incomes from sales of VFAs. This was evidenced in an increase of 8771 USD day^{-1} concerning to the nominal process, an 7 % increase when the system was disturbed in unfavorable conditions, concerning to the point of operation.

The results obtained from the experimental assays and from the simulation and control of the proposed mathematical model, showed the potential of methane production from food waste in Colombia, as well as the economic profitability of the VFAs production as a new perspective of anaerobic digestion. This study contributes to the transfer of knowledge of the process, practices for sustainable economy are promoted, opportunities are presented to obtain scenarios to obtain other value-added and in turn demonstrate the economic potential of non-conventional products in anaerobic digestion.

Keywords: Anaerobic digestion; Food waste; ADM1; Techno-economic analysis; Modeling and simulation.

Products

Journal papers

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2021. *Evaluation of anaerobic digestion beyond biogas*. Journal of Environmental Chemical Engineering. Status: submitted.

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2021. *Real-time optimization for enhanced closed-loop control of anaerobic digestion for VFAs production under disturbances.* Status: paper under development 80 %.

Academic awards

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2020. *Potential Volatile Fatty Acids production through controlled Anaerobic Digestion*. European Biosolids Bioresources VIRTUAL Conference, 24^{th} – 25^{th} November. AquaEnviro, Bristol-England. WINNER OF THE POSTER AWARD.

Project funding

- This work was carried out with the scholarship project: "Formación del talento humano de alto nivel para el fortalecimiento de necesidades estratégicas en ciencia, tecnología e innovación en el departamento Nariño" by Fundación Ceiba and Bécate Nariño program. 2019-2020.

Peer reviewed conference papers

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, (2020). *Valoración de la Digestión Anaerobia más Allá del Biogás*. In Proceedings of "XLI Encuentro Nacional de la AMIDIQ" (ISBN: en trámite). María del Rosario Enríquez Rosado (Editor). Pages: BIO-327-332. Academia Mexicana de Investigación y Docencia en Ingeniería Química (AMIDIQ).

Conference Presentations

Conference oral presentation

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2019. *Evaluación económica del proceso de digestión anaerobia para la producción de biogás y productos plataforma*. VI Feria Ambiental, 29^{th} and 30^{th} October, Manizales, Colombia.

Conference poster presentation

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2020. *Potential Volatile Fatty Acids production through controlled Anaerobic Digestion*. European Biosolids Bioresources VIRTUAL Conference, 24^{th} – 25^{th} November. AquaEnviro, Bristol-England.

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2020. *VALORACION DE LA DIGESTIÓN ANAEROBIA MÁS ALLÁ DEL BIOGÁS*. XLI Encuentro Nacional de la Academia Mexicana de Investigación y Docencia en Ingeniería Química A.C. (AMIDIQ), $22^{th} - 24^{th}$ October. Ixtapa Zihuatanejo, México.

- Oscar Dario Yepez-Ceron, Beatriz Aristizabal, Oscar Andrés Prado-Rubio, 2019. *Evaluación económica del proceso de digestión anaerobia para la producción de biogás y productos plataforma*. 8 Congreso Internacional de Desarrollo Sostenible y Medio Ambiente. Cambio climático en las perspectivas de los Objetivos de Desarrollo Sostenible - ODS, 22^{th},23^{th} and 24^{th} Octubre, Manizales-Colombia.

- Oscar Dario Yepez-Ceron, Andrea Jaramillo-Carmona, Rosa Camila-Parra, 2019. *Producción de biogás como aprovechamiento de residuos de alimentos en el departamento de Caldas*. 8 Congreso Internacional de Desarrollo Sostenible y Medio Ambiente. Cambio climático en las perspectivas de los Objetivos de Desarrollo Sostenible - ODS, 22^{th},23^{th} and 24^{th} Octubre, Manizales-Colombia.

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1 Introduction

About 80 % of global energy consumption comes from fossil fuels, which are considered the main source of acidifying pollutants and greenhouse gases that accelerate global warming and climate change (Jimenez et al., 2015). Hence, the importance of studying and evaluating new unconventional technologies to produce sustainable and self-sustaining energy without causing damage to the environment, following the philosophy of a circular economy. In a circular economy, unlike the linear economy, resources are regenerated within the biological cycle, recovered, and restored thanks to the technical cycle (Macarthur, 2006). Renewable energy that follows this philosophy, with great potential and that currently has great relevance worldwide, is the production of biogas through a biological process called anaerobic digestion.

Anaerobic digestion is a technology developed for the degradation of organic waste within biodigesters or anaerobic digesters. Four main steps for degradation occur in these: hydrolysis, acidogenesis, acetogenesis and methanogenesis, which, due to the action of different microorganisms, organic substrates such as food residues, pruning residues, domestic garbage, solid manure, sewage, agro-industrial residues, etc., are converted into energy in the form of biogas containing mainly methane (main component for energy production) and carbon dioxide (Guo et al., 2017).

Food waste is one of the most promising organic waste suitable substrate for anaerobic digestion due to its high energy content and its availability is relatively vast. The anaerobic digestion process is a proven and effective solution for the treatment and valorization of food waste (Zhang et al., 2014). In Colombian context, the characterization of food waste is limited, as well as its study in the anaerobic digestion process. Cadavid-Rodríguez L.S. and Bolaños-Valencia (2015), Guerrero Pinzón and Delgadillo Mirquez (2016), Solarte Toro et al. (2017), present some of the few studies with these local wastes for the production of biogas. The physico-chemical characterization of these wastes is arduous, however, it allows to know the potential for the generation of renewable energy, along with technology development for waste management.

Additionally, an alternative approach to the anaerobic digestion process is to target the production of Volatile Fatty Acids (VFAs): acetic acid, propionic acid, butyric acid and valeric acid. The direct recovery of these digestion products (which are produced in the acidogenesis process) or further processing to obtain other molecules (for example, polyhydroxyalkanoates (PHAs) or medium chain length fatty acids), can result in the production of end products with more added value than the conventional product, biogas (Kleerebezem et al., 2015).

Although the application of anaerobic digestion to degrade organic compounds and produce biogas has been successful (in addition to being a well-established process), the optimal design of anaerobic digesters for maximum methane production, and even for production of VFAs, remains a challenge. The above due to the variability of the substrate and its weak decomposition, the complexity of microbial consortium, destabilization, low biogas production, complicated biochemical, physical and chemical interactions involved in the processes and inhibitions that can destabilize the process (Donoso-Bravo et al., 2011; Yu et al., 2018). To address these drawbacks, increased efforts to optimize the process performance are crucial. One way to do this issue can be through the simulation and mathematical modeling of the anaerobic process (Manjusha and Beevi, 2016).

Recently, several mathematical models of AD have been proposed and in turn they have been implemented in different computer platforms for their simulations. The review document by Batstone et al. (2015) covers the latest studies and developments of mathematical models of the anaerobic digestion process that describe this process, being the ADM1 model (Anaerobic Digestion Model No 1) (Batstone et al., 2002) more complete and widely used. The use of this model allows a better understanding of the process, optimizing the production of biogas and alternative products and as a platform for the implementation of a control system.

In order to study the anaerobic digestion process for the production of biogas and VFAs, this study evaluates the potential of the production of biogas (biomethane) from local organic residues using Biochemical Methane Potential (BMP) assays. Compare through a rigorous economic model and the Net Present Value (NPV) index, the economic viability of the production of biomethane and VFAs in a local context. Finally, implement a closed loop control system, using ADM1 as a platform, to identify variables and conditions processes that can improve VFAs production, using a real-time optimization layer to ensure the highest profit from VFA sales.

1.1. Hypothesis

Upon completion of the proposed investigation, the following hypotheses are expected to be verified:

- It is possible to determine design and operation limitations of the anaerobic digestion process through rigorous dynamic modeling and simulation of the system.

- It is possible that the anaerobic digestion process together with the production of other compounds is a techno-economically viable option in a Colombian context.

Design limitations are related to operating conditions (i.e. temperature, pH, input substrate flow, soluble compounds and substrate particulates concentration).

1.2. Thesis objectives

1.2.1. General objective

- Investigate biogas production scenarios and value-added compounds using anaerobic digestion from local organic waste.

1.2.2. Specific objectives

- Propose and implement a mathematical model of anaerobic digestion using the MATLAB-SIMULINK platform.
- Determine the optimal biogas (biomethane) yield by simulating the mathematical model proposed using food waste as a substrate.
- Evaluate modifications to the mathematical model focused on the generation of alternative products.

Note regarding specific objective 3: during the research, it was noticed that VFAs accumulation was achieved using the original proposed model, when exploring the operational window in a broader spectrum. This makes it unnecessary to include structural changes in original model ADM1 for preliminary research of VFAs production by anaerobic digestion.

Although the thesis was planned to basically perform simulation, the scope of the project was increased due to the formulation and funding achieved through the project: "Formación del talento humano de alto nivel para el fortalecimiento de necesidades estratégicas en ciencia, tecnología e innovación en el departamento Nariño" by Fundación Ceiba and Bécate Nariño program, allowed to carry out part of the experimental part and complement the research focused on the production of methane from local organic waste.

1.3. Thesis content

This thesis is organized into chapters written in the form of a scientific article (except for the second chapter). Due to this distribution, some information is repeated so that each chapter is understandable to the reader. The thesis consists of the following chapters:

- Chapter 2 entitled: "Anaerobic Digestion Process" describes the fundamentals of the anaerobic digestion process and the potential for methane production from food waste form the Nariño region, Colombia, is evaluated through Biochemical Methane Potential (BMP) assays.
- Chapter 3 entitled: "Economic evaluation of the anaerobic digestion process" presents a techno-economic comparison of the products of the anaerobic digestion process: bio-methane and volatile fatty acids (VFAs), from waste in Colombian context, through a rigorous economic model, applying the Net Present Value (NPV) index.
- Chapter 4 entitled: "Modeling and simulation of the anaerobic digestion process" includes simulation of Anaerobic Digestion Model No 1 (ADM1) as a platform for the implementation of a control structure with real-time optimization (RTO) algorithm for enhance the VFAs bio-production under inlet disturbances.
- Chapter 5 entitled: "Conclusions and recommendations" shows an overview of the contributions to knowledge made in this thesis together with proposed recommendations for future research.

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2 Anaerobic Digestion Process

In this chapter, as a preamble, a literature review of the fundamentals of anaerobic digestion process was conducted, where information is collected on factors that affect the process, microorganisms that are involved, types of bioreactors, alternative products of anaerobic digestion and its benefits. Then, the Biochemical Methane Potential (BMP) of food waste samples collected from a restaurant (Nariño region, Colombia) was evaluated. Physico-chemical characterization of the food waste was performed, including proximate analysis, ultimate analysis, calorific value, among others. The methane yield was determined under mesophilic conditions, using two complementary assays. The first assay determined the methane yield using a German online biogas measurement equipment, Yieldmaster-Bluesense, and the second assay monitored process variables such as pH and soluble CODs through the sacrifice bottle method. The results of this chapter serve to understand the anaerobic digestion process, to identify variables that affect the process and to quantify the methane yield that food waste can generate. In addition, this chapter shows the methane concentration obtained through the anaerobic digestion of food waste (BMP assays), a necessary parameter for a techno-economic analysis that evaluates the economic viability when producing biomethane and Volttie fatty acids (VFAs).

2.1. Fundamentals of the anaerobic digestion process

Anaerobic digestion is a biological process where organic matter, in the absence of oxygen, is degraded and converted by microorganism families to macromolecules and then in methane and carbon dioxide, also called biogas (Toerien and Hattingh, 1969). This process occurs in biodigesters, which are hermetic and waterproof constructions that prevent the entry of air and supply the conditions for microorganisms to degrade organic matter. At the same time, this process is also known as an unconventional, environmentally sustainable technology, able to convert a variety of waste: municipal solid waste (organic part), animal manure, wastewater, and agricultural waste in the form of biogas (Horan et al., 2018).

Biogas, the main product of the anaerobic digestion process, is composed of 50 to 75 % methane, 25 to 50 % carbon dioxide and 2 to 8 % of other gases such as nitrogen, oxygen, and traces of gases (hydrogen sulfide (H_2S), ammonia (NH_3) and water vapor) (House and Surratt, 2013). A summary of the typical composition and properties of biogas is presented in Table **2-1**. The degradation of organic matter to methane is complex and is achieved through a sequence of reactions in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Gavala et al., 2003).

Table. **2-1**: Chemical composition of biogas, substances and component properties. (Braun, 2007)

Component	Concentration	Properties
CH_4	50-70 % (v/v)	Energy Carrier
CO_2	25-50 % (v/v)	Corrosive, especially in the presence of water
H_2S	0-5000 ppm	Corrosive, SO_2 emissions during combustion
NH_3	0-500 ppm	NO_x emissions during combustion
N_2	0-5 % (v/v)	Decrease heating value
Water steam	1-5 % (v/v)	Corrosive, decrease heating value

In the first stage, enzymatic hydrolysis, complex materials degrade in their monomers. In the acidogenesis or fermentation phase, volatile fatty acids (VFAs) are generated along with alcohols, lactic acid, CO_2, H_2, NH_3, H_2S, and new cellular material. Acetogenesis is the third step in which acetate and molecular hydrogen are produced through anaerobic oxidation of higher fatty acids and the conversion of propionate, butyrate, and valerate into acetate and hydrogen. Methanogenesis, the final stage, involves the production of methane from carbon substrates (Nguyen, 2014). An outline of the anaerobic digestion process is presented in Figure **2-1**.

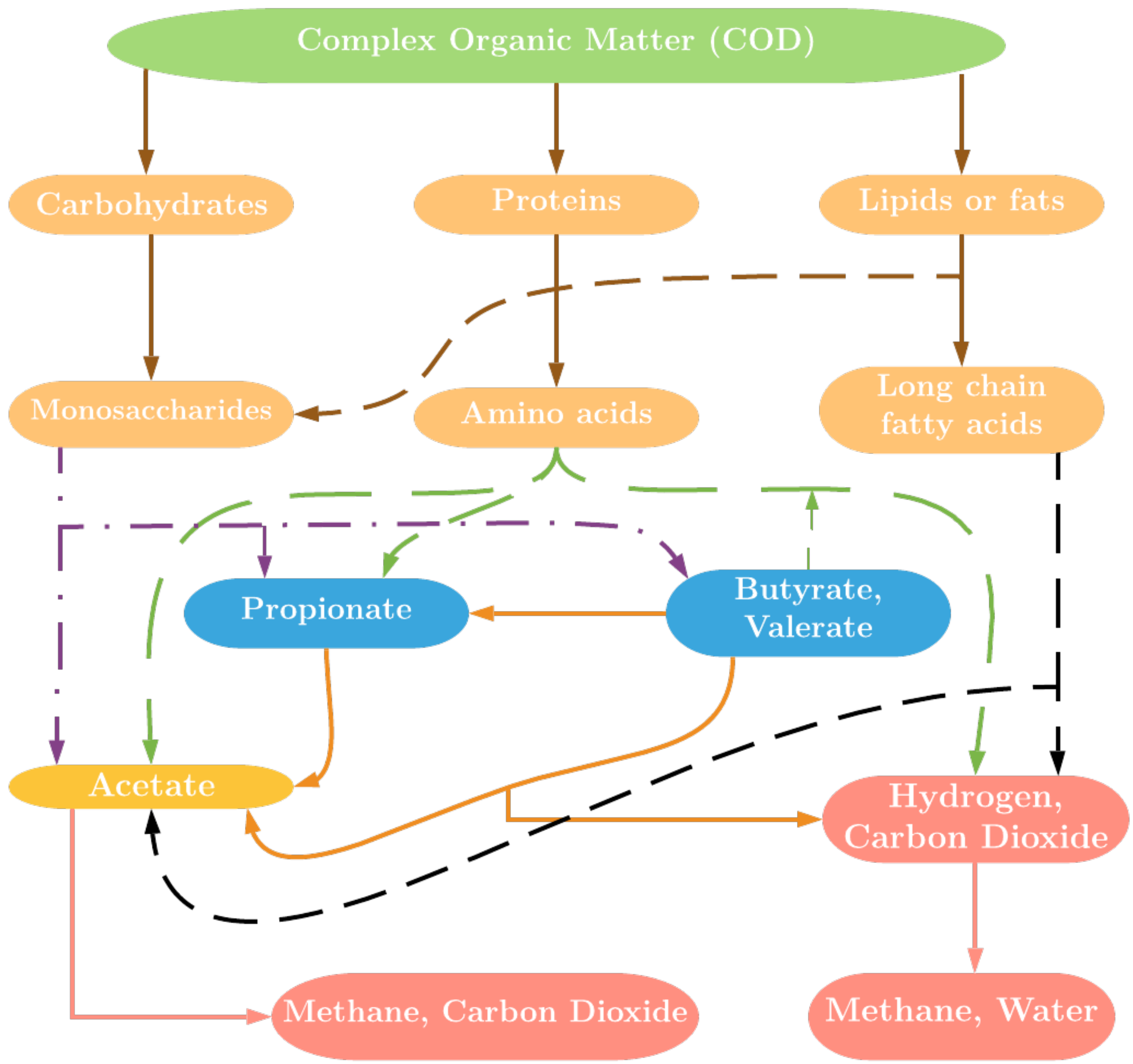


Figure. **2-1**: Sketch of the reaction pathways in the anaerobic digestion process. The brown dotted line represents the degradation of lipids in monosaccharides; the violet dotted line represents the breakdown of monosaccharides in acetate, propionate, butyrate, and valerate; the dashed green line represents the breakdown of amino acids into acetate, propionate, valerate, and butyrate, and hydrogen; the black dotted line represents the breakdown of long chain fatty acids in acetate and hydrogen. Adapted from Manchala et al. (2017).

Biogas can be used as a fuel for cooking, as heating and, as a cogeneration fuel, for the production of electrical energy (Guo et al., 2017). Besides the energy generated, the digestate or biol is the main side product of the anaerobic digestion process. This has been used as biofertilizer to provide nutrients to the plants and increase the organic composition of the soil (Kumar and Tuohy, 2018). Also, the use of biol as a raw material for the construction of ceramic materials has been studied, giving a new alternative for its use (Salazar, 2019). More recently, the anaerobic digestion process has gained attention as a cost-effective and ecological alternative for the production of VFAs, which include substances such as acetic acid, propionic acid, butyric acid, valeric acid, lactic acid, and caproic acid (Wang et al., 2014). As can be seen in Figure **2-1**, these compounds are intermediaries for the production of hydrogen thus for the production of biogas, being, second most limiting stage of the process, since the accumulation of these compounds would inhibit process. Their bioproduction from waste could become a sustainable alternative to petro and chemical synthesis of these platform compounds.

In developed countries of Europe, North America and Asia, biogas production is highly industrialised and large-scaled, where biogas is mainly used for energy generation in engines (combined heat and power plants) or burners. For a technical use of biogas, calorific value, and ignition temperature should be taken into account as some of the important physical properties. Table **2-2** shows the expected physical properties of biogas.

Table. **2-2**: Physical properties of biogas with an average composition of 60 % (v/v) CH_4, 38 % (v/v) CO_2 and 2 % (v/v) trace gas components (Braun, 2007)

Parameter	Unit
Net calorific value	21.48 MJ m^{-3}
Density	1.21 kg m^{-3}
Ignition temperature	700 °C
Explosive mixture límits of CH_4 with air	4.4-16.5 % (v/v)
Rate of flame propagation	0.25 m s^{-1}
Air requirement for combustion	5.71 m^3 m^{-3} biogas
Odor	500000 Odor units m^{-3}

In this way, organic waste can be transformed into valuable products following the circular economy philosophy. The circular economy aims to ensure that the value of products and materials is maintained for as long as possible in the production cycle. The ability and flexibility of the anaerobic digestion process to digest a large amount of organic waste, and in turn produce a variety of products, consolidate the role of the anaerobic digestion process in the circular economy.

2.2. Microorganisms involved in the anaerobic digestion process

The anaerobic digestion process is a complex bioprocess performed mainly by bacteria, but higher trophic groups such as protozoa and anaerobic fungi may also be present. The microbial population contains many genera (types) of strictly anaerobic bacteria and facultative anaerobic bacteria (Murphy and Thamsiriroj, 2013).

Currently, four different trophic groups are common in anaerobic processes. Figure **2-2** shows these groups. The coordinated activity of these trophic groups as a whole ensures the stability of the process.

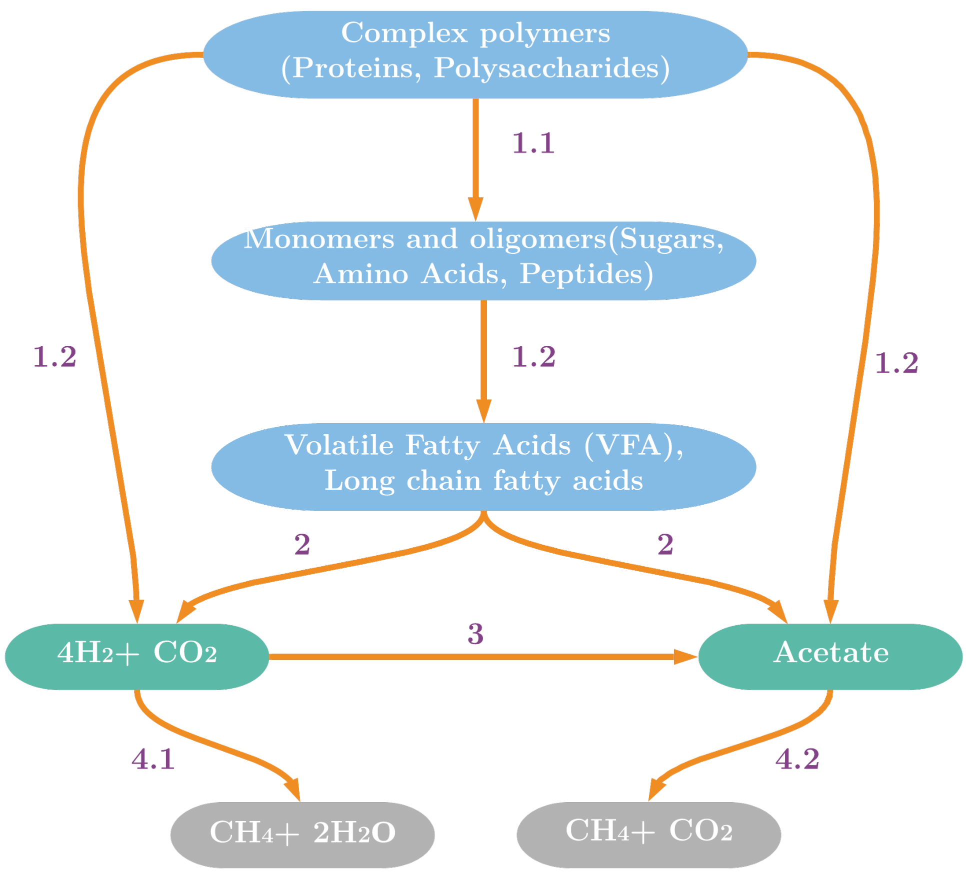


Figure. **2-2**: Four trophic groups involved in the anaerobic digestion process. 1. Acidogenic bacteria. 1.1. Hydrolytic bacteria 1.2. Fermentative bacteria 2. Acetogenic bacteria. 3. Homoacetogenic bacteria. 4. Methanogenic bacteria. 4.1. Methanogenic hydrogenotrophic bacteria. 4.2. Acetoclastic methanogenic bacteria. Adapted from Murphy and Thamsiriroj (2013).

Acidogenic bacteria: This group consists of fermentative and hydrolytic bacteria. Hydrolytic bacteria break down the carbohydrate into monomers and detects soluble material in particulate matter. Fermentative bacteria transform the resulting monomers in a wide range of products. The final products of the acidogenic stage include acetic acid, hydrogen and carbon dioxide. However, most of the products are volatile fatty acids with a greater number of carbons, such as propionate, butyrate, valerate, and also complementing substance as alcohols.

Acetogenic bacteria: This is a group of bacteria known as forced proton-reducing acetogenic microorganisms. This a syntropic group, which implies that they must act together with bacteria in a different trophic group to digest a substrate. A product of their own metabolism is hydrogen, which is toxic to them, thus, these bacteria require to interact with other species that can use hydrogen. These bacteria are fundamental in the anaerobic digestion process since they convert fermentative intermediates (VFAs) into methanogenic substrates: hydrogen, carbon dioxide, acetic acid, and uncarbonated compounds.

Methanogenic bacteria: This group consists of hydrogenotrophic methanogenic bacteria and acetoclastic methanogenic bacteria. The hydrogenotrophic bacteria utilise hydrogen which the acetogens produce. The relationship between acetogens and hydrogenotrophic methanogenic bacteria is a good example of syntropic mutualism: bacteria in different trophic groups converting propionate, butyrate, and long-chain acids into methane and water.

Species of only two genera *Methanosarcina and Methanothrix* can produce methane from acetic acid and are referenced to as aceticlastic. Hydrogenotrophic methanogens have relatively fast growth rates, which make them very efficient. The final product is methane and the contribution of the hydrogenotrophic pathway is from 27 to 30 % and by the acetoclastic route, it is 70 %.

Homoacetogenic Bacteria: They are strict bacteria that catalyze the formation of acetate from carbon dioxide and hydrogen. Hydrogen-consuming acetogens appear to be outcompeted by methanogens for hydrogen. The net result, however, is the maintenance of low hydrogen partial pressures and increased significance of acetate as an immediate methane precursor.

2.3. Types of anaerobic biodigesters

There are several types of biodigesters that are currently in use for biogas production. Table **2-3** shows the characteristics and description of the main biodigesters in which the anaerobic digestion process is carried out. Depending on the required application, the type of biodigester is chosen and used. For laboratory scale studies, Anaerobic Sequential Batch Reactor (ASBR) biodigesters are the most appropriate. The main considerations for the biodigesters design are substrate type, phase, product inhibition, bioenergy recovery, and mass transfer limitations (Uçkun Kiran et al., 2016).

There are three main biodigesters groups. The first is the discontinuous digester. These biodigesters are fed with organic raw materials and inoculum and then, the anaerobic degradation occurs. Once all the organic material has been degraded, the content of the reactor is discharged, cleaned and a new batch is added for digestion (Kumaran et al., 2016).

The second type is the continuous stirred tank digester, where all biochemical reactions take place in the same reactor. The substrate is fed constantly(continuously or in small batches with a defined interval of time), and as a direct consequence, the biogas production is almost stable. The main advantage of this biodigester is its simplicity in construction and operation (Gonzalez-Fernandez et al., 2015). Finally, there is the two-stage (or even multi-stage) continuous feeding system, where the hydrolysis/acidogenesis and acetogenesis/methanogenesis stage are separated in different reactors (Moo-Young, 2011).

Anaerobic biodigesters can also be classified as low rate or high-rate biodigesters. Table **2-4** shows a comparison of these types of reactors. The main difference between them is the application. High-rate biodigesters are used for bioenergy production, while low-rate biodigesters are used to treat and dispose of organic waste (sewage, feces, etc.). Some examples of low-rate biodigesters are anaerobic ponds, septic tanks and Imhoff tanks (Varnero Moreno, 2011). High-rate biodigesters have been used to formulate the mathematical models for biogas production.

On the other hand, the selection of the biodigester, the biomass retention capacity should be considered since anaerobic microorganisms slowly grow during the metabolic generation of methane and hydrogen. It is often essential to select a biodigester configuration that decouples the hydraulic retention time (HRT) from the solid retention time (SRT). Such decoupling can maintain a significantly high SRT/HRT ratio which favors a faster growth of anaerobic microorganisms (Khanal, 2008).

Table. **2-3**: Biodigesters used in the anaerobic digestion process

Biodigester	Description and characteristics	References
Anaerobic Contact Process (ACP)	▪ ACP is composed of a conventional anaerobic reactor with stirring ▪ The influent reactor is directly in contact with the anaerobic biomass ▪ HRT is 12 to 24 hours ▪ The SRT in the system is of the order of 25 to 40 days, producing the hydrolysis of solids and their subsequent mechanization	Varnero Moreno (2011); Khanal (2008)
Upflow anaerobic sludge blanket- (UASB)	▪ It is a suspended growth system in which adequate hydraulic and organic loading conditions are maintained to facilitate the formation of dense lumps of biomass known as granules ▪ The diameter of the granules varies from 1 to 3 mm ▪ An extremely long 200-day SRT can be achieved with a low HRT, approximately 6 h ▪ It is ideal for the production of biogas with a high concentration of methane from a feed stream with high solubility	Cruz-Salomón et al. (2017); Hulshoff Pol et al. (2004); Khanal (2008)
Anaerobic Sequential Batch Reactor (ASBR)	▪ It is a batch variation of the UASB, where a single reactor is used to fill, react, sediment and decant ▪ The ASBR process is recommended for bioenergy production from animal manure and another biowaste (wastewater, food waste) ▪ High levels of biomass can be achieved in the reactor regardless of HRT	Borja (2011); Mao et al. (2015); Khanal (2008)
Anaerobic Filter (AF)	▪ Upflow Anaerobic Filter (UAF): corresponds to a type of tubular anaerobic reactor that operates in a continuous and upward flow regime. Typically, HRT varies from 0.5 to 4 days and the loading rate varies from 5 to 15 kg COD m^{-3} ▪ Downflow Anaerobic Filter (DAF): it is similar to the UAF, only that it operates at a downstream flow	Meng et al. (2016); Khanal (2008)

Table. **2-4**: Comparison of high and low-rate biodigesters (Varnero Moreno, 2011; Fujihira et al., 2018; Rico et al., 2017)

Low-rate biodigesters	High-rate biodigesters
They are not mixed	They are mixed
Conditions such as Temperature, SRT and others are not controlled	They maintain a high level of biomass in the bioreactor
Organic load rate is a low range of 1-2 kg COD m^{-3} day^{-1}	Organic load rates vary from 5 to 30 kg COD m^{-3} day^{-1} or even higher
They are not suitable for bioenergy production	They are more appropriate for bioenergy production

2.4. Influence of operation conditions

In the anaerobic digestion process, microorganisms must remain in optimal-operating conditions to achieve maximum process performance. Depending on the component to be produced (biogas or VFAs), the factors that affect the process will determine the stability and the products quality. The following is a description of the most relevant factors that affect the process for the production of biogas, while Section 2.6.1 describes the factors that govern the process for the production of VFAs.

2.4.1. Anaerobic process temperature

Temperature is the most important physical factor affecting the kinetics of the biochemical reactions, especially methanogenic bacteria growth (Lier et al., 1997). The temperature ranges are classified into:

- **Psychrophilic:** less than 20 °C
- **Mesophilic:** between 20 °C and 40 °C
- **Thermophilic:** greater than 40 °C

Methanogenic bacteria reach a max growth rate of 60 °C for thermophilic conditions. For mesophilic conditions, optimal growth is between 30 and 36 °C. For the psychrophilic conditions, the worst growth conditions are found, reaching only 23 % at temperatures between 13 and 18 °C. Figure **2-3** shows how growth trend of methanogenic bacteria decreases exponentially when they exceed the specific temperature where the growth rate is maximum.

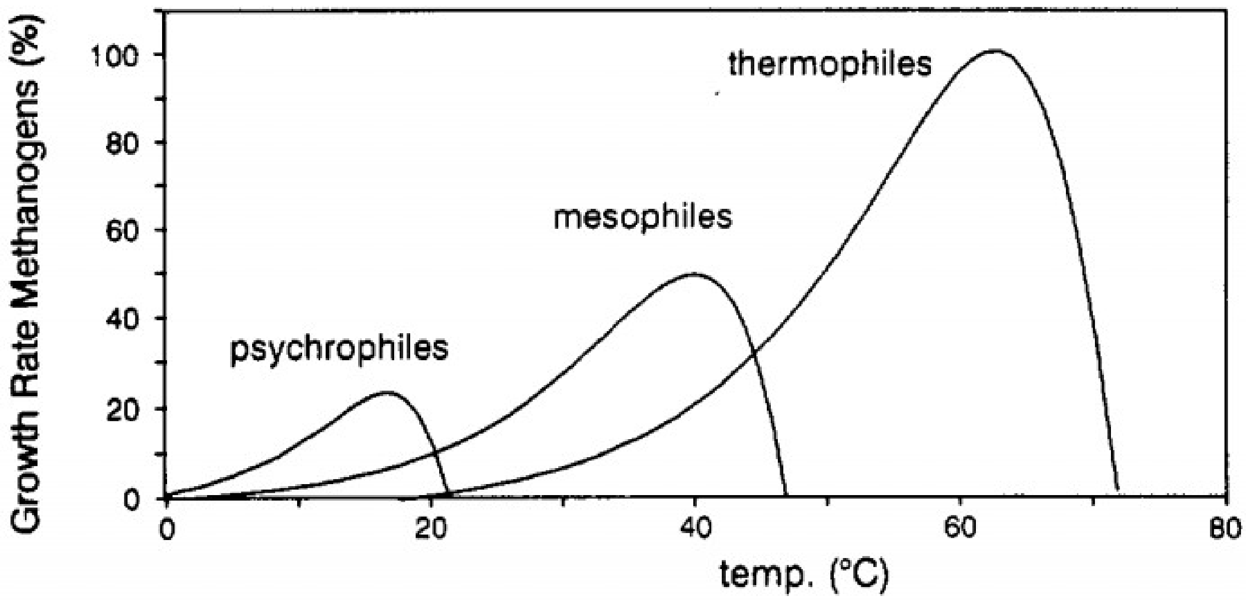


Figure. **2-3**: The relative growth rate of psychrophilic, mesophilic and thermophilic methanogens. Taken from Lier et al. (1997)

The thermophilic conditions, although the elimination of pathogenic microorganisms is higher, it is usually more sensible at any change in operating conditions. In addition, it exhibits inhibition problems due to the higher toxicity of certain compounds at high temperatures (i.e. ammoniacal nitrogen or long-chain fatty acids). Under thermophilic conditions, biogas production up to 30 % higher can be achieved, the biogas has more carbon dioxide concentration. For this reason, mesophilic conditions are considered as the optimal condition for the anaerobic digestion process (35-37 °C). In addition, small changes in temperature in this regime are less sensitive and do not influence the efficiency of the process.

2.4.2. pH and alkalinity

Small variations in pH cause the anaerobic digestion process to be negatively affected, especially for methanogenic microorganisms. To maintain the activity of methanogenic archaea, the optimum pH range should be between 6.8 and 7.5. For fermentative bacteria, the pH range is between 5.0 and 6.0, with tolerance for pH values of up to 4.5 (López-Hernández et al., 2017). A decrease in the pH value increases the activity of fermentative microorganisms, while consumers of their (slower) products are inhibited by the increase in acidity. The differences are one of the main operational problems in the anaerobic digestion process.

The pH value affects both biogas production and methane composition. When the pH is below 6, the biogas has low percentage of methane, negatively affecting its energy capacity.

Studies suggest that for anaerobic digestion at mesophilic conditions, the optimal pH range should be between 6.5-7.5 (Ishida et al., 1982; Van Ginkel et al., 2001; Khalid et al., 2011). The pH is controlled primarily by the natural alkalinity as a buffer system. Each mole of organic nitrogen theoretically generates an alkalinity equivalent. Ammonia reacts with carbon dioxide to produce ammonium bicarbonate. Bicarbonate ions (HCO_3^-) are the main contributors to the alkalinity of the system. On the other hand, under unfavorable conditions (accumulation of VFAs), the pH also decreases if the system has a small buffer capacity which can cause process failures due to inhibitions (Nguyen, 2014).

To maintain the pH within the optimal ranges in the biodigester, it is often necessary to add substances that provide alkalinity to the system, such as sodium bicarbonate (preferred due to its high solubility and low toxicity), sodium carbonate, ammonium hydroxide, gas ammonia, lime, sodium, and potassium hydroxide.

2.4.3. Total and volatile solids

For the process to develop normally, the percentage of total solids (TS) contained in the substrate is an important factor to account for. Mobility of microorganisms is very limited as the amount of total solids increases, affecting efficiency and biogas production.

Experimentally, it has been shown that a load in semicontinuous digesters should not have more than 8 to 12 % of total solids to ensure the proper functioning, unlike discontinuous digesters, which have between 40 to 60 % of TS (Varnero Moreno, 2011). Volatile solids (VS) indicates the amount of material that can be used as food by microorganisms and theoretically be converted to methane.

2.4.4. Carbon/Nitrogen ratio

The substrate is the main source of carbon and nitrogen to microorganisms. However, the microbiological process also requires mineral salts (nutrients) such as sulfur, phosphorus, potassium, calcium, magnesium, iron, manganese, molybdenum, zinc, cobalt, selenium, tungsten, nickel and another minor. Residues such as manures and sewage sludge contribute to these elements in an adequate proportion, however, with the use of some industrial organic waste, the addition of these nutrients may be necessary (Varnero Moreno, 2011).

The Carbon:Nitrogen (C/N) ratio is a factor that relates the proportion of these two compounds present in the organic material. Carbon is the energy source (catabolism) and nitrogen is used for the formation of new cells (anabolism). Normally, bacteria consume 30 times more carbon than nitrogen, so the optimal ratio of these two elements in the raw material is considered in a range of 30:1 to 20:1 (Varnero Moreno, 2011).

If the C/N ratio is too high, nitrogen is rapidly consumed by methanogenic microorganisms to supply their protein requirements and is no longer available to react to the excess carbon content in the material. As a result, biogas production decreases. On the other hand, if the C/N ratio is very low, the nitrogen is released and accumulates in the form of ammonia, causing the pH to increase creating a toxic effect on methanogenic bacteria (Abbasi et al., 2012).

2.4.5. Food waste as substrate

Conventionally, the anaerobic digestion process can use organic waste of animal, vegetable, agroindustrial, domestic origin among others. Table **2-5** shows a classification of the different organic substrates used for the process.

Table. **2-5**: Organic waste from different origins Varnero and Arellano (1990).

Residue	Example
Animal origin	Manure, urine, guano, slaughterhouse waste
Vegetable origin	Weeds, crop stubble, straws, spoiled fodder
Human origin	Stool, trash, urine
Agribusiness	Crops, molasses, seed residues
Forestry	Leaves, stems, branches, and barks
Aquatic crops	Seaweed and aquatic weeds

Food waste is interesting as substrate for the anaerobic digestion process since its energy content is high, large quantity and the availability of this is relatively high. The anaerobic digestion process is an effective solution for the treatment and recovery of food waste (Zhang et al., 2014). Compared to other organic residues, food waste could be a good substrate for anaerobic digestion process due to their high degradability and physicochemical characteristics, where a high methane yield can be obtained. Table **2-6** shows a comparison of food waste with other organic substrates, where a favorable methane yield for food waste is estimated.

According to the different eating habits, the food waste composition depends on the region from which it is obtained and the presence of: rice, vegetables, meat, eggs, and other main components. Table **2-7** shows the composition and characteristics of food waste from different regions of the world. As shown in the table, the contents of total solids (TS) and volatile solids (VS) of food waste are in the ranges of 18.1-30.9 % and 17.1-26.35 %, respectively. This indicates that water represents 70- 80 % of waste.

Table. **2-6**: Substrate characteristics for the anaerobic digestion (House and Surratt, 2013)

Substrate	Organic content	C/N	Volatile Solids (%)	Methane yield (m^3CH_4 $kgVS^{-1}$)
		Animal waste		
Pig manure	Carbohydrates, proteins, lipids	7	4	0.3
Beef manure	Carbohydrates, proteins, lipids	13	6.4	0.2
Bird droppings	Carbohydrates, proteins, lipids	7	4	0.3
		Vegetable waste		
Straw	Carbohydrates, lipids	90	56-81	0.15-0.35
Pruning waste	Carbohydrates, lipids	125	54-63	0.2-0.5
Pasture	Carbohydrates, lipids	18	18-23	0.3-0.55
		Agroindustrial Waste		
Serum	75-80 % lactose, 20-25 % protein	-	4.5	0.33
Soy oil	90 % vegetable oil	-	85.5	0.8
Olive pulp		-	18	0.33
Food waste	Carbohydrates, proteins, lipids	24	20	0.5-0.6
		Sewage sludge		
Sewage sludge		-	3.7	0.4
Sewage sludge concentrate		-	7.5	0.4

The highest methane potential of food waste is in the range of 0.5-1.1 m^3 of CH_4 $kgVS^{-1}$, generally higher than other food waste substrates such as lignocellulosic biomass, animal manure and sewage sludge (Mao et al., 2015). The highest methane yield is obtained from household and restaurant food waste since it has a relatively high lipid content and also a balanced nutrient composition. Carbohydrates and proteins are generally considered rapidly degradable, thus residues of lipid-rich foods (i.e, used oil, ice cream) and easily degradable carbohydrates can achieve high methane yields. In contrast, food waste with a high ligno-cellulosic fraction and low lipid content, such as fruit and vegetable residues and brewery residues, have methane potentials of less than approximately 0.16-0.35 m^3 $kgVS^{-1}$ (Grimberg et al., 2015).

Table. **2-7**: Composition and characteristics of food waste reported in the literature for different regions

Parameter	Zhang et al. (2011)	Zhang et al. (2013)	Zhang et al. (2007)	Solarte Toro et al. (2017)
Region	Korea	China	USA	Colombia
TS %	18.1	23.1	30.9	29
VS %	17.1	21	26.35	25.3
VS/TS (%)	0.94	90.9	85.3	87.2
pH	6.5	4.2	NR	NR
C (ppm)	46.67	56.3	46.78	48.3
N (ppm)	3.54	2.3	3.16	2.1
C/N	13.2	24.5	14.8	27
S (ppm)	0.33	NR	2508	0.2
P (ppm)	1.49	NR	NR	NR
Methane yield ($mLCH_4$ gVS^{-1})	479	540	440	240

TS are the total solids (%), VS are the Volatile Solids (%), C is Carbon, N nitrogen, S Sulfur, P Phosphorus. NR is not reporting.

2.4.6. Retention Time

As previously mentioned, retention time is the period for which organic material (substrate) or microorganisms (solids) remain together in a digester to degrade the substrate to get a high consumption of carbon, nitrogen, and nutrients. A biodigester is more efficient when the retention time is shorter (Abbasi et al., 2012). However, to achieve low "substrate retention times" it is necessary to simultaneously achieve high micro-organism ("solids") retention times as explained in the following sub-sections.

Hydraulic retention time: The hydraulic retention time (HRT) is the time that an organic material spends in a digester from the instant of its entry into the digester to its exit to be degraded (Abbasi et al., 2012). Aiming for a complete degradation under mesophilic conditions, the optimal hydraulic retention time is 15-30 days and for thermophilic conditions is necessary 12-14 days (Mir et al., 2016).

Solids Retention Time: "Solids" is the term used to denote microorganisms in the anaerobic process. So, solids retention time (SRT) is microorganisms retention time. In conventional low-rate digesters and Continuously Stirred Tank Reactors (CSTR), there is no disposal to retain "solids". In those systems, HRT is the same SRT due to the solids pass out of the digesters at the same rate as the substrate to be degraded. On the other hand, for high-rate digesters, SRT > HRT since suspended growth systems allow microorganisms retention. In a typical high-rate anaerobic digester, SRT=3HRT (Mir et al., 2016).

2.5. Inhibition and toxicity effects

The inhibition is conceived as a reversible reduction of the activity of the microorganisms, while, the toxicity imposes an irreversible effect on population death. Compounds present in the organic material (feedstock) and subproducts of the metabolic activity, can affect negatively the population in the digester, causing partial or total cessation of their activity. Some effects on the anaerobic digestion process of specific feedstock compounds are presented in Table **2-8**.

Some minor compounds are present such as: sodium, calcium, potassium, magnesium, iron, chromium, manganese, selenium, iodine, lead, molybdenum, nickel, cobalt, arsenic. Their salts and heavy metals serve as micronutrients to the bacteria's activity. A high concentration of these substances, or interaction with other species, could cause toxic effect. Table **2-9** resumes salts and heavy metals that present toxicity to anaerobic metabolism.

Concerning anaerobic treatment, the most critical substances are oxygen, ammoniacal nitrogen, sulfurized compounds, and organic acids. Table **2-10** shows the inhibitory concentrations of these compounds and some descriptions.

Table. **2-8**: Feedstock compounds and their effect on the digestion process (Steffen et al., 1998; House and Surratt, 2013)

Compound	Digestibility	Feedstock source	Process disturbing effects	Process inhibition
Fats	Very good	Slaughterhouses Rendering plants	Foaming Layering Poor water solubility	High VFAs levels Low pH
Proteins	Very good	Dairy processes Pharmaceutical industry	Foaming	pH decrease High ammonia concentrations
Carbohydrates Sugars	Very good			
Starch	Very good	Agro-industries Crop residues Animal manures	Foaming	pH decrease
Cellulose	Poor			
Volatile fatty acids (VFAs)	Very good	Rendering plants Oil mills	Poor water solubility	High VFAs levels
Organic pollutants Pesticides Antibiotics Detergents	Poor	Animal manures Crop and crops residues Organic wastes	Foaming	Antibiotic effects

Table. **2-9**: The concentration of inhibitory salts and heavy metals of the anaerobic digestion process (Appels et al., 2018)

Compound	Stimulating concentration (mg L^{-1})	Moderately inhibitory concentration (mg L^{-1})	Strongly inhibitory concentration (mg L^{-1})
Na^{+}		3500-5500	8000
K^{+}	200-400	2500-4500	12000
Ca^{2+}	100-200	2500-4000	8000
Mg^{2+}	75-150	1000-1500	3000
S^{2-}		200	200
Cu^{2+}			0.5 (soluble) 50-70 (total)
Cr^{6+}		10	3(soluble) 200-250(soluble)
Cr^{3+}			2 (soluble) 180-240 (total)
Ni^{2+}			30 (total)
Zn^{2+}			1 (soluble)
Chlorides		6000	
Lead compounds		5	
Cyanide		1–2 (acclimatization possible up to 50)	
Copper compounds		1	
Potassium chloride		>10000 (acclimatization possible up to 40000)	

Table. **2-10**: Inhibitory substances for the anaerobic digestion (Appels et al., 2018).

Inhibitor	Inhibitor concentration	Description
Oxygen	>0.1 mg L^{-1}	Inhibition of anaerobic methanogenic bacteria
Hydrogen sulfide	>50 mg L^{-1}	The inhibitory effect increases with the decrease of the pH value
Volatile Fatty Acids	>2000 mg L^{-1} (pH=7)	The effect of inhibitors increases with the decrease in the pH value High adaptability of bacteria
Ammonium nitrate	>35000 mg L^{-1} (pH=7)	The inhibitory effect increases with the increase in the pH value (due to the formation of ammonia), as well as the temperature High adaptability of bacteria
Antibiotics, disinfectants	Does not apply	The inhibitory effect is product specific

2.6. Alternative products from the anaerobic digestion process

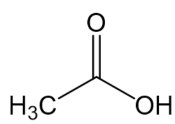
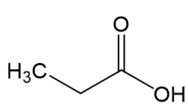
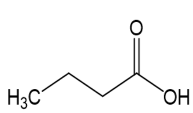
2.6.1. Volatile Fatty Acids

Conventionally, the anaerobic digestion process has been a study point and interest mainly in biogas production. However, other products can be obtained. An alternative approach to conventional anaerobic digestion process is to target the production of Volatile Fatty Acids (VFAs). These are building block chemicals with high demand in the market. Traditionally, their production is based on non-renewable petrochemical sources that cause serious negative effects on health and the environment.

VFAs are linear molecules of short-chain aliphatic monocarboxylate, having two (acetic acid) to six (caproic acid) carbon atoms. In general, they have a wide range of applications, such as a carbon source for: biogas, polyhydroxyalkanoate biopolymers (PHAs), biofuel precursors, chemical components for industries or used for the biological removal of phosphorus or nitrogen (Jankowska et al., 2017).

The most common VFAs produced from the anaerobic digestion process are acetic, propionic, and butyric acid. These are important intermediates produced in acidogenesis and acetogenesis steps of the digestion process. Properties, applications, market size, and production methods are summarized in Table **2-11**. VFAs are mostly used in fields of food and beverages as acidifiers, but also in the cosmetic industry, tanning industry, and pharmaceutical industry.

Table. **2-11**: Volatile Fatty acids general properties. Atasoy et al. (2018); Zacharof and Lovitt (2013).

VFAs	Chemical formula	Market size (kton $year^{-1}$)	Market Price (USD ton^{-1})	Application	Production methods
Acetic acid		3500000	400-800	Vinyl acetate monomer(polymers, adhesives, dyes), food additive, solvent, vinegar, ester production, chemicals	**Chemical synthesis:** Carboxylation of methanol, Acetaldehyde oxidation, Ethylene oxidation **Bioprocess:** oxidative and anaerobic
Propionic acid		180000	1500-1650	Animal and human food additive, Chemical intermediate, Solvent, Flavouring agent	**Chemical synthesis:** Hydrocarboxylation of ethylene, Aerobic oxidation of propionaldehyde **Bioprocess:** Anaerobic process
Butyric acid		30000	2000-2500	Ester used food industry as aroma additive, Food additive, flavoring, Pharmaceuticals, Animal feed supplement, Fishing bait additive	**Chemical synthesis:** oxidation of Butyraldehyde **Bioprocess:** Fungal fermentation of glucose

Usually, VFAs are obtained from petrochemical derivates synthetically and biologically process using the fermentation process. Although bio-based production methods are environment-friendly, currently these can not compete economically with the petro-based production methods (Liu et al., 2018). The lower manufacturing cost of oil-based production methods and the lower efficiency of bio-based production methods are the main reasons why petro-based production methods are dominant (Atasoy et al., 2018). However, adverse effects on the environment such as Greenhouse Gas emissions, high energy requirements, chemical requirements, and large waste and wastewater production are the driving forces shift from petrol-based production to bio-based methods (Besselink et al., 2017). For the study of bio-based VFAs production methods have particular importance nowadays. Research has been focused on increasing efficiency, enhancement the operation conditions, providing renewable sources as substrate, characterizing and assessing the microbial communities with their interactions, and new separation processes.

The optimization of the operating conditions is the most significant topic of bio-based VFAs production methods. Table **2-12** shows operation conditions in terms of pH, temperature, type of substrate, retention time, and reactor type effects on VFAs production through bio-based process. pH has the biggest impact on concentration and composition of VFAs. pH values between 5 and 11 favor the production of VFAs, having a wide range compared to the optimum pH for the production of biogas that is between 6.5 and 7.5. Regarding temperature, as well as for the production of VFAs and biogas, mesophilic conditions promote the production of these compounds. The type of substrate influences the production of VFAs, the degree of acidification being an important characteristic to be considered. On the other hand, the C/N ratio influences directly the biogas production. Alternatively, VFAs production requires a lower SRT than biogas oriented process, because low SRT can prevent methanogen dominance.

Table. **2-12**: Parameters that affect VFAs production.

Operation parameter	Influence of operational parameter on VFAs production	Study cases	References
pH	pH is one of the most critical parameters that have a very strong effect on the VFAs concentration and composition. Also, pH assumes an important role in increasing the production rate and yield of VFAs in the anaerobic digestion process. pH affects the microorganism activity because of the majority of enzymes do not tolerate acidic (pH<3) or alkaline (pH>12) environments[a]. Any change in pH value can control the type of VFAs produced from acidogenesis fermentation[b].	The optimal pH values for the production of VFAs are mainly in the range of 5.25–11, but the specific ranges are dependent on the type of waste used[b]. The stepwise pH fermentation strategy envelopment by Zhao et al. (2018)shows that the activity of acid producing bacteria (pH 9) was improved, as well as inhibition of the activities of methanogens (pH 11), which resulted in an increased production of VFA. Huang et al. (2018) studied the effect of pH (3, 5, 7, 9, 10 and 12) on VFAs production. Their results concluded that under pH 10, the optimal VFAs production occurred. Optimal pH for a specific VFAs production is highly dependent on the type of substrate used.	a. Liu et al. (2012) b.Lee et al. (2014)

Temperature	Temperature is a key parameter that improves VFAs production due to that it affects the enzyme activity, the growth of microorganisms, and hydrolysis rate[c]. A change of operation temperature can alter the microbial structure of the microbial consortium involved in acidogenic fermentation[d]. Also, temperature affects the type of main VFAs product in fermentation.	VFAs yields are pretty similar at both thermophilic and mesophilic conditions. However, the mesophilic temperature (35 °C) is the most optimum and economical favorable condition for VFAs production[e]. Jiang et al. (2013) stated that butyric acid was the main product at a working temperature of 55 °C, meanwhile acetic and propionic acids were the main product at 35 °C.	c. Zhou et al. (2018) d. Strazzera et al. (2018) e. Gruhn et al. (2016)
Substrate	The production of VFAs is significantly influenced by the type of substrate used. The degree of acidification is an important factor in the fermentation process for VFAs production and it is defined as the percentage of initial Chemical Oxygen Demand (COD) converted into organic acids[f]. This factor indicates the amount of VFAs produced in the anaerobic digestion process. The VFAs composition produced from waste streams is due to the characteristics (carbohydrate, lipid and protein content) of the organic matter content of the waste stream[g].	Silva et al. (2013) studied the fermentation of eight organic wastes streams. These presented significant variance in the degree of acidification, resulting in different VFAs productions. Cheese whey, sugarcane molasses and organic fraction of municipal solid waste streams presented the highest degree of acidification (up to 40 %) with total VFAs production of 2700-3300 mg L^{-1} as COD. On the other hand, landfill leachate produced 634 and 240 mg L^{-1} as COD with the lowest degrees of acidification of 2 %.	f. Jin et al. (1999) g.Atasoy et al. (2018)

Retention time	Retention time includes hydraulic retention time (HRT) and solid retention time (SRT). VFAs production depends more on the hydraulic retention time compared to the temperature of a reactor[h]. SRT can prevent the dominance of methanogens in the anaerobic process as the growth rate of methanogens is lower than that of acidogensi. This makes that a lower STR, the production of VFAs is beneficial. A higher HRT could be advantageous to VFAs production due to the microorganisms have more time to react with the waste. However, prolonged HRT could lead to stagnant VFAs production[j].	Feng et al. (2009) stated that increasing the STR from 4 d to 12 d produced a 44 % higher VFAs concentration because of the high soluble substrates amount. However, further, an increase in SRT to 16 d led in lower VFAs concentration, although there were even more soluble substrates. Lim et al. (2008) demonstrated that the production of VFAs increased as the HRT increased from 96 h to 192 h, but there was no further increase in VFAs production once the HRT exceeded to 288 h.	h. Kim et al. (2013) i. Ferrer et al. (2010) j. Lee et al. (2014)

2.6.2. Digestate or biol as organic fertilizer

In addition to generating biogas as fuel, anaerobic digestion of organic matter produces an organic residue with excellent properties as fertilizer. The solid or liquid digester or biol has no bad smell, does not attract flies, and can be applied directly to the field in liquid form. This applications are limited to the presence of pollutants like pathogens, heavy metals, etc. Otherwise, the solid biol can be dehydrated and stored for later use. In general, biol contains N_2 (1.8 %), P_2O_5 (1.0 %), K_2O (0.9 %), Mn (188 ppm), Fe (3550 ppm), Zn (144 ppm) and Cu (28 ppm) (Surendra et al., 2014).

Biol does not leave toxic residues in the soil, raises the quality of the soil, and can be considered as a good fertilizer that can compete or be complemented with chemical fertilizers (Fregoso Soria et al., 2001) This results in money and time savings on fertilizers and also helps regenerate the land.

2.7. Benefits of the anaerobic digestion process

2.7.1. Health benefits

In many rural areas, direct biomass burning (wood, crop residues) is used as fuel in traditional cookstoves. This activity results in higher emissions of carbon monoxide and carbon dioxide, hydrocarbons, and particulate matter. These emissions result in severe health issues due to indoor pollution (IAP), mainly indoors without proper ventilation. Additionally, IAP has been linked to other health problems, such as child pneumonia, chronic obstructive pulmonary diseases, lung cancer, asthma and cataracts, tuberculosis among others (Surendra et al., 2014). Women and children are more susceptible to IAP due to prolonged exposure to smoke when they spend hours cooking and doing other household chores.

Through the traditional and economical construction of digesters, organic waste from farms (which are more accessible than firewood) is used to produce biogas. Unlike burning biomass, biogas (H_2S from biogas should be removed previously) can provide a clean and smoke-free environment and could significantly reduce IAP.

2.7.2. Environmental benefits

The use of firewood as fuel has an important negative impact on local forests. Fuel wood contribute to deforestation and have negative impacts on forest health and biodiversity. Worldwide deforestation causes 17-25 % of all anthropogenic Greenhouse gas emissions (Strassburg et al., 2009). Also, unlike the carbon dioxide emission of firewood, the carbon dioxide emissions that originate from the use of biogas are equal to the amount of carbon dioxide that affects plants to grow and produce renewable resources. Therefore, no additional carbon dioxide is produced, which is considered harmful to the climate.

Thus, when replacing firewood with biogas can reduce deforestation, mainly in developing countries. In the same way, Greenhouse gas emissions can be mitigated.

2.7.3. Social Benefits

In rural areas, collecting firewood can be a task that requires time and a lot of human effort. Commonly, women and children can get to travel more than 5 km and spend nearly 6 hours a day gathering firewood (Topa et al., 2004). This labor is difficult and may cause neck-pain, back-pain, and other physical issues. Likewise, the time spent by women and children in this labor, deprive them of opportunities for education and social activities(Surendra et al., 2014).

With the implementation of biodigesters to produce biogas, greater and better opportunities can be provided for the beneficiaries. In addition, the quality of life of people can improve, since, in areas where there is no electricity, biogas (through a cogenerator) can meet this need.

2.8. Case study: Food waste from the Nariño region as a substrate for anaerobic digestion

The type, composition, and amount of food waste is defined by economic development and population growth, where the main sources are collection centers, agribusinesses, hotels, restaurants, family homes, dining rooms and companies (Zhang et al., 2014). Currently, the problem of food waste is rising. Worldwide, it is estimated that about 1.3 billion tons year^{-1} of solid waste are generated and this amount is expected to increase to 2.2 billion tons by 2025 (One third corresponds to food waste) (Han et al., 2016). Loss refers to food that occurs in the stages of agricultural production, post-harvest and industrial storage, and processing. On the other hand, waste is food that occurs in the stages of distribution and retail and consumption.

In Colombia, this problem is not foreign. According to a study by Departamento Nacional de Planeación (2016), Colombia lost 9.96 million tons of food per year, and in the Pacific region (i.e. Chocó, Nariño, Cauca, Valle del Cauca) appears in fourth place with 1’063.159 (17.1 %) tons year^{-1} and in third place with 488.539 (13.8 %) tons year^{-1} of wasted food.

The disposal and elimination of this waste is a problem that affects environmental, economic and social aspects. Traditional approaches for food waste disposal and elimination are mainly in landfills, by incineration, and to a limited extent by aerobic decomposition (compost). However, it is relevant to mitigate this type of practice due to adverse consequences. Incineration is high energy demanding since these wastes have high water content and often pollute the air (Zhang et al., 2014). On the other hand, sanitary landfills disposal have been banned in many countries due to serious pollution problems because of high chemical and biological oxygen demand (COD and BOD) (Lin et al., 2013). At the same time, a series of problems arise that include the increase in the cost of waste disposal, the lack of space on the ground, the contamination of groundwater by leachate and the emission of toxic and greenhouse gases (Uçkun Kiran and Liu, 2015).

According to the study carried out by Superintendencia de Servicios Públicos Domiciliarios (2016), in Colombia the number of final waste disposal sites has been reduced in the last 3 years of evaluation with respect to 2016, in 2014 there are 400 sites, in 2015 a total of 227 sites and in 2016 there were 269 sites. To dispose of waste, there are adequate and inadequate sites. Figure **2-4** shows the number of adequate sites (sanitary landfill and contingency cell) and inadequate sites (transitional cell, open-air dump, burial, dumping of water bodies, burning of solid waste). In Colombia, landfills were and still a priority, however, the lifespan of many of these are ending. In 2016, the country had 275 sites between adequate and inadequate (related to operation and management), mainly are landfills (158 sites), open-air dumps (54 sites) and transitional cells (34 sites). The Nariño department has 17 final disposal sites, of which 11 are suitable sites in the form of landfills, of which it is estimated that the useful life of these is between 3 to 15 years (Superintendencia de Servicios Públicos Domiciliarios, 2016).

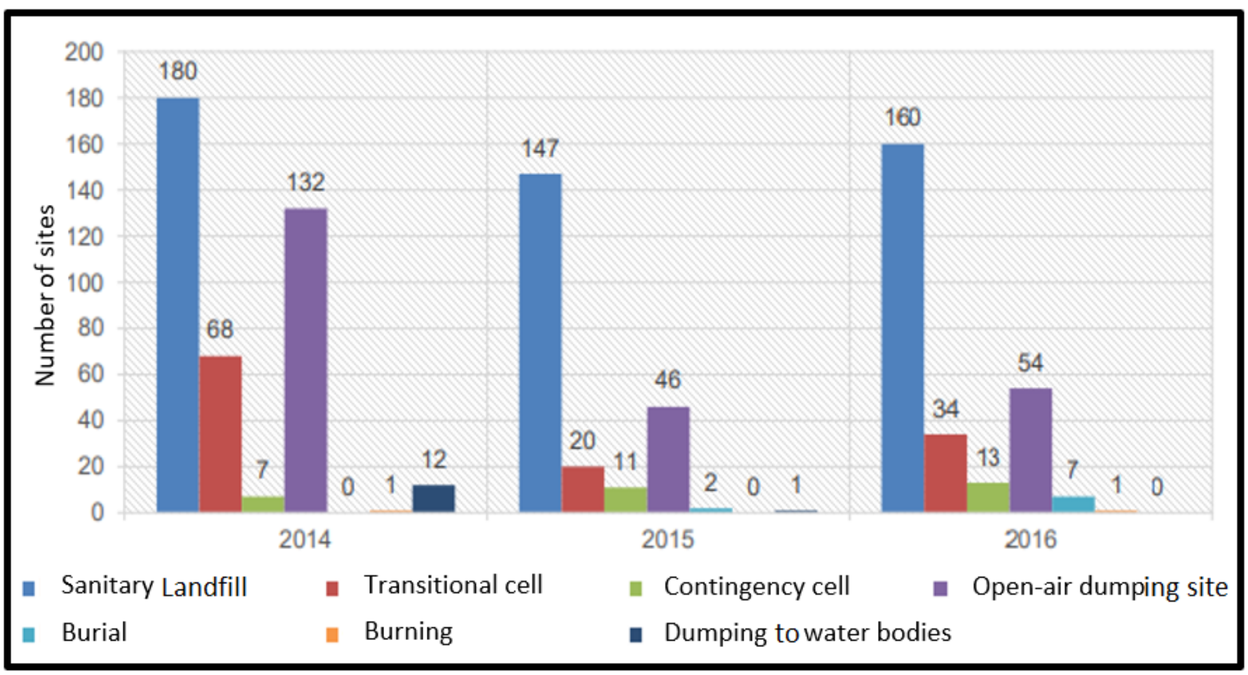


Figure. **2-4**: The number of final disposal sites in Colombia for 2014, 2015 and 2016 validities. Adapted from: Final Disposal of Solid Waste-National Report-2016 (Superintendencia de Servicios Públicos Domiciliarios, 2016)

The Nariño region generates 235.322 ton year^{-1} of solid waste (Superintendencia de Servicios Públicos Domiciliarios, 2016), of which, it is generally estimated that about one third is food waste (Han et al., 2016). Then, it could be said that per year, approximately 84.500

ton year^{-1} of food is wasted in Nariño. The generation of food waste is expected to increase every year since this is proportional to the population increase, where Nariño since 1985, each year has had a change in the average population of +1.3 % (DANE, 2017).

Considering the negative environmental impact, the potential decrease and high costs of adequate waste disposal sites, as well as the unfeasibility of incinerating them, the anaerobic digestion process has been proposed as a technology relatively profitable to dispose and take advantage of this organic waste aimed primarily at the production of renewable energy. Tables **2-13** and **2-14** present situations in which the biogas produced by food waste generated in the Nariño department can be used. It should be noted that these calculations are very ideal, but it helps to have an overview of the maximum extent of biogas.

Table. **2-13**: Ideal generation of electricity from food waste in the Nariño department (this study).

Food waste (Ton year^{-1})	Biogas produced (m^3)	Electricity generated (kWh-year)	Satisfied Colombian houses
235 322	47 064 400	282 386 400	47 064

Equivalences: Biogas contains 60 % methane, 1 m^3 biogas equals 6 kWh Colombian house consumes approximately 6000 kWh year-house .

Table. **2-14**: Ideal equivalence of natural gas from food waste in the Nariño department (this study).

Food waste (Ton year^{-1})	Biogas produced (m^3)	Equivalence to natural gas produced (m^3)	Satisfied Colombian houses
235 322	47 064 400	28 238 640	67 234

Equivalences: Biogas contains 60 % Methane, 1 m^3 Biogas equals 0.6 m^3 of natural gas (Varnero Moreno, 2011), *Colombian house consumes approximately 420 m^3 year^{-1} of natural gas.*

The development of organic waste management through anaerobic digestion technology would articulate the environmental and energy aspects, promoting the implementation of a circular economy, aiming that the value of products and materials is maintained during the productive cycle (Consejo Nacional de Política Económica y Social, 2016). The circular economy provides multiple value creation mechanisms not linked to the consumption of finite resources. As shown in Figure **2-5**, in a circular economy, unlike the linear economy, resources are regenerated within the biological cycle, recovered, and restored thanks to the technical cycle. Within the biological cycle, the anaerobic digestion process allows the discarded materials to be regenerated. In the technical cycle, with sufficient available energy, human intervention recovers the different resources (reuse, use, treatment, among others) and recreates the order within the time scale that arises (Macarthur, 2006).

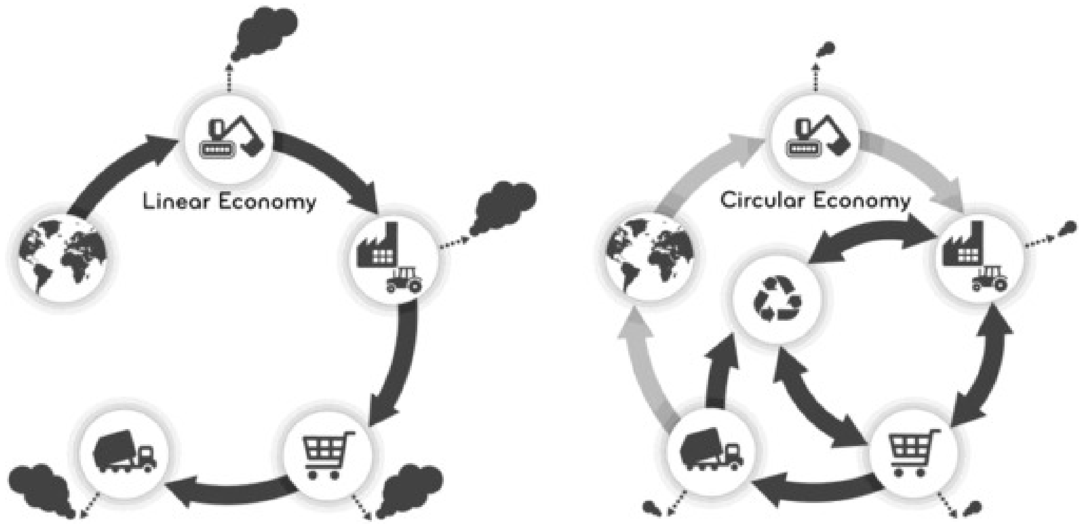


Figure. **2-5**: The linear economy(left) ignores the environment impacts hat come with resource consumption and waste disposal, and results in too much virgin resource extraction, pollution, and waste. In contrast, the circular economy (right) takes into account the impact of resource consumption and waste on the environment. The objective of the circular economy is to optimize the use of virgin resources and reduce pollution and waste at each step, inasmuch as possible and desirable (Sauvé et al., 2016)

For a specific study, it was decided to analyze the panorama of food waste generation in the city of Ipiales-Nariño. The "Instituto de Servicios Varios de Ipiales" (ISERVI) provided information on the current state of solid waste generation and the current state of the landfill "La Victoria" in the city of Ipiales. Table **2-15** shows these characteristics for the year 2019. The data reveal that 60 % of solid waste is organic waste, making the city have a great chance of taking advantage of this waste.

As mentioned, anaerobic digestion is a process that produces biogas as renewable energy and VFAs as economically attractive products. Factors such as pH, temperature, type of substrate, and type of digester can define the desired product. To evaluate the anaerobic digestion of an organic mixture, parameters to determine the quantity and quality of the products obtained are necessary: characterization of the substrate, evaluation of the Biochemical Methane Potential, monitoring of variables such as pH, COD, temperature, and concentration of VFAs throughout the process. Food waste is a promising substrate for the production of biogas and

VFAs, an evaluation of this waste with the anaerobic digestion process at the local context, will give a vision of the potential uses, producing compounds with energy value and added value. Thus, in this study, the potential for methane and VFAs production from food waste from the Department of Nariño, Colombia was evaluated. The substrate was characterized and the evaluation of methane production was carried out, using the assay of the biochemical potential of methane in batch digesters. To monitor the abovementioned process variables, and this test was complemented with a sacrifice bottle assay.

Table. **2-15**: The current state of generation and management of solid residues in Ipiales, Nariño. Data provided by ISERVI

Item	**Description**
Solid residues amount	1450 Ton month^{-1}
Organic residues amount	870 Ton month^{-1}
Landfill use time	8 years
Landfill lifetime	15 years
Municipalities served	10
Landfill area	26.34 hectares
Type of solid residues treatment	Combined landfill: area and trench type
Leachate Treatment	2 UASB reactors 2 Mechanical oxidation lagoons 2 sedimentation tank 2 maturation lagoons

2.9. Methodology

2.9.1. Substrate sampling: Food Waste

Food waste (FW) was obtained at the Casa Colombia restaurant, located in the city of Ipiales-Nariño Department. They were collected considering sampling protocol ASTM D5231-92. Six samples (FW1, FW2, FW3, FW4, FW5 and FW6) were collected daily for six consecutive days in the afternoon. Additionally a composite sample (CFW) of the six previous samples was prepared. They were stored in Ziploc plastic bags and no physical or chemical treatment was performed. They were weighed using a weighing hook and preserved in a freezer at a temperature of -15 ° C until use. The samples taken were transported to the city of Manizales using portable expanded polystyrene refrigerators with dry ice to keep them at a low temperature.

In the Laboratory of Productive Processes of Universidad Nacional de Colombia-Manizales, the low biodegradability compounds separation of each sample was carried out, characterizing and identifying qualitatively the type of organic matter. Next, a JAVAR industrial blender was used to crush each sample until a particle size of 0.2 to 1 cm was achieved, as recommended by Sharma SK, Mishra IM, Sharma MP (1988). The average grinding time was 20 seconds. Each sample was weighed with a FEMTO ABT series analytical balance. Finally, the samples were stored at a temperature of -15 ° C until use.

2.9.2. Food Waste characterization

The analyzes that were carried out were: total solids (TS), volatile solids (VS), proximate analysis: total humidity, dry matter, ash, volatile matter and fixed carbon, ultimate analysis: the amount of carbon, hydrogen, oxygen, and nitrogen and calorific Value. The analyses were carried out in the Waste Exploitation laboratory and Water Laboratory at Universidad Nacional de Colombia-Manizales. All analyses were performed with a replica.

- **Total solids and volatile solids:** TS are used to describe the dry matter of a substrate, and VS represent the amount of material that can be used as food by microorganisms, and which theoretically must be converted to methane. For the quantification of TS and VS of food waste, the protocol of Standard Methods for the examination of water and wastewater (APHA, 2008) was followed. Table **2-16** shows the methods used.

Table. **2-16**: Methods used to determine the parameters of TS and VS

Parameter	Unit	Method	Technique
TS	mg TS mg sample^{-1}	S.M.2540 B	Gravimetry
VS	mg VS mg sample^{-1}	S.M.2540 E	Gravimetry

- **Proximate analysis:** The proximate analysis of CFW separates the products into four groups: (1) moisture (M), (2) volatile Matter (VM) consisting of gases and vapors released during pyrolysis, (3) fixed Carbon (FC), non-volatile fraction and (4) ash content (ASH), inorganic residue after combustion. A summary of the standard methods used to perform the proximate analysis is presented in Table **2-17**.

- **Ultimate analysis:** The ultimate analysis provides information about the content of elements such as carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). From the proximate pnalysis and through correlations developed by Shen et al. (2010) it is possible to give an approximation of the content of these elements.

Table. **2-17**: Standard methods used to carry out the Proximate analysis of CFW

Analysis	Method
Moisture	ASTM E871-82 (2013)
Volatile Matter	ASTM E872-82 (2013)
Ashe	ASTM E1755 - 01(2015)
Fixed Carbon	ASTM E870 – 82 (2013)

$$\%C = 0.635(\%FC) + 0.460(\%VM) - 0.095(\%ASH) \tag{2-1}$$
$$\%H = 0.059(\%FC) + 0.060(\%VM) + 0.01(\%ASH) \tag{2-2}$$
$$\%O = 0.340(\%FC) + 0.469(\%VM) - 0.023(\%ASH) \tag{2-3}$$

According to Shen et al. (2010), equations 2-1, 2-2 and 2-3 are valid for raw materials containing:

$$9.2\,\% \leq FC \leq 32.79\,\%$$
$$57.2\,\% \leq VM \leq 90.6\,\%$$
$$0.1\,\% \leq ASH \leq 24.6\,\%$$
$$36.2\,\% \leq C \leq 53.1\,\%$$
$$4.7\,\% \leq H \leq 6.61\,\%$$
$$31.37\,\% \leq O \leq 48.0\,\%$$

These values are expressed in mass fraction (% wt.) on dry basis.

For the purposes of this study, it will be assumed that the rest of the composition is nitrogen. This is because nitrogen is a compound that is present in this class of waste in a larger quantity in relation to other components that this residue contains (Na, S, K, P, etc) (Esteves and Devlin, 2010). The nitrogen content is calculated with equation 2-4.

$$\%N = 100 - \%C - \%H - \%O \tag{2-4}$$

- **Calorific value:** It is the amount of energy emitted by a raw material when it is submitted a combustion process. To determine the calorific value, a calorimetric technique was used by means of an immersion bath in the SDACM3100 Bomb Calorimeter unit with pressurization of the sample with oxygen at 3 MPa and operating temperatures of 24 to 42 ° C.

2.9.3. Inoculum

The inoculum is an important part of the start-up of the anaerobic digestion process since it is the one that contributes most of the microbial consortium in the process (Demirel and Scherer, 2011). The inoculum should preferably be fresh and extracted from an anaerobic reactor in operation (stirred tank, UASB, etc.) in the proportion (or volume) desired for the tests (Angelidaki et al., 2009).

For this study, an inoculum from the UASB of a coffee industry was used. The company Buencafé (Chinchiná, Caldas) supplies this inoculum. It was required to homogenize and acclimation for 10 days at a temperature of 36 °C in a thermostatic bath until the remaining organic matter was consumed (Angelidaki et al., 2009). During the acclimation process, 0.5 g L^{-1} day^{-1} of food waste was added to adapt the inoculum to the substrate used (Solarte Toro et al., 2017). Additionally, the inoculum was characterized in terms of volatile solids, total solids, and pH following the methods presented in Table **2-17**.

2.9.4. Biochemical Methane Potential (BMP)

To evaluate the application of anaerobic treatment systems in the degradation of an organic substrate, it is necessary to determine its methanogenic potential (Angelidaki et al., 2009). Through a discontinue essay known as Biochemical Methane Potential (BMP) is possible to evaluate the methanogenic potential on a laboratory scale. BMP is widely used to determine the concentration of organic matter present in a residue that can be anaerobically converted to methane (CH_4). As well as BMP can evaluate the efficiency of an anaerobic process in the degradation of specific wastes. This test has an approximate duration of 30 days where methane production is followed and registered, which is related to the reduction of organic matter expressed as COD (Chemical Oxygen Demand) (Esposito et al., 2012).

Several norms aimed at standardization of BMP tests such as DIN 38414 TL8 (1985), ASTM D 5210 (1992), ASTM D 5511 (1994), ISO 11734 (1995), ISO 14853 (1998), and ISO 15985 (2004). However, to perform the BMP test with food waste as substrate, the German standard VDI_4630 was used (VDI-Handbuch Technik Biomasse, 2016). In order to analyze the stages and development of the anaerobic digestion of food waste, two BMP assays were carried out. In the first experiment, only methane production was monitored on-line and in the second, methane production, COD, VFAs, and pH were monitored by sacrifice bottle every 3 days on average. The following is the process used for these experiments.

Macronutrients and micronutrients solution: To guarantee the most favorable conditions that enhance the anaerobic degradation of the substrate, it is necessary to use a solution of macronutrients and micronutrients (Owen et al., 1979). As suggested by Angelidaki et al.

(2009), a ratio of 1:100 v/v of macronutrients, 0.1:100 v/v of micronutrients, and 0.2:100 v/v of yeast extract was added in the liquid phase volume for the BMP assays. NaOH and HCl solutions were used to adjust the pH. The solutions used in the BMP assays are presented in Table **2-18**.

Table. **2-18**: Composition of the nutrient solution for the BMP assay (Angelidaki et al., 2009)

Solution	Solution:liquid phase ratio (v/v)	Chemical compound	Unit	Concentration
Macronutrients	1:100	NH_4Cl	$g\ L^{-1}$	100
		$NaCl$		10
		$MgCl_2$ -6H_2O		10
		$CaCl_2$ -2H_2O		5
		K_2HPO_4 - 3H_2O		200
Micronutrients	0.1:100	$ZnCl_2$	$g\ L^{-1}$	0.05
		$AlCl_3$		0.05
		$CoCl_2$ -6H_2O		0.05
		H_3BO_3		0,05
		$(NH_4)6Mo_7O_{24}$ -4H_2O		0.05
		$C_{10}H_{16}N_2O_8$		0.5
		$FeCl_2$- 4H_2O		2
Other	0.2:100	Yeast extract (source of vitamins)	$g\ L^{-1}$	0.2
	-	HCl	N	2
	-	NaOH		2

Methane production by on-line measurement assay: The on-line methane quantification was carried out using the German Yieldmaster by BlueSense equipment which performs real-time measurements of methane concentration and volume produced. It measures up to 80 mL min^{-1} with a resolution of 1 mL and consists of a volume measurement cell as well as temperature and pressure sensor. The sensor contains the infrared light source and detector. The infrared light beam is reflected by the gas-filled measuring adapter and the light weakened by the analyte gas is measured by the detector. Yieldmaster equipment sensors report methane concentration data at 0.8 bar gauge pressure and at an average temperature of 20 °C. Figure **2-6** shows the equipment used. Two bottles were used under the same experimental conditions (inoculum, macronutrient, micronutrient, and yeast extract solution). One corresponds to the blank (without substrate) only with water to determine the endogenous activity of the inoculum. The other using food waste as a substrate. The measurements were taken every 30 minutes and the data is saved in a computer, using the equipment software BACVis®.

Figure. **2-6**: On-line methane measurement assay setup.

The bottles have a volume of 300 mL (working volume of 200 mL). The bottles consist of an upper nozzle that attaches to the methane sensor of the Yieldmaster equipment. They also have an upper side nozzle through which the biogas leaves the bottle to be quantified. The assay was performed under mesophilic conditions of 37 °C in a Memert WNB 22 thermostatic bath with daily manual stirring for 31 days. The pH was adjusted to 7.0 before the operation. According to the VDI_4630 standard, the substrate-inoculum ratio was set on 0.4 $gVS_{substrate}$:$gVS_{inoculum}$ and for every 500 mL of digestion volume, the inoculum should provide 7.5 gVS (VDI-Handbuch Technik Biomasse, 2016). The amounts of inoculum, substrate, and nutrients can be seen in Table **2-19**. The bottles were made up to working volume with tap water. To ensure removal of the oxygen content within the bottle, nitrogen was bubbled into each bottle for 3 minutes. Then the bottles were sealed and capped ensuring that there were no leaks. The assay had no duplicate. The pH, CODs, VFAs were evaluated at the beginning and end of the assay.

Table. **2-19**: Conditions for the BMP assay with on-line methane production measurement

Item	Units	Value
Inoculum	g	24.42
Substrate	g	3.4
Macronutrient solution	mL	2
Micronutrient solution	mL	0.2
Yeast extract solution	mL	0.4

Methane production by sacrifice bottle assay: To monitor several operational parameters throughout the anaerobic digestion process such as CODs and pH, a sacrifice bottle assay was performed. 30 bottles of 120 mL (working volume of 80 mL) was used, of which 20 contain substrate, inoculum and nutrients and the rest only inoculum and nutrients (blank). The bottles consist of a small upper nozzle that is hermetically closed with a rubber lid and aluminum cap. The assay was carried out under mesophilic conditions of 37 ° C in a BINDERED 260 incubator. Each day manual stirring was performed on each bottle. The assay lasted 31 days.

The substrate-inoculum ratio was set on 0.4 $gVS_{substrate}$:$gVS_{inoculum}$ and for every 500 mL of digestion volume, the inoculum should provide 7.5 gVS (VDI-Handbuch Technik Biomasse, 2016). The amount of inoculum, substrate, and nutrients can be seen in Table **2-20**. The pH was adjusted to 7.0 before operation and the bottles were made up to working volume with tap water. Nitrogen was bubbled into each bottle for 3 minutes. The volume of methane was measured every 2 days by the alkaline displacement method(Cárdenas et al., 2016). Figure **2-7** shows the setup of the assay and the methane quantification from each bottle. Every 3 $\pm$ 1 days, 3 bottles were discarded (2 bottles contained substrate and 1 bottle was the blank) and subsequently, pH and CODs were measured. For the initial value of CODs, a 5 mL sample was taken from a bottle with substrate before starting the assay.

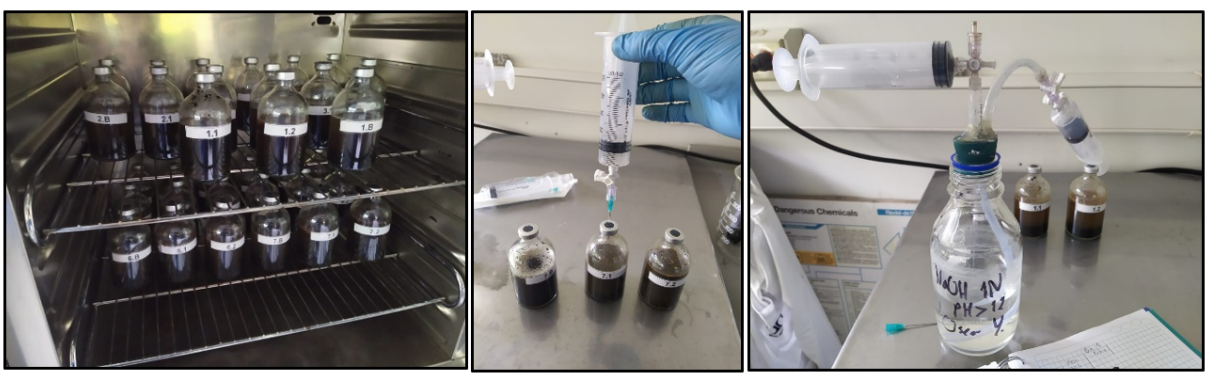


Figure. **2-7**: Sacrifice bottle assay setup

Soluble chemical oxygen demand (CODs): Chemical oxygen demand (COD) is a measure of the quantity of carbon present in the sample. Specifically, soluble chemical oxygen demand (CODs) allows to periodically monitor the development of the biodegradation process of organic matter (Owen et al., 1979). For the CODs measurement, the Standard Method "5220 CHEMICAL OXYGEN DEMAND (COD)" was followed (APHA, 2008). Previously, each sample was subjected to centrifugation at 5500 rpm for 10 min in an INDULAB Ref 004 dynamic centrifuge.

Table. **2-20**: Conditions for the BMP assay with sacrifice bottles

Item	Units	Value
Inoculum	g	9.77
Substrate	g	1.36
Macronutrient solution	mL	0.8
Micronutrient solution	mL	0.08
Yeast extract solution	mL	0.16

Theoretical biochemical methane potential: The theoretical BMP of an anaerobic digestion process is limited by stoichiometry and can be calculated if the elemental composition of the substrate is known. For this study, a stoichiometric model proposed by Buswell and Mueller (1952) was used. Likewise, knowing the theoretical BMP and experimental BMP (obtained from the previous tests) it is possible to estimate the biodegradability index (%B) as described by Sosnowski et al. (2003), Equations 2-5-2-7 were used to calculate the theoretical BPM and the index of biodegradability.

Noticed that the analyzes performed corresponds to preliminary exploration since at this stage it was not possible to perform triplicates.

$$C_nH_aO_bN_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{8}\right) H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4} + \frac{3c}{8}\right) CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right) CH_4 + cNH_3 \tag{2-5}$$

$$BMP_{theoretical}(mL\ CH_4\ gVS^{-1}) = \frac{22,4\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)1000}{12n + a + 16b + 14c} \tag{2-6}$$

$$\%B = \frac{BMP_{experimental}}{BMP_{theoretical}} * 100 \tag{2-7}$$

In these equations, n,a,b and c indicate the number of moles of carbon, hydrogen, oxygen, and nitrogen respectively, 22.4 corresponds to the volume (L) occupied by an ideal gas under standard conditions, 1000 is the volume conversion factor for conversion from L to mL, and 12, 1, 16, and 14 are the molecular weights (g mol^{-1}) of C, H, O and N, respectively.

2.10. Results and discussion

2.10.1. Characterization of food waste and inoculum

Table **2-21** shows the characteristics of the samples collected. Potato, rice, and chicken were the common foods in each food waste sample. On the other hand, fruit peel, chicken skin, and bones were the predominant low biodegradability waste (compounds that cannot be or are hardly degraded in the anaerobic digestion process) in the samples, which were removed. The physical pretreatment of food waste by reducing the particle size was carried out to homogenize the substrate and improve the performance of the process in an increase in biogas. According to the study by Hajji and Rhachi (2013), this pretreatment can improve biogas production by 20 % when the particle size is reduced to 10 mm. Figure **2-8** shows food waste before and after size reduction.

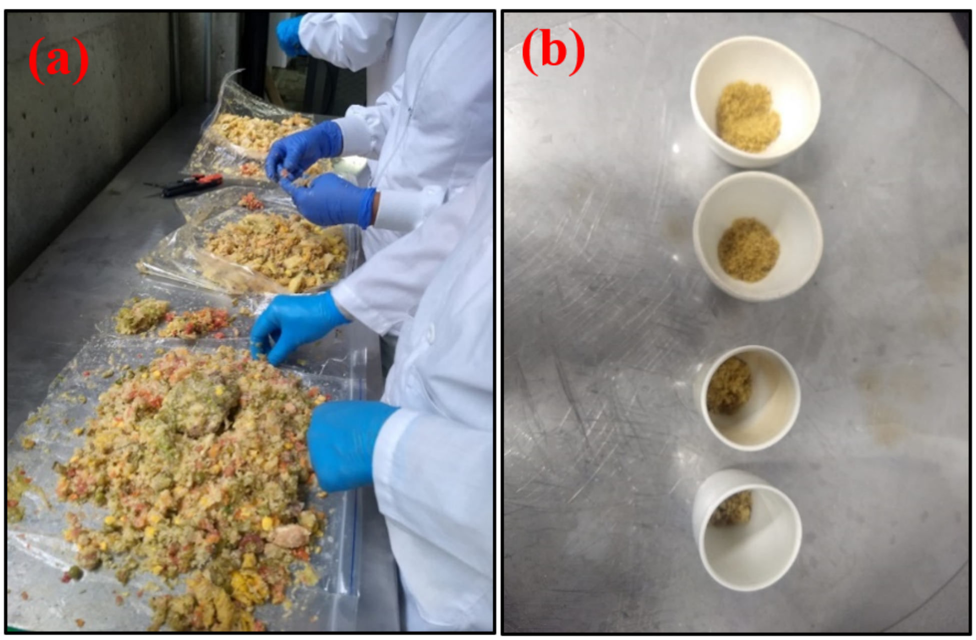


Figure. **2-8**: (a): Separation of organic matter and low biodegradability waste from the substrate. (b): Food waste after size reduction.

Table. **2-21**: Food waste amples

Sample	Organic Matter	Organic matter weight (g)	Low biodegradability waste	Weight organic matter without low biodegradability waste (g)	Weight for composite sample * (g)
FW2	Pea, potato, beef, chicken, carrot, banana, fish, beans, lettuce, pumpkin	1500	Lulo peel, paprika peel, thorns, seeds	983	191.2
FW3	Banana, potato, rice, peas, cassava, beans, noodles, fish, chicken, carrots	1500	Onion, tomato peel, paprika, cucumber, thorns, chicken skin	1120	217.9
FW4	Cassava, potato, rice, banana, corn, beef	1250	Paprika, corncob, fish skin, chicken skin	1143	222.3
FW5	Potato, pork, beef, banana, beans, arepa, rice, tomatoes, carrots, onions, cassava	1500	Tomato, lettuce, fish skin	1166	226.8
FW6	Banana, rice, peas, fish, meat, potatoes, corn, carrots, beans	1500	Tomato, lettuce, fish skin, thorns, orange peel	729	141.8

FW1 was discarded due to the decomposition of the waste.
**A composite sample (CFW) with a total weight of 1000 g was made*

Table **2-22** shows the results of the physicochemical characterization of food waste and inoculum. To determine the moisture content, the food waste was initially subject to a predrying at 60 °C for 24 h. The decrease in moisture by this process is not depicted in Table

2-23. The moisture of 10 % should be interpreted as the remaining moisture of partially dry food waste. The VS/TS ratio (94 %) shows similarity with the values reported by various authors, which are between 87 % - 95 % (Zhang et al. (2013),Solarte Toro et al. (2017),Pramanik et al. (2019)). This relationship suggests that the wastes have a high potential for biodegradability and are suitable for use in the anaerobic digestion process. Regarding the inoculum, it is a granular inoculum and the results show a VS/TS ratio > 80 %, which indicates a high content of active biomass present, making it a reliable inoculum for use in the anaerobic digestion process.

Table. **2-22**: Physicochemical characterization of food waste and inoculum

Parameter	Unit	Food Waste	Inoculum
Total solid	% wt	37.50 ± 1.63	13.82 ± 1.23
Volatile Solid		35.33 ± 1.62	12.28 ± 1.22
VS/TS	%	94.23	88.861

Concerning the proximate analysis of food waste, the results are in agreement with the results reported by the authors of Table **2-23**. Ash content represents the minerals remaining when moisture and organic matter are driven off from a sample. The study by Lo et al. (2012) showed that the addition of ash can improve the anaerobic digestion process. Nevertheless, ash also can increase the concentration of metals resulting in detrimental effects on the process (Lo et al., 2010). The value of 3 % of ashes for this waste does not represent relevance in the improvement or decline in the production of biogas. On the other hand, when calculating the combustibility index (VM/FC) of the food waste, a value of 5 was obtained. A low value like this suggests that the waste has a higher percentage of fixed carbon, which favors longer combustion and higher caloric power (Rojas-González et al., 2019). The above suggests that food waste can be incinerated and used as fuel, however, the calorific value of methane is 53 MJ kg^{-1} (Scott, 2000), 2.7 times higher than that found in this study (19 MJ kg^{-1}), therefore, the anaerobic digestion process for the production of methane suggests being the most indicated to take advantage of these wastes.

The C/N ratio of food waste is 13. Haug (1993) proposed an optimal ratio of 15-30. The differences between the elemental composition of food waste are determined by the region of origin. As mentioned before, this food waste was composed mainly of rice, potatoes, and chicken, indicating a lower content of animal protein and in turn, high content of carbohydrates. As can be seen in Table **2-7**, similar methane yields were obtained when the food waste presents different C/N ratios. Therefore, the substrate for this study indicates the potential to be used in the anaerobic digestion process in the production of biogas.

Table. **2-23**: Elemental and proximate analysis of food waste

Parameter	Unit	This study	Chae et al. (2020)	Singh and Yadav (2021)
C	% wt.	47.14 ±0.16	51.74	45.71
H		5.83 ± 0.009	6.79	6.72
O		43.34 ± 0.065	36.53	44.66
N		3.68 ± 0.47	3.36	2.91
C/N	-	12.81	15.4	15.70
Moisture*	% wt.	9.69 ± 0.28	NR	NR
Ash	% wt.	3.01 ± 0.37	9.9	3.62
Volatile matter (VM)		80.88 ± 0.064	68.9	73.78
Fixed Carbon (FC)		16.11 ± 0.13	12.1	13
Calorific power	MJ kg^{-1}	19.02 ± 0.003	16.87	16.07

*NR: Not reporting. wt: weight fraction on dry base. *Pre-dried at 60 °C for 24 h.*

2.10.2. Biochemical methane potential of food waste

The behavior of the evolution of biogas production and its quality (%v/v methane) for the anaerobic digestion of food waste is shown in Figure **2-9**(a). Similarly, the accumulated and daily methane production is seen in Figure **2-9**(b). These data were obtained from the online measurement of the YieldMaster equipment every 30 minutes for 31 days.

The total volume of biogas generated in 31 days of the process was 306 mL gVS^{-1} for the degradation of food waste, with a methane content of 73 % v/v. 80 % of the total biogas generated is produced after 9 days. Solarte Toro et al. (2017) report that this percentage is reached after 22 days of digestion, with a total biogas production of 450 mL gVS^{-1} and with a theoretical methane content of 52.5 % v/v at 37 °C and 40 days. Similary, Zhang et al. (2007) obtained 600 mL gVS^{-1} of biogas and 73 % v/v methane at 50°C after 30 days. For this study, the high methane content in the biogas produced may be because the food waste was relatively easy to degrade (low amount of lignocellulosic components) and therefore a large amount of soluble organic compounds is available for rapid conversion into CH_4, generating the high content of CH_4. In turn, this is also related to the low moisture content and particle size of the substrate. Likewise, according to the data in Table **2-2**, an energy content of 26,13 MJ m^{-3} could be estimated for the biogas produced with 73 % methane concentration.

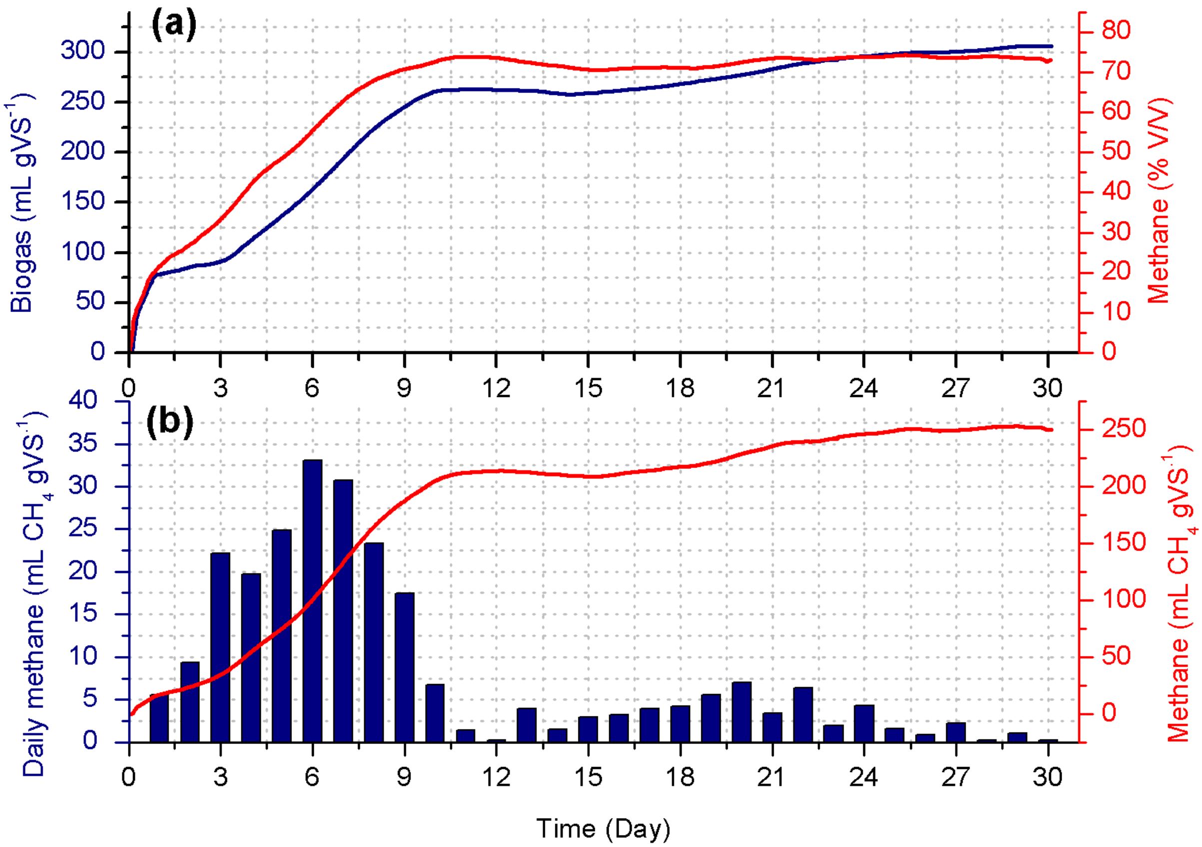


Figure. **2-9**: BMP assay by on-line measurement of methane during anaerobic digestion of food waste. (a) Accumulated biogas production and methane concentration. (b) Accumulated BMP and daily methane production.

From Figure **2-9**(b) it can be seen that a yield of 251 mL gVS^{-1} of methane is produced. The highest daily methane production (33 mL gVS^{-1}) occurs on day 6, suggesting that the adaptation time of the microbial biomass present in the inoculum was short, rapidly degrading the substrate. This is because the inoculum had an adequate conditioning process. Methane production increased until day 10 and then remained almost constant at a low level until the end of the assay (day 31). This pattern can be explained because the substrate, due to its high biodegradability, begins to quickly deplete. The methane yield generated in this study (251 mL gVS^{-1}) was lower than that reported by Heo, Park, Kang, (2004) who obtained 489 mL gVS^{-1} in 40 days under mesophilic conditions using food waste as substrate.

For the BMP test of food waste by on-line measurement of methane, pH and CODs were monitored at both the beginning and end of the assay. Table **2-24** presents these parameters.

Regarding pH, the process remained in the optimal range of 6.5-7.5 (Khalid et al., 2011). This indicates that there was no inhibition by pH, which was to be expected due to the amount of biogas generated. At the beginning of the test, a few drops of 2N NaOH had to be added, since the pH of the food waste with inoculum was 6.8. The pH of the blank was not adjusted. The CODs at the end of the assay shows a decrease concerning the initial one, giving an indication of degradation of organic matter in the digestion process. Usually, the percentage of CODs removal efficiency is reported as an indicator of the effectiveness of the anaerobic treatment on the stabilization of the biodegradable organic waste (Cendales Ladino, 2011). For this study, at the end of the assay, a CODs removal efficiency of 62 % was obtained.

Table. **2-24**: Control parameters for BMP assay of food waste by on-line measurement

Parameter	Food Waste		Blank (inoculum)	
	Initial	Final	Initial	Final
pH	7.02*	7.257	7.15	7.25
CODs (mg L^{-1})	13354.2	5054.2	2062.5	1829.2

**Value adjusted with NaOH (2N).*

Obtaining the initial and final control parameters of the anaerobic digestion process is useful to give a general evaluation of the process. However, the process can be periodically monitored using sacrifice bottle. A sacrifice bottle assay was performed simultaneously with the BMP assay by online measurement of methane. Table **2-25** shows the day on which sacrifice bottle are discarded for their corresponding characterization. This assay aims to evaluate the behavior of the control parameters (pH, CODs, VFAs) along the anaerobic digestion process.

Table. **2-25**: Sample collection during BMP assay using the scarified bottle method

Samples	A	B	C	D	E	F	G	H	I	J
Sacrifice day	5	10	12	14	17	20	24	26	28	31

Figure **2-10**(a) shows accumulate BMP production for each sample as a function of the sacrifice day. As expected, the highest methane yield produced was that of sample J (31 days) with 129 mL gVS^{-1} of methane, because it was the last to be discarded (day 31). Sample A (5 sacrifice day) shows the lowest methane yield with 16 mL gVS^{-1} and after discarding sample F (20 sacrifice day) the accumulated methane yield stabilizes at an average value of 123.5 mL gVS^{-1}. Compared with the yield found in the on-line methane measurement assay (Figure **2-9** (a)), the yield obtained from sample J is 1.9 times lower. The methane concentration in the biogas generated by each sample had a stable value throughout the assay, which was 61.9 % (v/v), 1.18 times lower than that reported in the assay by on-line measurement of methane. Therefore, the two assays (methane online measurement and sacrifice sample) should not be interpreted as comparable, but as complementary, being the sacrifice bottle assay that provided information on the behavior of the relevant variables throughout the process and the on-line methane measurement assay who provides the methane yield produced by food waste.

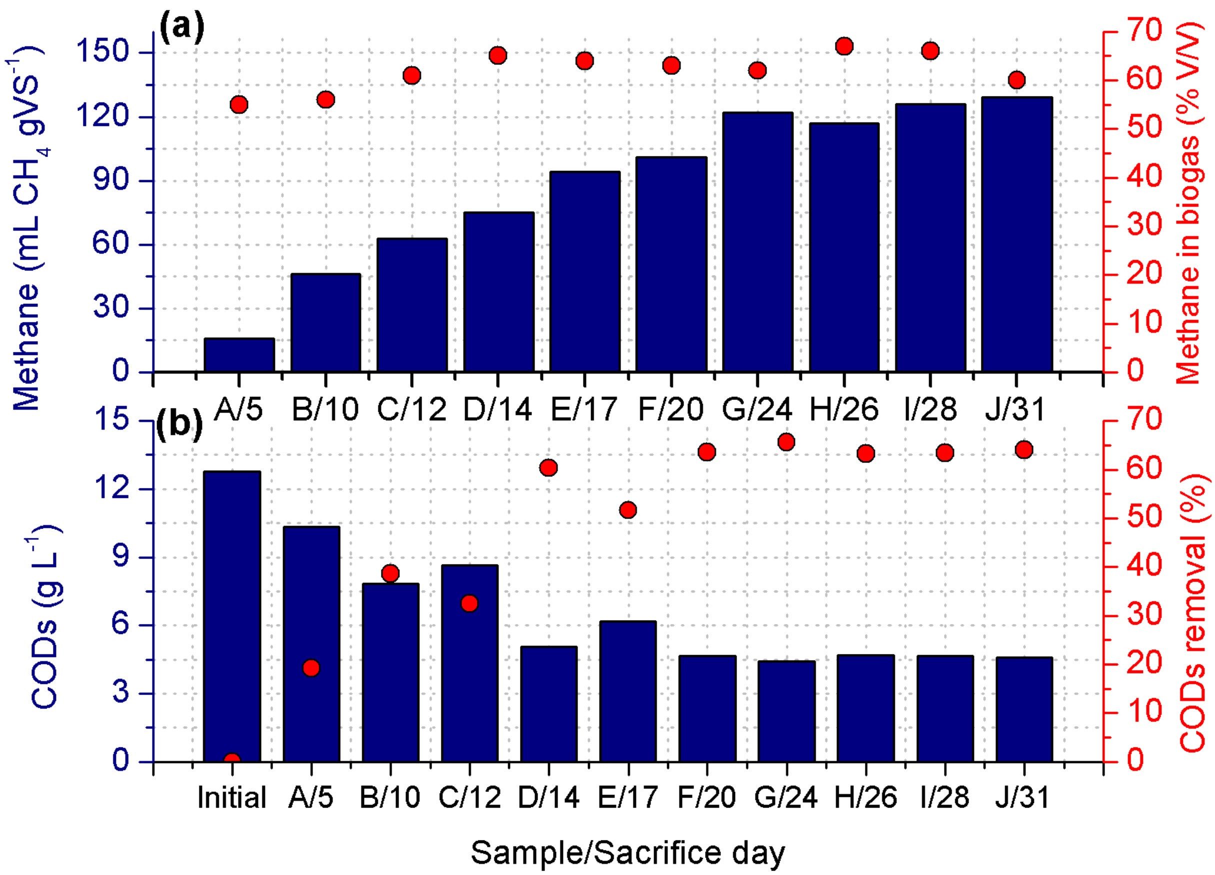


Figure. **2-10**: BMP assay by sacrifice bottle during anaerobic digestion of food waste. (a) Accumulate BMP and methane concentration in biogas of each sample on its sacrifice day. (b) CODs concentration and % CODs removal of each sample on its sacrifice day.

Organic substances in food waste are degraded and transformed into biogas during the anaerobic digestion process, resulting in fluctuations in the concentration of CODs. Figure 8 (b) shows the CODs values obtained for each sacrifice sample, with the percentage of CODs removal. At the beginning of the trial, the CDOs reported a value of 12.8 g L^{-1}, while, from sample F (day 20) to the end of the assay, a stable average value of 4.6 g L^{-1} was reported. A maximum COD removal of 65.6 % was obtained for sample G, which was discarded on day 24. However, after discarding sample C (day 14), it can be seen that the % CODs removal tends to stabilize and an average value of 61.7 % of CODs removed was obtained. % CODs removal obtained in this study was lower than the values reported by Ma et al. (2018) who obtained 89 % CODs removal at 35 °C and 12 days. The high percentage of CODs removal is mainly since the authors carry out a pretreatment of food waste with fungal mash rich in various enzymes. Nevertheless, similar values were obtained to those reported by Wijayanti et al. (2018), who obtained 59,45 % CODs removal at 28°C in 60 days.

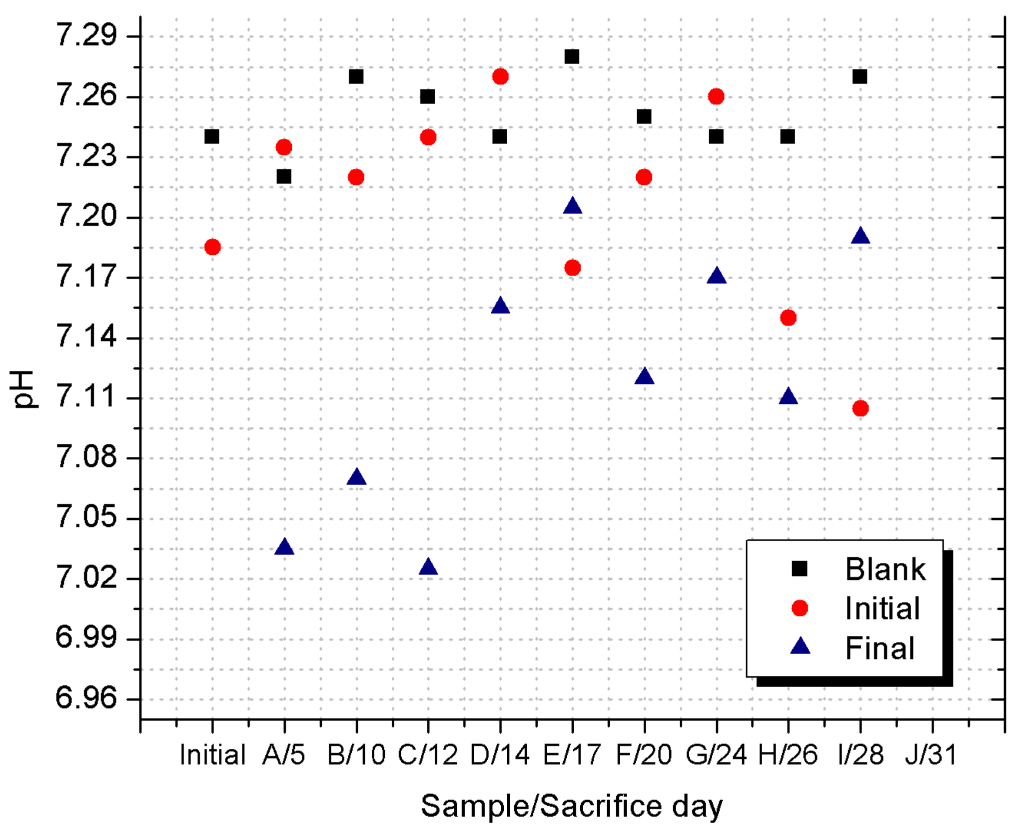


Figure. **2-11**: pH variation in BMP assay by sacrifice bottle during anaerobic digestion of food waste. *The initial pH values reported were adjusted to pH 7 with 2N HCl.*

In Figure **2-11** it can be seen that until sample E (day 17) was discarded, there is a slight decrease in pH. This decreasing at the beginning of the digestion process is due to volatile fatty acids production from the substrate. This shows the hydrolysis and acidogenesis stages in the process. Subsequently, the stability of the pH at an average value of 7.12 suggests that the acids are decomposed until the end of the assay. The pH range throughout the assay was 6.9-7.2, which is within the optimal operating range for the anaerobic digestion process between 6.5-7.5 (Khalid et al., 2011). The behavior of the pH of this study reports similar results to those reported by Solarte Toro et al. (2017), who reported pH ranges of 6.8-7.5 where the minimum value recorded occurs in the first 5 days of the assay. The fact that the behavior of the pH did not show large fluctuations, indicates that food waste provides the necessary nitrogen to control the pH by natural alkalinity as a buffer system since ammonia reacts with carbon dioxide to produce ammonium bicarbonate. Bicarbonate ions (HCO_3^-) expected to be the main contributors to the alkalinity of the system.

2.10.3. Theoretical Methane Yield

According to the element contents of food waste shown in Table **2-26**, the organic matters in this waste could be expressed as formulations of $C_{15}H_{22}O_{10}N$, similar to that reported by Browne and Murphy (2013) for food waste of $C_{16.4}H_{29}O_{9.8}N$, but different from that reported by Solarte Toro et al. (2017) $C_{27}H_{45}O_{16}N$. The similarity or difference in the empirical formula for food waste is because food preferences and cuisine may vary from one region to another. Table **2-26** presents the theoretical and experimental BMP, as well as the biodegradability index obtained for the food waste used in the anaerobic digestion process reported in this study and by various authors.

Table. **2-26**: Theoretical and experimental BMP for food waste during anaerobic digestion

Item	Unit	This study	Solarte Toro et al. (2017)	Browne and Murphy (2013)
Theoretical BMP	$mL\ CH_4\ gVS^{-1}$	439.49	517.06	550
Experimental BMP		251	240	529
Biodegradability index (B)	%	58.4	46.4	96.1

For this study, a biodegradability index of 58.4 % was obtained, 1.64 less than that reported by Browne and Murphy (2013), who mentions that the high reported value was associated with acclimatized inoculum and wet samples of food waste. However, it was favorable compared to those reported by Solarte Toro et al. (2017) 46.4 %). This result can be attributed to the content of elements of the waste, where the authors report almost double the carbon, obtaining a theoretically optimal C:N ratio (30:1) for biogas production, which generates that the theoretical BMP is a high value, decreasing the value of Biodegradability index.

2.11. Conclusions

Food waste from the Nariño region presented mainly the presence of rice, potatoes, chicken, and meat. The characterization of these waste showed great similarity to those reported in the bibliography, with a VS/TS ratio of 0.94 and a C/N ratio of 12.81. The proximate analysis found a calorific value of food waste of 19 MJ kg^{-1} and a low value of combustibility index (VM / FC) of 5. The experimental results of the anaerobic digestion of food waste showed a biogas production of 306 mL gVS^{-1}, and a methane concentration of 73 % at 37 ° C in 31 days. The hydrolysis phase occurs in the first 8 days, where the highest daily methane production was obtained on day 6 (33 mL gVS^{-1}), obtaining a methane yield of 251 mL CH_4 gVS^{-1}. A biodegradability index of 58.4 % was obtained, considering that the theoretical BMP calculated for these waste was 429.49 mL CH_4 gVS^{-1}. Likewise, the control parameters to monitor digestion show that the percentage of CODs removal was 62 % and the pH remained within the optimal operating range for the anaerobic digestion (6.5-7.5).

The sacrifice bottle assay was convenient and complementary to the behavior analysis during the anaerobic digestion process. The pH and COD control helped to identify the hydrolysis and fermentation phase and rule out inhibitions throughout the process. A similar percentage of COD elimination (62 %) was presented in the two proposed tests, which allowed complemented the analysis of the biogas production from food waste.

Finally, these results show that this food waste can be used for the production of renewable energy through the anaerobic digestion process, which, according to this study, the biogas produced (73 % methane) could theoretically contribute 26.13 MJ m^{-3}, being able to supply energy to interconnected areas and, in turn, reducing environmental problems by replacing firewood with biogas.

The following experimental information served to implement the economic model that compares the economic viability of the production of biomethane and VFAs from food waste by the anaerobic digestion process: methane concentration of 73 % (v/v) and process pH of 7.2.

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3 Techno-economic evaluation of anaerobic digestion beyond biogas

In this chapter, a technical comparison and an economic evaluation of the products that can be generated in the anaerobic digestion process was carried out. First, biomethane is presented, and on the other hand platform products such as volatile fatty acids (VFAs) are obtained. For this analysis, the Net Present Value method was used under different conditions of supply (available food waste) and demand (natural gas consumption in the transport sector and VFAs exports) in a Colombian context. Besides, the results of this chapter serve as a perspective towards the enhancement of the VFAs production, justifying the study of new methodologies to guide the anaerobic digestion process towards the production of platform compounds. The content of this chapter is presented in article format.

TECHNO-ECONOMIC EVALUATION OF ANAEROBIC DIGESTION BEYOND BIOGAS

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ABSTRACT
The anaerobic digestion process has been an object of study and interest mainly for the production of biogas, referred to as biomethane. However, the production of platform products, such as volatile fatty acids (VFAs), has a growing interest due to its high economic potential and positive environmental impact by harnessing organic waste within the circular economy philosophy. In the present work, a rigorous techno-economic analysis is performed comparing production scenarios for anaerobic digestion using food waste as substrate in the Colombian context. The Net Present Value (NPV) index was used to evaluate the economic viability of the process when producing biomethane and VFAs, using as inputs construction costs, logistics and services costs, amount of substrate available, inflation rate and product selling prices, among others. Eight production scenarios were investigated at different scales from the available food waste and ve production scenarios for the demand of potential products. It was found that the anaerobic digestion process oriented towards VFAs production can be 11 times more lucrative than biomethane generation. In turn, biomethane could replace and satisfy as much as 15 % (545455 m^3 biomethane $year^{-1}$) of natural gas consumption in the transport sector and 5 % (378 Ton VFAs $year^{-1}$) of VFAs exports in Colombia, being also an interesting production scenario. These results indicate that the anaerobic digestion process could contribute to harnessing food waste for the production of renewable energy and high-added platform components and these scenarios can be extrapolated to other developing countries.

Keywords: Anaerobic Digestion; Biomethane; Volatile Fatty Acids (VFAs); Techno-economic analysis; Viability.

3.1. Introduction

Currently, the Latin American economy can be considered basically based on the linear concept, where goods from raw materials are bought by consumers. Once the products have been used or consumed, consumers discard the remaining materials, without being reused. As the world population grows and new industrial and developed areas expand, it is evident that linear economy is already producing scarcity of commodities and energy, including food. This is leading to financial hardship, human suffering, and conflict (Sariatli, 2017).

In accordance with the 2030 Agenda for Sustainable Development and the Sustainable Development Goals (SDGs), Goal 7 includes: “Ensure access to affordable, reliable, sustainable and modern energy for all”. Therefore, the sustainable management of the environment and natural resources is a commitment assumed for economic growth and human well-being. Only through proper management of natural resources, a society can develop in a sustainable way, with a healthy ecosystem where water, air, and land are not contaminated as a result of residual discharges generated in the linear economy. In this sense, the circular economy is proposed as an alternative to avoid the drastic consequences that may arise from continuing to apply the linear economy (Macarthur, 2006).

The circular economy is defined as an economic-environmental strategy that aims to reduce both the entry of materials and the production of waste, creating a closed-loop or circle where the materials that have been discarded are treated to reduce re-entering the production system (Sauvé et al., 2016). The circular economy is an economic concept directly related to sustainability. Its main objective is that the value of products, materials, and natural resources remain in the economy for as long as possible, considerably reducing the generation of waste (Rizos et al., 2017). Anaerobic digestion process matches within this concept since it transforms bio-based waste such as food waste, pruning waste, household waste, solid manure, wastewater, agro-industrial waste, among others, into valuable products. Anaerobic digestion is carried out in hermetic containers called biodigesters. The bioprocess takes advantage of the degrading action of the biological material that certain microorganisms carry it out in the absence of oxygen, conventionally aimed to obtain biogas, which is mainly composed of carbon dioxide (40 %) and methane (60 %) (House and Surratt, 2013). Biogas is a renewable energy resource that does not add dioxide carbon load in the atmosphere and it has many uses in a sustainable society. Biogas can be used as a fuel for cooking, for heat and electricity production through co-generation (Hengeveld et al., 2016; Guo et al., 2017), upgraded biogas (biomethane) is used as vehicle fuel (Cucchiella et al., 2017; Balkenhoff et al., 2010) and also in injection into the gas grid (Wall et al., 2018; Aryal and Kvist, 2018).

During the anaerobic digestion process, four stages are carried out: the hydrolysis of carbohydrates in simpler soluble compounds that, later through acidogenesis, are metabolized producing volatile acids. Subsequently, in the acetogenesis stage, these compounds are transformed into acetic acid, hydrogen and carbon dioxide, to finally obtain the main compound of interest in methanogenesis, biogas (Diaz-Baez et al., 2002). Once the organic matter complies with the anaerobic digestion process and the biogas is extracted, a wet organic residue called digestate or biol is produced, which is pumped out of the biodigester. Digestate consists of slow degradable, stable organic components such as lignin, nitrogen, and phosphorous in various forms, inorganic salts containing phosphate, ammonium, potassium, and other minerals (Fagerström et al., 2018). Digestate has no bad smell, does not attract flies, and can be applied directly to the field in liquid form as fertilizer, as long as it complies with the soil application regulations.

An alternative approach to increase anaerobic digestion profitability is to target the production of Volatile Fatty Acids (VFAs): acetic acid, propionic acid, butyric acid, valeric acid and caproic acid (Wang et al., 2014). Previous research indicate that pH, temperature, type of substrate and retention time are parameters that favor the production of VFAs instead of biogas (Feng et al., 2009; Lee et al., 2014; Silva et al., 2013; Jiang et al., 2013). The direct recovery of these products from fermentation broth or the subsequent processing to produce other molecules (for example, polyhydroxyalkanoates (PHAs) or fatty acids of medium chain length), can result in valorization of the process beyond biogas and digestate (Kleerebezem et al., 2015). As advantages, the storage and transport of VFAs are easier and safer than biogas, and the added value of VFAs is 1.650 USD ton^{-1} (Calt, 2015), greater than the value of purified biogas (95 % methane), which is 996 USD ton^{-1} (Zhou et al., 2018). VFAs have a wide range of applications, valuable industrial chemicals for cosmetics production, the pharmaceutical industry, petrochemical synthesis, and the food and beverage industries (Zacharof and Lovitt, 2013). Additionally, VFAs production has created an opportunity for novel applications, such as polyhydroxyalkanoate biopolymers (PHA) production (Bluemink et al., 2016) nutrient removal in wastewater treatment plants (Lim et al., 2008), chain elongation (Cabrera Rodríguez et al., 2017), or bulk fuel and solvent production (Agler et al., 2011). Therefore, VFAs have the potential to be one of the main platforms in the new biorefineries, which can be used to produce biofuels and valuable chemicals by transforming biomass-based raw materials (Satinder et al., 2017).

In this sense, focusing on the production of VFAs through the anaerobic digestion process could turn the process into a system with a higher net income compared to the process destined to generate biogas. The process focused on biogas production has a limited financial profitability because biogas is not as efficient as fossil fuels, the biogas purification process is costly and the biogas is cheaper than VFAs. Despite VFAs potential, there is few techno-economical assessment studies focused on the production of VFAs through the anaerobic digestion process, and even less on the economic comparison of the production of biogas and VFAs by this process (Kleerebezem et al., 2015).

Therefore, this contribution aims to perform a rigorous techno-economic analysis of the anaerobic digestion comparing the net economic income depending on the product of interest to provide a comprehensive view of the conventional anaerobic digestion process (biogas production), assessing the economic advantages and disadvantages of VFAs recovery compared to biogas production. The investigated production scenarios are based on substrate offer and products demand. This assessment shows the anaerobic digestion economic viability in short and long term as a function of the production scale. The simulation results are particularly relevant since by the year 2025, 2.2 billion tons per year of urban municipal waste will be generated in the world, 46 % of which represents organic waste, which could be used by implementing technologies that promote the circular economy (Hoornweg and Bhada Tata, 2012). Moving towards a more circular economy could deliver benefits such as reducing environmental issues, preserve the supply of raw materials, increasing competitiveness, stimulating innovation, boosting economic growth, and creating jobs.

3.2. Methodology

In the present work, an a model-based techno-economic assessment in Colombian context is performed using technologies validated for the production of biomethane and VFAs through anaerobic digestion, using food waste as substrate. Food waste was chosen as substrates because of their high energy content (oriented to biogas production), low buffer capacity (oriented to VFAs production), high degradability, and large quantity and abundant availability (Zhang et al., 2014). In addition, food waste has better yields for biogas production and VFAs production compared to other types of waste (House and Surratt, 2013; Mao et al., 2015; Zhou et al., 2018).

From a general perspective, the same base process was considered but with a different objective product. The first was focused on biomethane production and the second on VFAs production (acetic acid, propionic acid, butyric acid and valeric acid). Depending on the focus, the process varies in design parameters such as: solids retention time (determines the size of the biodigester), operating pH, operating temperature, and volatile solids content of the substrate.

For the economic analysis and scaling up of anaerobic digestion, two approaches are considered. First, the amount of food waste available in Colombia (supply) to be used as a substrate in the anaerobic digestion process. Second, the demand for biomethane and VFAs in Colombia. When biomethane is produced, the income was calculated by comparing the consumption of natural gas in the transportation sector in Colombia, and when VFAs is generated, the income was determined by comparing the export of industrial monocarboxylic fatty acids. Figure **3-1** shows the flow diagram that summarizes the methodology of the study carried out. It consists of 4 main steps: 1) Systematic literature review, 2) Design of the process, 3) Economic model development and 4) Scenario based techno-economic analysis. Each main step composed of complementary items that are developed for the implementation and analysis.

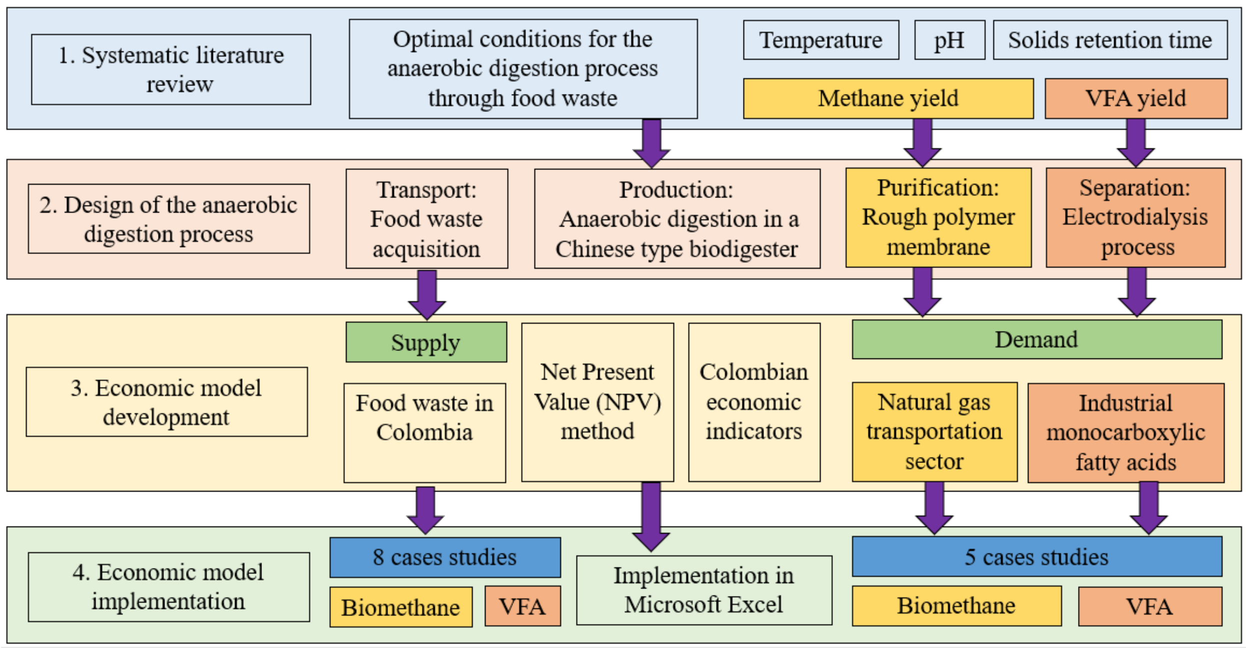

Figure. **3-1**: Methodology for the economic study of the anaerobic digestion process.

3.2.1. Economic potential evaluation

A systematic literature review was carried out to identify the optimal conditions of the anaerobic digestion process, using food waste as substrate, in order to obtain the maximum yields for biogas and VFAs reported. For this purpose, 3 scientific search engines were used to find information: Science Direct, Scopus, and Web of Science. The application of the scheme to explore databases was carried out using a search equation that limits the results to the words: “anaerobic digestion”, ”biogas”, “volatile fatty acids”, “VFAs”, “methane, “biomethane”, “yield”, ”production”, “efficiency”.

The economic feasibility is evaluated through the Net Present Value (NPV) index, which makes possible to analyze the profitability of a long-term investment. NPV (measured in USD) is defined as the sum of the present values of the individual cash flows, and it considers only cash inflows and outflows. In addition, the determination of these flows is based on the incremental approach. This method is described below (Gebrezgabher et al., 2010):

$$NPV = -I_o + \sum_{t=1}^{n} \frac{I_t - O_t}{(1+IRR)^t} \tag{3-1}$$

Where I_o: *Initial investment*, I_t: *Discounted cash inflows*, O_t: *Discounted cash outflows*, n: *Lifetime of investment*, t: *Time of the cash flow*, and IRR: *Internal Rate of Return*.

a. **Cash flows**

The costs, revenues, and investment calculations are based on the methodology used by Cucchiella and D'Adamo (2016) and Ferella et al. (2019). For the revenues side (discounted cash inflows), purified biogas (biomethane) is considered as vehicle fuel. While for the VFAs production process, the main revenue was from the sale of the sum of individual VFAs. Additionally, another part of the revenues is represented by the disposal of organic waste. In Colombia, the final disposal of urban waste in landfills is a paid service and for this study, it was taken into account as income for the two processes.

For the costs side (discounted cash outflows), three phases were considered: (i) substrate acquisition (transport), (ii) production (maintenance, operation, and services), and (iii): purification (biogas) or separation (VFAs). Figure **3-2** depicts these 3 phases of biomethane process, where the acquisition of substrate, the production stage in a Chinese-type biodigester and the purification stage are identified. Likewise, for the process to obtain VFAs, the acquisition of substrate, the production (Chinese-type biodigester) and the separation of the product stage are observed. For both processes, the initial investment costs are the construction of a Chinese type concrete biodigester with integrated polyester membrane gas-holder, with two concrete tanks for the storage of the input and output of the substrate.

For the first process, the biogas purification system was carried out using a non-rough polymer membrane, which uses the driving force generated by pressure difference for separation (Cucchiella and D'Adamo, 2016). While for the second process, VFAs separation was performed by an electrodialysis process (Moresi and Sappino, 2000). For the substrate acquisition, only the cost of transporting the waste to the biodigester was considered. For both biomethane production and VFAs production, the estimated costs were: maintenance and operation of the biodigester, cost of electricity service and the biodigester depreciation. For the purification of biogas into biomethane, the cost of maintenance and operation of the purifier, the cost of electricity service of the purifier, and depreciation of the purifier were considered. For the separation of the VFAs, the costs of maintenance and operation, the cost of electricity, and the depreciation of the electrodialysis system were included. Finally, labor costs were considered in both processes. For one worker, it was estimated 1 legal minimum wage in force, along with a transport subsidy, as stipulated by the Colombian standards.

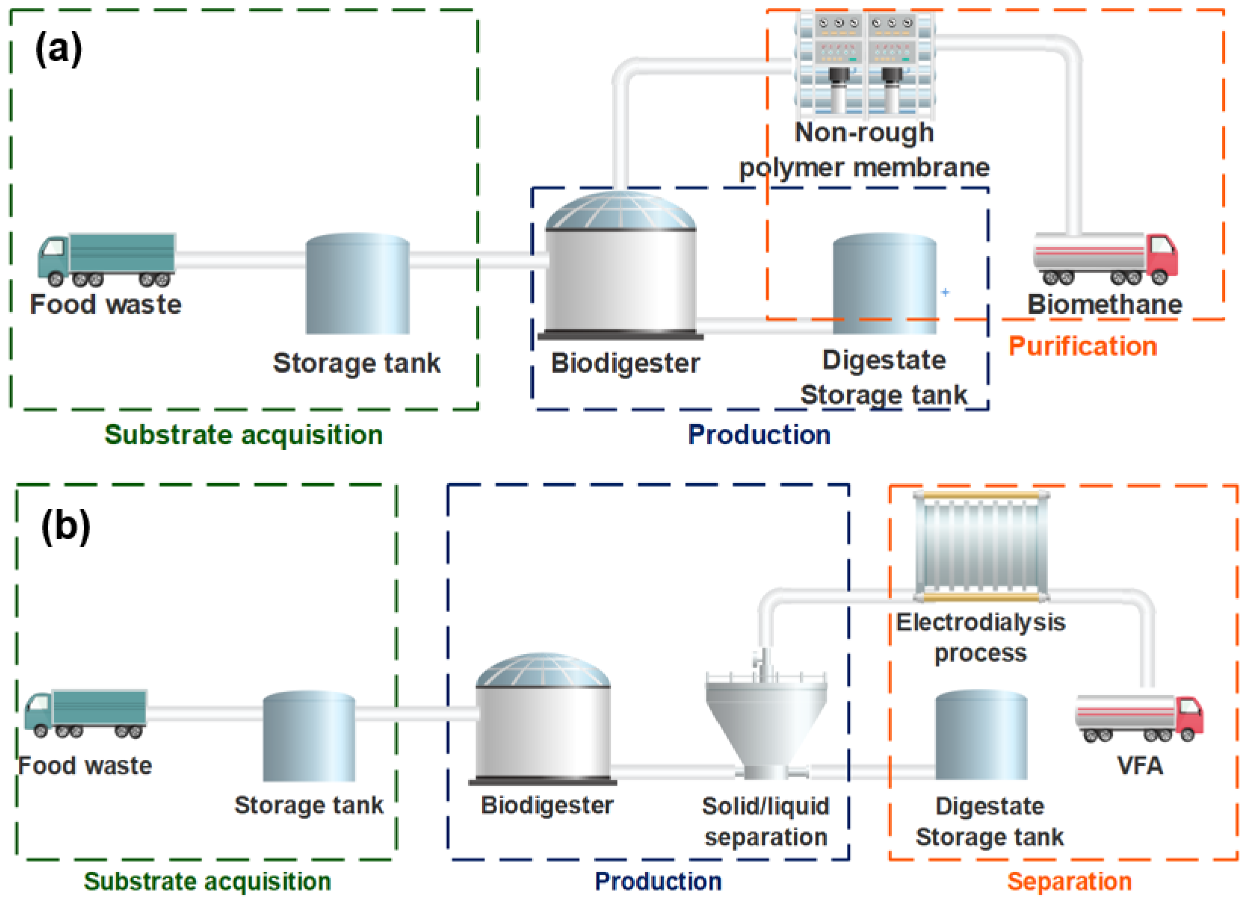

Figure. **3-2**: Phases of the anaerobic digestion process from food waste for the production of: (a) biomethane (b) VFAs.

b. **Economic model description**

In order to use equation 3-1, the economic model was implemented in Microsoft Excel and corresponds to an adjusted version of the model to the economic model proposed by Cucchiella et al. (2018), where the main differences lies on the scale of the process, local economic indices, and the design of separation and purification processes.

- Process oriented to the production of biomethane

$$I_o = C^{inv}_{B+ST} + C^{inv}_{BP} \tag{3-2}$$

$$I_t = R_{FWD} + R_{Biomethane} \tag{3-3}$$

$$O_t = C_{BOM} + C_{Bd,t} + C_{Be,t} + C_{L,t} + C_{FWT,t} + C_{POM,t} + C_{Pd,t} + C_{Pe,t} \tag{3-4}$$

- Process oriented to the production of VFAs

$$I_o = C^{inv}_{B+ST} + C^{inv}_{E} \tag{3-5}$$
$$I_t = R_{FWD} + R_{VFA} \tag{3-6}$$
$$O_t = C_{BOM} + C_{Bd,t} + C_{Be,t} + C_{L,t} + C_{FWT,t} + C_{EOM,t} + C_{Ed,t} + C_{Ee,t} \tag{3-7}$$

- Initial investment: Biodigester and storage tanks

$$SR_B = (\eta_{VSR})(H_B)(NW_{SR}) + 2\pi(\eta_{hSR})(r_B)(NW_{SR}) \tag{3-8}$$
$$\eta_{VSR} = \frac{4\pi r_B}{d_{SR}} \tag{3-9}$$
$$\eta_{hSR} = \frac{2H_B}{d_{SR}} \tag{3-10}$$
$$SR_{ST} = (\eta_{VSRST})(e_{ST})(NW_{SR}) + 4(\eta_{HSRST})(e_{ST})(NW_{SR}) \tag{3-11}$$
$$\eta_{VSRST} = \frac{16(e_{ST})}{d_{SR}} \tag{3-12}$$
$$\eta_{HSRST} = \frac{4(e_{ST})}{d_{SR}} \tag{3-13}$$
$$V_{STC} = 10(e_{ST})^2(t_B) \tag{3-14}$$
$$V_{ST} = \frac{(FW)(f_o)}{D_{FW}} \tag{3-15}$$
$$a_M = 2\pi(r_B)^2 \tag{3-16}$$

- Initial investment: Biogas Purification

$$C^{inv}_{BP} = (C_{UBP})(S_{biomethane}) \tag{3-17}$$
$$S_{biomethane} = \frac{(FW)(VS_{FW})(Y_{methane})}{24000D_{FW}} \tag{3-18}$$

- Initial investment: VFAs separation - electrodialysis equipment

$$C^{inv}_{E} = C_{EU} + C_{EM} + C_{EC} \tag{3-19}$$
$$C_{EU} = \alpha + \beta A_M \tag{3-20}$$
$$A_M = \frac{(e_f)(S_{VFA})}{2(t_w)(J_s)} \tag{3-21}$$
$$S_{VFA} = \frac{\eta_L(FW)(Y_{VFA})(SRT)}{D_{FW}} \tag{3-22}$$
$$C_{EM} = \gamma A_M \tag{3-23}$$
$$C_{EC} = \delta A_M \tag{3-24}$$

- Revenue: Final disposal of organic waste

$$R_{FWD} = (FW)\,(R_{FWDU})\,(t_W) \tag{3-25}$$

- Revenue: Biomethane sale

$$R_{Biomethane} = 24\,(S_{Biomethane})\,(P_{Biomethane})\,(t_w) \tag{3-26}$$

$$P_{Biomethane} = (P_{PTV})(C_{fgas})(1 - \%rp_{PTV}) \tag{3-27}$$

- Revenue: VFAs sale

$$R_{VFA} = 12\,(S_{VFA})\,(P_{VFA}) \tag{3-28}$$

- Costs: Production costs

$$C_{BOM} = \left(C^{inv}_{B+ST}\right)(OMF)\,(1 + RPI\_OM)^{t-1} \tag{3-29}$$

$$C_{Bd,t} = \frac{\left(C^{inv}_{B+ST}\right)(P_{df})}{100\eta_{debt}} \tag{3-30}$$

$$C_{Bd,t+1} = C_{Bd,t}\left(1 + \frac{inf}{100}\right) \tag{3-31}$$

$$C_{Be,t+1} = (C_{UeB})\,(Q_{biogas})\,(P_e) \tag{3-32}$$

$$Q_{Biogas} = \frac{100}{60}\,(S_{Biomethane})\,(t_w) \tag{3-33}$$

$$C_{Be,t+1} = C_{Be,t}\left(1 + \frac{inf}{100}\right) \tag{3-34}$$

$$C_{L,t} = 12\,(C_{UL})\,(\eta_{op}) \tag{3-35}$$

$$C_{L,t+1} = C_{L,t}\left(1 + \frac{inf}{100}\right) \tag{3-36}$$

$$C_{FWT,t} = (C_{UFWT})\,(FW)\,(t_w) \tag{3-37}$$

$$C_{FWT,t+1} = C_{FWT,t}\left(1 + \frac{inf}{100}\right) \tag{3-38}$$

- Costs: Biogas Purification

$$C_{POM,t} = \left(C^{inv}_{BP}\right)(P_{mo}) \tag{3-39}$$

$$C_{POM,t+1} = C_{POM,t}\left(1 + \frac{inf}{100}\right) \tag{3-40}$$

(3-41)

$$C_{Pd,t} = \frac{\left(C_{BP}^{inv}\right)\left(P_{df}\right)}{100\eta_{debt}} \tag{3-42}$$

$$C_{Pd,t+1} = C_{Pd,t}\left(1 + \frac{inf}{100}\right) \tag{3-43}$$

$$C_{Pe,t} = \left(C_{UeP}\right)\left(Q_{Biogas}\right)\left(P_e\right) \tag{3-44}$$

$$C_{Pe,t+1} = C_{Pe,t}\left(1 + \frac{inf}{100}\right) \tag{3-45}$$

$$\tag{3-46}$$

- Costs: VFAs separation - electrodialysis equipment

$$C_{EOM,t} = 0.03\left(C_E^{inv}\right) + \frac{C_{EM}}{\eta_m} \tag{3-47}$$

$$C_{EOM,t+1} = C_{EOM,t}\left(1 + \frac{inf}{100}\right) \tag{3-48}$$

$$C_{Ed,t} = \frac{C_E^{inv}}{\eta_{debt}} \tag{3-49}$$

$$C_{Ed,t+1} = C_{Ed,t}\left(1 + \frac{inf}{100}\right) \tag{3-50}$$

$$C_{Ee,t} = 12\left(E_{Wh}\right)\left(P_E\right)\left(P_e\right) \tag{3-51}$$

$$E_{Wh} = \frac{S_{VFA}}{\left(J_s\right)\left(A_M\right)} \tag{3-52}$$

$$C_{Ee,t+1} = C_{Ee,t+1}\left(1 + \frac{inf}{100}\right) \tag{3-53}$$

c. **Model assumptions and limitations**

For both processes, the initial investment, revenues, and costs were estimated at the Colombian setting. The investment cost was covered with bank financing. An Internal Rate of Return (IRR) of 10 % was chosen and the lifetime of investment was 15 years. Eight cases were investigated for the substrate supply, i.e. the production of these compounds (biomethane and VFAs) depends on the available substrate. The substrate was estimated from the food waste that can produce a small city to a large city in Colombia. Inflow varied between 5 $Ton\ day^{-1}$ (small city) to 200 $Ton\ day^{-1}$ (large city).

On the other hand, for the production of biomethane and VFAs, five cases were investigated based on the demand for these products. For the process oriented to the production of biomethane, studies were carried out to satisfy between 0.1 % and 15 % of the demand for natural gas in the transportation sector for Colombia in 2019. On the other hand, for the process oriented to the production of VFAs, between 5 % and

50 % of the export of industrial monocarboxylic fatty acids from Colombia in 2017 was taken into account. In addition, it was assumed that there are no production interruptions and that both biomethane (purification) and VFAs (electrodialysis separation) were obtained at 100 %. 330 days of annual production were used for all processes.

In terms of costs, the price of pre-treatment and conditioning of the food waste was not taken into account. Tools and equipment such as solid/liquid separator pipes, ducts, pumps, mixers, among others, were considered negligible expenses that, out of the costs included, make up the plant of the anaerobic digestion process. Likewise, the purchase and conditioning of the land for the plant was not contemplated in the economic study. On the revenue side, it was estimated that the purchase of biomethane and VFAs is total for the project duration. The sales price of VFAs was estimated as an average of the sales price of acetic acid, propionic acid, and butyric acid. The final specifications of the biomethane (like composition and pressure) are adjusted to be in line with their final use, therefore these costs were not taken into account. Economic and technical inputs are proposed in Table **3-1**.

This study can be considered as a conceptual analysis to evaluate different production scenarios, where it is assumed that the production of biomethane and VFAs through the process of anaerobic digestion is ideal according to the yields found in literature (Jiang et al., 2018; Wang et al., 2016).

3.3. Results and discussion

Through the systematic literature review, 36 articles were selected with relevant information on the production of biogas and VFAs through anaerobic digestion, using food waste as a substrate. For the production of biogas, yields between 142 to 926 $mL\ biomethane\ gVS^{-1}$ were reported, while for the production of VFAs, yields between 21.54 to 47.31 $gVFAs\ L^{-1} digestate$ were found. For this study, the best yields reported was selected, along with the ideal processing conditions to achieve that yield. A summary of the operating conditions of the both process are shown in Table **3-2** and Table **3-3**. These conditions remain constant for each of the cases to be economically evaluated.

Table. **3-1**: Input data for economic model

Variable	Value	Unit	Reference
$\% \ rP_{PTV}$	5	–	Ferella et al. (2019)
C_C	143.85	$USD\ m^{-3}$	Gobernación del Cauca (2016)
C_{fgas}	0.0105	$MWh\ m^{-3}$	Ferella et al. (2019)
C_M	8.63	$USD\ kg^{-2}$	Alibaba.com
C_{SR}	1.18	$USD\ kg^{-1}$	Gobernación del Cauca (2016)
C_{UBe}	0.13	$KWh\ m^{-3}$	Cucchiella and D'Adamo (2016)
C_{UFWT}	5.17	$USD\ Ton^{-1}$	Mintransporte (2018)
C_{UL}	293.70	$USD\ month^{-1}$	This study
C_{UP}	0.29	$MWh\ m^{-3}$	Cucchiella et al. (2018)
C_{UPB}	5428.57	$USD\ m^{-3}\ h^{-1}$	Cucchiella et al. (2018)
d_{SR}	0.3	m	This study
E_{Wh}	600	$h\ month^{-1}$	This study
e_f	1.1	–	Moresi and Sappino (2000)
e_{ST}	0.2	m	This study
f_o	1.1	–	This study
$f_{H/r}$	2	–	This study
inf	3.86	%	Portafolio (2019)
J_S	0.529	$kg\ m^{-2}\ h^{-1}$	This study
NW_{SR}	0.56	$kg\ m^{-1}$	Gobernación del Cauca (2016)
OMF	0.04	–	Lauer et al. (2018)
P_{df}	20	%	Cucchiella and D'Adamo (2016)
P_E	1.7	KW	This study
P_e	0.16	$USD\ m^{-3}$	Enel Codensa (2019)
P_{mo}	5	%	Ferella et al. (2019)
R_{FWDU}	9.12	$USD\ Ton^{-1}$	Grupo EPM (2019)
RPI_OM	0.065	–	Lauer et al. (2018)
P_{PTV}	28.17	$USD\ MWh^{-3}$	Ferella et al. (2019)
P_{VFA}	1.83	$USD\ kg^{-1}$	Zhou et al. (2018)
t	15	$year$	This study
t_B	0.2	m	This study
t_W	330	day	This study
α	185587.3	USD	Moresi and Sappino (2000)
β	843.4	$USD\ m^{-2}$	Moresi and Sappino (2000)
δ	742.3	$USD\ m^{-2}$	Moresi and Sappino (2000)
γ	327.7	$USD\ m^{-2}$	Moresi and Sappino (2000)
η_{debt}	15	$year$	Cucchiella and D'Adamo (2016)
η_L	3	$Batch\ month^{-1}$	Moresi and Sappino (2000)
η_m	3	$year$	Moresi and Sappino (2000)
η_{op}	4	–	This study

Table. **3-2**: Operating conditions of the anaerobic digestion of food waste for the production of biomethane.

Item	Units	Value	Reference
Substrate	-	Food waste	-
Density substrate	kg L^{-1}	0.514	Assumed
Operation temperature	°C	55	Jiang et al. (2018)
pH	-	7.2	
Solids Retention Time	day	29	
Volatile Solids substrate	gVS L^{-1}	20.12	
Product	-	Biomethane	
Biomethane Yield	mL Biomethane gVS^{-1}	556	
Concentration product	% v/v	100	Assumed
Sale Price product	USD kg^{-1}	0.28	Ferella et al. (2019)

Table. **3-3**: Operating conditions of the anaerobic digestion of food waste for the production of VFAs.

Item	Units	Value	Reference
Substrate	-	Food waste	-
Density substrate	kg L^{-1}	0.514	Assumed
Operation temperature	°C	35	Wang et al. (2016)
pH	-	7	
Solids Retention Time	day	8.75	
Volatile Solids substrate	gVS L^{-1}	20.12	
Product	-	VFAs	
VFAs Yield	gVFAs L^{-1}digestate	47.31	
Concentration product	% v/v	100	Assumed
Sale Price product	USD kg^{-1}	1.833	Zhou et al. (2018)

Regarding the scale of the process, in Table **3-4** can be seen the amount of substrate (supply), which defines the capacity of the plant, and which was taken into account for the 8 cases of the process focused on the production of biomethane and VFAs. The total amount of food waste in Colombia per year was used as a reference. On the other hand, Table **3-5** summarizes the 5 cases with the estimated amounts of biomethane and VFAs production, in order to satisfy a percentage of the natural gas for the transportation sector and industrial monocarboxylic fatty acids, respectively demand in Colombia.

Table. **3-4**: Amount of substrate for the case studies based on the supply of food waste in Colombia for the production of biomethane and VFAs through anaerobic digestion.

Food waste in Colombia ($Ton\ day^{-1}$)	Reference
26575	Departamento Nacional de Planeación (2016)
Case	**Substrate inflow ($Ton\ day^{-1}$)**
1a	5
2a	10
3a	20
4a	30
5a	50
6a	100
7a	150
8a	200

Applying the economic model proposed together with the NPV method for each situation and case study of the process proposed, the surface curve for supply and demand of biomethane production (Figure **3-3**) and VFAs production (Figure **3-4**) were obtained. Taking into account the supply (amount of substrate), the process oriented to VFAs production presents a positive accumulated NPV when 10 $Ton\ day^{-1}$ of substrate are used onwards. With a smaller amount of substrate, the accumulated NPV is unfavorable until the final year of the project. For the biomethane process, favorable NPVs are seen from 20 $Ton\ day^{-1}$ of substrate used. Substrate values lower than this will generate losses profits until the final year of the project. The time since it generates economic profit varies with respect to the amount of substrate to use. For the biomethane process, a maximum of 7 years (from 20 $Ton\ day^{-1}$) and at least 4 years (from 100 $Ton\ day^{-1}$) are required to start generating economic profit. However, in the case of VFAs production, profit is made from the first year when an amount of substrate greater than or equal to 20 $Ton\ day^{-1}$ is used. Thus, the project to produce VFAs from the anaerobic digestion process is more economically attractive. This is mainly because the time in which it begins to generate profits is shorter compared to the biomethane process. The above is concluded taking into account the same amount of substrate to be used.

Table. **3-5**: Amount of products for the case studies based on the demand for natural gas and industrial monocarboxylic fatty acids in Colombia.

Gas natural demand in the transport sector for Colombia ($m^3 year^{-1}$)		Reference	Export of industrial monocarboxylic fatty acids from Colombia ($Ton\ year^{-1}$)	Reference
3 636 364		Unidad de Planeación Minero Energética (2017)	7 556	Datawheel (2017)
Case	Natural gas demand percentage (%)	Biomethane ($m^3 year^{-1}$)	VFAs demand percentage (%)	VFAs ($Ton\ year^{-1}$)
1b	0,1	3636	5	378
2b	1	36364	10	756
3b	5	181818	25	1889
4b	10	363636	40	3022
5b	15	545455	50	3778

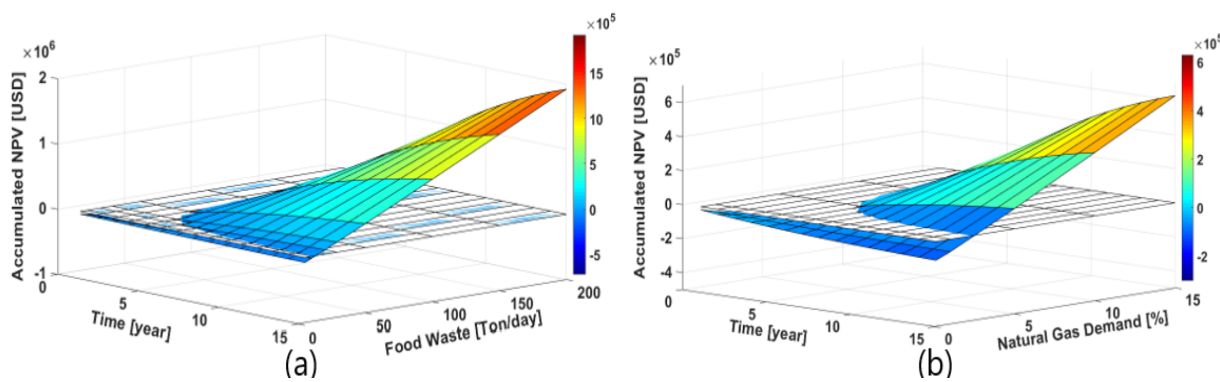

Figure. **3-3**: Accumulated NPV of biomethane production through the anaerobic digestion process. (a): Supply. (b): Demand. White surface is zero.

Comparing results individually, the process aimed at VFAs production has an overall investment (equipment, maintenance, depreciation, labor, services) 3.5 times higher than the biomethane process. This is mainly due to the cost of the electrodialysis equipment, which represents 89 % of the total investment. Compared to biogas purification, the costs of electrodialysis equipment are on average 6 times higher (depending on the scale of the process the investment costs are inversely proportional to the waste in flow). From the bioreactor point of view, due to the low solids retention time of the VFAs process, the smaller size of the biodigester is needed compared to the biomethane process. This results in lower costs in the construction of the biodigester (2 times smaller than the biodigester needed for the production of biomethane), mitigating the overall investment costs of the process aimed at the production of VFAs. The costs of labor, maintenance, and services make a similar value between the two processes in all evaluated scales.

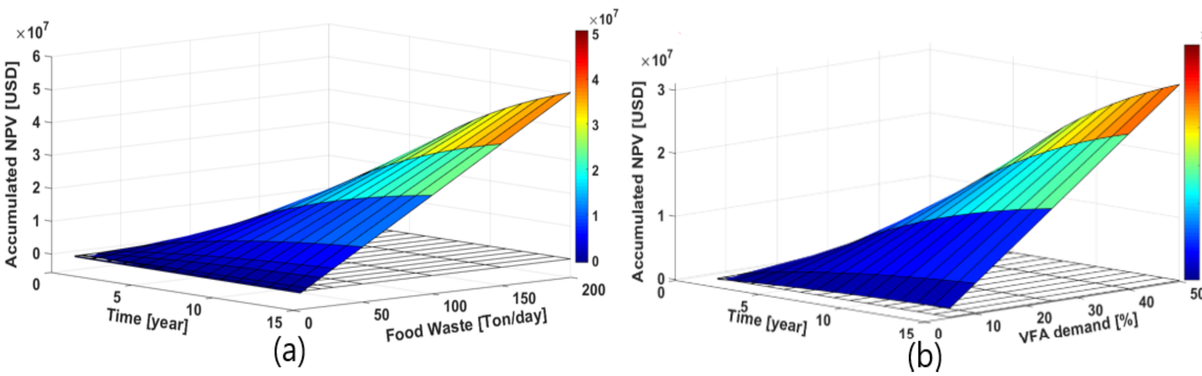

Figure. **3-4**: Accumulated NPV of VFAs production through the anaerobic digestion process. (a): Supply. (b): Demand. White surface is zero.

From a product point of view, revenue from final VFAs products sales is on average 11 times higher than sales per biomethane. As a result, the initial investment cost can be recovered in a few years (less than 3) as long as the substrate flow is greater than 10 $Ton\ day^{-1}$. In contrast, for biomethane production, a positive NPV was reflected when the substrate flow is greater than 18 $Ton\ day^{-1}$. As a consequence, profits were noticed after the maximum evaluated period (15 *years*).

Cucchiella et al. (2018) conducted an economic study using the NPV method on small-scale plants (50, 100, and 150 $m^3\ h^{-1}$ of substrate) for the production of biomethane through the anaerobic digestion process. As substrate, corn waste and municipal organic waste generated in Italy were employed. The results showed that a positive NPV is generated for biogas plants that can treat at least 50 $m^3\ h^{-1}$ of substrate equivalent to 600 $Ton\ day^{-1}$. In comparison to this study, positive results were obtained when treating an organic waste rate from 100 $Ton\ day^{-1}$. This difference could be partially explained since the availability of the substrate and process factors such as storage, compression, and distribution of the methane which are taken into account by the authors and which were not considered here since that information was not available in our context. This makes the process economically feasible when treating larger substrate flows, as the scale is inversely proportional to the process costs. Besides, another difference can be seen in the cost of methane production. The authors report production cost between 0.74 and 0.97 € m^{-3} of methane produced (Cucchiella et al., 2018).

For this study, the methane production price ranges from 0.32 to 0.63 € m^{-3}. Production costs for this study are derived from annual costs without taking into account the cost of fixed capital investment, these being inversely proportional to the scale of the process, as mentioned above. According to Arteconi et al. (2017), the cost of biomethane production depends by the feed-stock composition, which is related to the biomethane yield that can be obtained from the substrate, suggesting a higher production cost for low-yield substrates. In this study, the highest biomethane yields for food waste reported in the literature were used, thus generating low biomethane production costs.

On the other hand, Kleerebezem et al. (2015) have performed also a study s comparing the economic feasibility of the products of the anaerobic digestion. Although the authors did not make an in-depth assessment of the revenues and costs of the entire process, as done in this contribution, they report that the VFAs oriented anaerobic digestion process can be 5.6 times more profitable than when oriented to biogas production (Kleerebezem et al., 2015). For this study, it can be seen from the accumulated NPV as a function of the supply scale (see Figure **3-5** (a)) that VFAs production is more economically attractive. Specifically for the last year of the economic study (15 day), the scale of the process is directly proportional to the income generated. As a result, net profits are up to 28 times higher when the process is oriented to VFAs production rather than to the production of biomethane (when 200 *Ton* day^{-1} of substrate are treated). On average, the percentage increase in net revenues from the process aimed at VFAs production with respect to the process for generating biomethane is 97 %, as shown in Figure **3-5** (b). This is mainly due to the difference in sales price of the Figure **3-5** (b) products, which approximately VFAs have 13 times the commercial value of biomethane. This means that the investment costs are recouped in less time, quickly generating a positive NPV and therefore higher net profits.

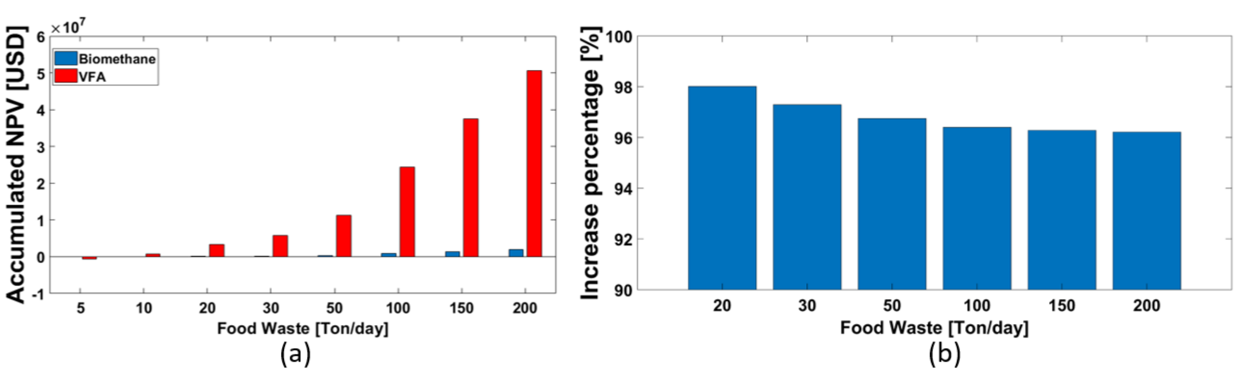

Figure. **3-5**: Cumulative NPV of biomethane and VFAs production for the year of project completion (15 years) taking into account the supply of substrate. (a): Comparison of net revenues. (b): Percentage increase of net revenues from the VFAs production process with respect to the biomethane production process

3.4. Conclusions

The results of this study showed that the economic investment feasibility of the project aimed at producing VFAs from the anaerobic digestion process is more attractive than the investment project focused on biomethane production. Despite the fact that the former requires a higher initial investment. Technically, it is possible to valorizate the supply of food waste utilization of at least 20 $Ton\ day^{-1}$ and a percentage from 5 % of the national demand for natural gas for the transport sector, with a favorable economic balance in a period of 15 years. While for the production of VFAs by means of the process of anaerobic digestion, the supply of the reuse of food waste of minimum 9 $Ton\ day^{-1}$ can be supplied and could satisfy 5 % of the annual VFAs exported by Colombia, generating profitable income for the implementation of the process within a period of 15 years.

The study of these scenarios is important because it can encourage and promote the analysis and improvement of the anaerobic digestion process for VFAs production. The methodology used in this study can be implemented in regions that have information on at least economic indicators (inflation rate), amount of substrate, prices of construction materials, services and logistics, as well as sale prices of products. At the same time, it theoretically demonstrates the economic sustainability of the anaerobic digestion process at a national level, opening the doors to a circular economy with a great capacity for profit, providing a response to the current problems derived from non-renewable energies, such as environmental pollution, limited availability of resources and the supply of energy to interconnected areas.

3.5. Acknowledgments

We thank the Fundación Ceiba and Becate Nariño, with the project: "Formación del talento humano de alto nivel para el fortalecimiento de necesidades estratégicas en ciencia, tecnología e innovación en el departamento Nariño", for funding this work. We also express our gratitude to the Universidad Nacional de Colombia-sede Manizales for providing the tools and resources for this research.

Nomenclature

A_M	Membrane area for electrodialysis, m^2
a_M	Polyester membrane area, m^2
C^{inv}_{B+ST}	Cost biodigester + 2 storage tanks, USD
C_{Be}	Biodigester electricity cost, $USD\ year^{-1}$
C_{Bd}	Biodigester depreciation fund, $USD\ year^{-1}$
C_{BOM}	Biodigester operation and maintenance cost, $USD\ year^{-1}$
C^{inv}_{BP}	Biomethane purification investment cost, USD
C_C	Concrete cost 3000 PSI (includes installation), $USD\ m^{-3}$
C^{inv}_{E}	Electrodialysis equipment investment cost, USD
C_{EC}	Electrodialysis cell cost, USD
C_{Ed}	Electrodialysis depreciation, $USD\ year^{-1}$
C_{Ee}	Electrodialysis electricity cost, $USD\ year^{-1}$
C_{EM}	Electrodialysis membrane cost, USD
C_{EOM}	Electrodialysis operation and maintenance cost, $USD\ year^{-1}$
C_{EU}	Electrodialysis equipment unit cost, USD
C_{fgas}	Conversion factor biogas, $MWh\ m^{-3}$
C_{FWT}	Substrate transportation cost, $USD\ year^{-1}$
C_L	Labor cost, $USD\ year^{-1}$
C_M	Polyester membrane cost, $USD\ m^{-2}$
C_{Pd}	Purification biomethane depreciation fund, $USD\ year^{-1}$
C_{Pe}	Purification biomethane electricity cost, $USD\ year^{-1}$
C_{POM}	Purification operation and maintenance cost, $USD\ year^{-1}$
C_{SR}	Steel rod $3/8'$ cost (includes installation), $USD\ kg^{-1}$
C_{UBe}	Biodigester electricity consumption unit, $KWh\ m^{-3}$
C_{UP}	Unit purification biomethane electricity consumption, $MWh\ m^{-3}$
C_{UPB}	Biomethane purification unit cost, $USD\ m^{-3}\ h^{-1}$
C_{UL}	Unit labor cost USD, $month^{-1}$
C_{UFWT}	Unit substrate transportation cost, $USD\ Ton^{-1}$
d_{SR}	Distance between steel rods, m
D_{FW}	Food Waste density, $kg\ L^{-1}$
e_f	Correction factor for safety over design of the required membrane surface area
e_{ST}	Edge of storage tank, m^2
E_{Wh}	Electrodialysis equipment working hour, $h\ month^{-1}$
$f_{H/r}$	Height-radius ratio
f_o	Oversizing factor
FW	Food waste flow, $Ton\ day^{-1}$
H_B	Biodigester height, m
inf	Rate of inflation, %
I_o	Initial investment, $USD\ year^{-1}$
I_t	Discounted cash inflows, $USD\ year^{-1}$

Nomenclature

J_S	VFA flux, $kg\ m^{-2}\ h^{-1}$
n	Lifetime of investment, *year*
N_{hSR}	Number of horizontal steel rods
NW_{SR}	Nominal weight steel rods $3/8'$, $kg\ m^{-1}$
O_t	Discounted cash outflows, $USD\ year^{-1}$
OMF	Operation and maintenance cost annual factor
$P_{Biomethane}$	Selling price of biomethane, $USD\ m^{-3}$
P_{PTV}	Price of biomethane in the virtual trading point, $USD\ MWh^{-3}$
P_{df}	% of depreciation found
P_e	Unit price of electricity, $USD\ m^{-3}$
P_E	Electrodialysis power, KW
P_{mo}	% of maintenance and overhead cost
P_{VFA}	Selling price VFAs, $USD\ kg^{-1}$
Q_{bogas}	Biogas flow, $m^3\ h^{-1}$
$\%\ rP_{PTV}$	% reduction of the price in the PTV
r_B	Biodigester radius, m
$R_{Biomethane}$	Biomethane sale revenue, $USD\ year^{-1}$
R_{FDFW}	Food waste disposal revenue, $USD\ year^{-1}$
R_{FWDU}	Food waste disposal price unitary, $USD\ Ton^{-1}$
RPI_OM	Rate price increase operation and maintenance costs
R_{VFA}	VFAs sale revenue, $USD\ year$
$S_{biomethane}$	Biomethane production, $m^3\ h^{-1}$
SRT	Solid retention time, *day*
SR_B	Amount of steel rod $3/8'$ for the biodigester, kg
SR_{ST}	Amount of steel rod $3/8'$ for 2 storage tanks, kg
S_{VFA}	VFAs production, $kg\ month^{-1}$
t	Time of the cash flow, *year*
t_B	Wall thickness, m
t_W	Working time, *day*
V_B	Biodigester volume, m^3
V_{BC}	Biodigester concrete volume, m^3
V_{BFC}	Biodigester floor concrete volume, m^3
V_{BWC}	Biodigester wall concrete volume, m^3
V_{ST}	Storage tank volume, m^3
V_{STC}	Storage tanks concrete volume (2), m^3
V_{TG}	Biodigester volume-gas phase , m^3
V_{TL}	Biodigester volume-liquid phase , m^3
VS_{FW}	Volatile solid food waste, $gVS\ L^{-1}$
$Y_{biomethane}$	Biomethane yield, $mL\ methane\ gVS^{-1}$
Y_{VFA}	VFAs yield, $gVFAs\ L^{-1}$

Greek symbols

α	Constant for electrodialysis equipment unit cost, *USD*
β	Constant for electrodialysis equipment unit cost, *USD* m^{-2}
δ	Constant for electrodialysis cell cost, *USD* m^{-2}
γ	Constant for electrodialysis membrane cost, *USD* m^{-2}
η_{debt}	Period of loan, *year*
η_{hSR}	Number of horizontal steel rods for biodigester
η_{L}	Number of monthly loads, *Batch month*$^{-1}$
η_{hSRST}	Number of horizontal steel rods for 2 storage tanks
η_{m}	Membrane shelf life, *year*
η_{op}	Number of operators
η_{VSR}	Number of vertical steel rods for biodigester
η_{VSRST}	Number of vertical steel rods for 2 storage tanks

References

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4 Modelling and simulation of the anaerobic digestion process

The linear system of production and consumption worldwide has not undergone changes and is still based on the extraction of raw materials, the production of goods, consumption and the generation of waste. The circular economy starts from the change in this system towards a more sustainable approach avoiding waste and mitigating negative impacts for the environment, the climate and human health. Anaerobic digestion is a technology governed by the circular economy, which in addition to producing biogas as renewable energy, can produce added value products such as Volatile Fatty Acids (VFAs).

In this chapter, a model-based techno-economic investigation was proposed to enhance the VFAs bio-production through anaerobic digestion process. The Anaerobic Digestion Model No 1 (AMD1) was used to design and implement a control system based on an override strategy where pH is the controlled variable, and a real-time optimization algorithm finds the best production scenarios under inlet disturbances such as protein particle components. With this simulation approach, the understanding of the system is improved, and an integral vision is given to the conventional anaerobic digestion process, promoting and contributing to the study of the generation of non-conventional products in the anaerobic digestion. The implementation of the model was carried out from the research presented by Rosen and Jeppsson (2006). The content of this chapter is presented in article format.

Real-time optimization for enhanced closed-loop control of anaerobic digestion for VFAs production under disturbances

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ABSTRACT
Anaerobic Digestion have shown to play an important role in circular economy considering its ability to transform waste in biogas. Beyond that, the production of platform substances through the anaerobic digestion process, such as volatile fatty acids (VFAs) is of growing interest due to the expected higher process profitability. However, the production and extraction of these compounds are still challenging. Computational simulation is considered a relevant tool to provide process understanding and improve the design and operation of the anaerobic digestion process. This work proposes a model-based techno-economic investigation to enhance the VFAs bio-production form waste under disturbance. Anaerobic Digestion Model No 1 (AMD1) is implemented for designing and evaluating a control structure based on an override strategy. pH is the controlled variable, and a real-time optimization (RTO) algorithm finds the best production scenarios under inlet disturbances. Through simulation it was possible to obtain concentration of 34 times larger of total sum of VFAs, and increase of 8771 USD day^{-1} (concerning to the nominal value) for sales of VFAs was obtained (by implementing the VFAs production improvement), and through the RTO layer implementation, 7 % increase on process profit could be obtained when the system was disturbed in unfavorable conditions (concerning to the point of operation). The results show that it is possible to improve VFAs production compared to an uncontrolled reactor and demonstrate that the control structure with real-time optimization guarantees the maximum possible income when the system is subject to disturbances, finding the optimal operation point for this purpose. Modeling efforts showed the production potential of VFAs through the anaerobic digestion process, opening the doors to new perspectives of the process, being an important step to implement profitable renewable technologies.

4.1. Introduction

The rapid development of modern society and the constantly increasing population are factors that cause the generation of organic waste to increase significantly annually. Worldwide, 2.01 billion tons per year^{-1} of solid waste is generated, and this amount is expected to increase to 3.4 million tons by 2025 (Paes et al., 2019). Improper waste management is not only harmful to humans and the environment, but also increases climate change and makes the sanitation system compel nations and governments to invest more financial and material resources for its remediation (Wainaina et al., 2020). Consequently, renewable technologies for waste management are necessary to promote environmental protection, sustainable development and are also essential to implement and project a circular economy. The main objective of the circular economy is that the value of products, materials and natural resources remain in the economy for as long as possible, considerably reducing the generation of waste (Rizos et al., 2017).

One technology that implements the philosophy of the circular economy is the anaerobic digestion process. Anaerobic digestion is a biological process where organic matter, in the absence of oxygen, is degraded by microorganisms families through a sequence of reactions in four stages: hydrolysis, acidogenesis (or fermentation), acetogenesis, and methanogenesis and is mainly converted into methane and carbon dioxide, also called biogas (Toerien and Hattingh, 1969). The anaerobic digestion process for biogas production has been highly successful and well-established. Nevertheless, biogas is not one of the most valuable products that can be obtained form anaerobic digestion. Then, this process has recently gained attention as a cost-effective and environmentally friendly alternative for volatile fatty acids (VFAs) production (Wang et al., 2014). VFAs including acetic acid, propionic acid, butyric acid, valeric acid are potentially renewable carbon sources that have applications in the pharmaceutical industry, precursors for polyhydroxyalkanoates (PHAs), cosmetic production, petrochemical synthesis, and food and beverage industries (Zacharof and Lovitt, 2013). Besides, production and extraction of VFAs during the anaerobic digestion process, though is a technical challenge, could offer an economic advantage compared to biogas due to market value for VFAs is 1.650 USD ton^{-1} (Calt, 2015), greater than the market value for purified biogas (95 % methane), which is 996 USD ton^{-1} (Zhou et al., 2018a).

Several strategies to enhance VFAs production through the anaerobic digestion process have been investigated. According to Zhou et al. (2018b), the production of VFAs can be improved based on the stages of anaerobic digestion, and these can be generally classified into: I) Improving hydrolysis rate to produce more soluble substrates for further fermentation. Optimization of key operational factors such as pH, temperature, and substrate pretreatment before fermentation are methods that enhance hydrolysis (Kim et al., 2005; Zhang et al., 2005; Wang et al., 2014). II) Promoting the acidogenic process: experimentally, it has been shown that substrate, inoculum, hydraulic retention time (HRT), organic loading rate (OLR), pH, temperature, and headspace gas are critical factors that determine the efficiency of VFAs production and quality of VFAs (Lim et al., 2008; Chen et al., 2013; Jiang et al., 2013). III) Removing the inhibiting factors: the accumulation of VFAs may cause the acidogenic reactions thermodynamically unfavorable, resulting in the shift of metabolic pathway to produce other products (Pind et al., 2003). This limitation can be overcome if the VFAs were removed from the system continuously through precipitation, extraction, crystallization, distillation, and, primarily, electrodialysis technique (Redwood et al., 2012; Jones et al., 2015; Arslan et al., 2016) .

Despite previous research efforts, the optimal design, control, and operation of the anaerobic digestion process VFAs production remain as challenge due to the variability of the substrate and its weak decomposition, the complexity of the microbial consortium, the destabilization by inhibition, pH variability, inhibition by ammonia, complicated biochemical, physical, and chemical interactions involved in the process (Donoso-Bravo et al., 2011; Yu et al., 2018). To address these drawbacks, the computational simulation of mathematical models is and interesting approach to improve the design and efficiency of the anaerobic digestion process (Manjusha and Beevi, 2016). The computational simulation allows a better understanding of the system, formulation, and validation of some hypotheses, prediction of the behavior of the system under different conditions, thereby reducing experimental information requirements, costs, risk, and time (Donoso-Bravo et al., 2011). On the other hand, according to Nguyen et al. (2015), implementing an anaerobic digestion process control system enables quick process stabilization with less operation and maintenance inconveniences, maximizing the efficiency of the process.

Research in the last two decades has focused on implementing sophisticated models to simulate and understand the complex degradation of organic matter that occurs in anaerobic processes. These models are developed to discover specific aspects of the composite substrate degradation process, taking into account the identification of key factors that affect system performance (Batstone et al., 2002). Possibly the most widely applied model in the area of anaerobic digestion process research is the Anaerobic Digestion Model No. 1 (ADM1) developed by the modelling task group of the International Water Association IWA (Batstone et al., 2002). ADM1 takes into account the main steps of disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. It consists of descriptions of 7 groups of bacteria and archaea, 19 biochemical process rates, 24 components (12 soluble and 12 particulate elements), 3 gas-liquid transfer kinetic processes (CH_4, CO_2, H_2), and 6 acid-base balances in association with the pH calculation together with a set of 105 kinetic and stoichiometric parameters/variables (Batstone et al., 2002; Kleerebezem and van Loosdrecht, 2006).

ADM1 has been applied and validated by simulating the digestion of various organic waste

(Batstone and Keller, 2003; Lohani et al., 2016; Jurado et al., 2016; Nordlander et al., 2017). Likewise, ADM1 modifications have been made to improve and optimize the biogas production by anaerobic digestion process (Pessoa et al., 2019; Li et al., 2020; Sun et al., 2021), as well as the implementation of control systems with ADM1 as a test platform, where these studies focused on the design of control strategies that avoid the accumulation of VFAs to guarantee the process stability and optimal production of biogas (García-Sandoval, 2009; Ramirez et al., 2019; Zhou et al., 2020). In contrast, research on the implementation and control of ADM1 to enhanced VFAs production is limited. Bai et al. (2015) developed a modified ADM1 to simulate anaerobic fermentation of waste activated sludge degradation and evaluate the influence of pH on VFAs production. The authors used particle swarm optimization (PSO) to improve acidogenic reactor design and optimize the operation parameters. They found that alkaline conditions are beneficial for VFAs production through anaerobic fermentation, being one of the few studies conducted that focuses on improving VFAs production through modeling and simulation of the anaerobic digestion process.

Due to the lack of understanding of the factors that enhance VFAs production in anaerobic digestion systems, a study to predict and improve VFAs production by anaerobic digestion using a robust mathematical model such as ADM1 is required. Additionally, mentioned above, orienting the anaerobic digestion process toward the production of VFAs can be a more economically attractive process than when producing biogas. A strategy that allows implementing these two purposes is to include a real-time optimization (RTO) layer to a control structure to estimate the optimal anaerobic digestion conditions under input disturbances. A RTO layer is a framework that continuously evaluates the process operating conditions to maximize the economic productivity of a process (Mirlekar et al., 2018), thus it could be used to find the best production scenarios when the substrate change properties and the control structure guarantee stable operation. In this study, ADM1 model is used to simulate and evaluate possible VFAs production scenarios using the RTO strategy coupled with a control structure. The implementation and manipulation of this model proposes strategies to obtain VFAs instead of biogas. Through the Matlab/simulink® tool, a sensitivity analysis is performed to identify the input variables of the model that promote the increase in VFAs concentration and decrease methane production. Likewise, the implementation of closed-Loop control with an RTO layer (economic optimizer) is designed and investigated to guarantee, not only the optimal operation of VFAs production under potential disturbances but also to maximizes the economic income from the sale of VFAs produced.

4.2. Methodology

The methodology that was proposed to implement a closed-loop real-time optimization for ADM1 to increase the production and incomes from sales of the VFAs consists of 4 primary steps: 1. Mathematical implementation of ADM1, 2. Operation point estimation that enhances VFA production under inlet standard conditions, 3. Control structure design where manipulated and controlled variables are selected and 4. Hierarchical control structure: real-time optimization layer implementation for closed-loop control. Figure **4-1** shows the flow diagram that summarizes the methodology of the study carried out.

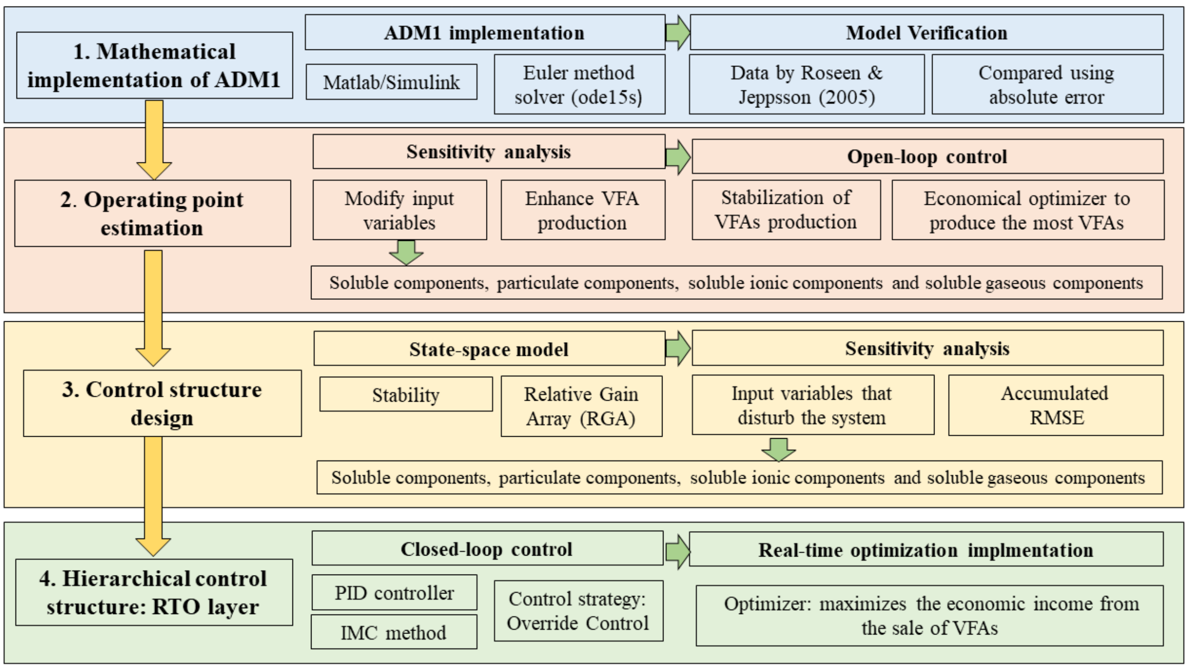

Figure. **4-1**: Methodology for the implementation of closed-loop real-time optimization that enhances VFAs production in anaerobic digestion.

4.2.1. Mathematical implementation of ADM1 and verification

ADM1 model was programmed in Matlab/simulink® R2018a through an Ordinary Differential Equations (ODEs) system as well as a Differential-algebraic equation (DAE) system. The equations covering the biological kinetic rate expressions and coefficients were obtained from the Peterson matrix (Batstone et al., 2002). All of the parameters and initial conditions necessary for the implementation of the model come from Rosen and Jeppsson (2006). Because ADM1 is a very stiff system with time constants ranging from fractions of a second to months (Rosen and Jeppsson, 2006), ODEs were solved with the Euler method solver (ode15s) available in Matlab® . The in-house implementation was done since the open-source implementation is available in C++ connected with Matlab® , which limits the potential of model adaptations

In order to verify the model implementation, simulation outputs were compared to (Rosen and Jeppsson, 2006)) simulations. The comparison between the benchmark data and the results derived from the simulation of the model of this study was carried out by calculating the absolute error of each output variable of the model. The simulation time (t_{span}) for the model verification was 2000 days, it was also used to obtain final values at steady-state conditions.

4.2.2. Optimal operating point determination

The optimal operating point corresponds to the sum of the highest concentration of each VFA that can be produced. To determine this, a sensitivity analysis was first performed to determine the input variables: soluble components, particulate components, soluble ionic components and soluble gaseous components (presented in the nomenclature) that promote the generation of VFAs and inhibit the generation of methane. Each of the input variable was individually modified in a range of 5 times less and 5 times more than the initial value. This sensitivity analysis allowed to define the operative window and potential numerical problems for the subsequent optimization.

Due to the process unstability, it was necessary to implement an open-loop control that allows stabilizing the production of VFAs, where the manipulated variables were the input variables found from the sensitivity analysis carried out before. To optimize the reactor with the open-loop control, equation 4-1 presents the economic objective function that allow finding the highest economic income from selling VFAs. The optimization problem depicted in Equation 4-1 was solved using the Matlab® function “Fmincon” with the “interior-point” algorithm. This solver is a powerful tool able to minimize non linear objective functions, considering inequality and equality constraints (Pataro et al., 2020). The prices of the VFAs: valeric acid, butyric acid, propionic acid, and acetic acid are presented in Table **4-1**. The extraction and purity of the VFAs obtained from the anaerobic digestion process were considered ideal.

Table. **4-1**: VFAs sale prices. (Zhou et al., 2018b)

VFA	unit	value
Valeric acid	USD kg^{-1}	2.5
Butyric acid	USD kg^{-1}	2
Propionic acid	USD kg^{-1}	1.65
Acetic acid	USD kg^{-1}	0.8

$$min \left\{ -q_{in} \sum_{i=1}^{4} (PriceVFA_i)([VFA]_i) + \left[VFA^-\right]_i \right\} \quad (4\text{-}1)$$

Where: q_{in}: *Flow rate* m^3 *day*$^{-1}$, *Price VFA*$_i$: *VFAs sale prices USD kg*$^{-1}$, $[VFA]_i$: *VFAs concentration kgCOD m*$^{-3}$, $[VFA^-]_i$: *ions VFAs concentration kgCOD m*$^{-3}$

4.2.3. Control structure design

Once the operating point of the system is found, a control structure must be designed, i.e., identify potential controlled and manipulated variables to achieve the control objective. For this, the system controllability and stability is determined through the evaluation of the Kaman's controllability matrix (Seborg et al., 2010). For this purpose, it was necessary to calculate the linear representation of the system through numerical approach (MathWorks, 2021). For determining the best pairing of controlled and manipulated variables, Bristol's Relative Gain Array (RGA) method was used (Bristol, 1966; Skogestad and Postlethwaite, 2005).

Due to the non linear nature of the model, the potential manipulated variables: soluble components, particulate components, soluble ionic components and soluble gaseous components (presented in the nomenclature), were identified through a sensitivity analysis instead of using a linear approach. The sensitivity analysis was carried out using step disturbances on each input variable of (-50 %: 5: 50 %) at time 0 and t_{span} of 500 days. The interest output variable is the pH, because pH is one of the factors that most affects the concentration and composition of VFAs (Liu et al., 2012; Lee et al., 2014). Through the sensitivity analysis, this statement was corroborated. To quantify output sensitivity, the accumulated root-mean-square error (RMSE) was calculated, which was calculated according to equations 4-2 and 4-3.

$$RMSE_k = \sqrt{\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n}} \quad (4\text{-}2)$$

$$RMSE_{ac} = \sum_{k=1}^{21} RMSE_k \quad (4\text{-}3)$$

Where $RMSE_k$: *Root-mean-squeare error for a k % disturbance*, P_i: *Operating point value*, O_i: *Observable point value, n: Data number*, $RMSE_{ac}$: *Root-mean-square error accumulated for a disturbed input variable.*

4.2.4. Hierarchical control structure: real-time optimization and closed-loop control

In practice, the control system is usually divided into several layers. Typically, layers include scheduling (weeks), site-wide optimization (day), local optimization (hour), supervisory/predictive control (minutes) and regulatory control (seconds) (Larsson and Skogestad, 2000). Referring to local optimization, the purpose of this is to identify the active constraints and recompute optimal set points for the controlled variables (Skogestad, 2004). This optimization is the task of the real-time optimization (RTO) layer.

Initially, the linear relation between controlled and manipulated variable is required. A linear representation of first order plus time-delay (FOPTD) model is obtained by optimal parameter estimation using the step response method with 10 % and -10 % input disturbance (Seborg et al., 2010). This is approach is preferred to exploit knowledge of input disturbances and to have a better representation of the non linear response.

$$y(t) = KM\left(1 - e^{-\frac{t}{\tau}}\right)(t - t_d) \tag{4-4}$$

Where *K: Gain*, *M: Amplitude of the input step disturbance*, τ: *Time constant*, *t: Time*, t_d: *Time delay*

The PID controller implemented was a parallel type with a derivative filter. Derivative filter reduces the sensitivity of the control calculations to noisy measurement (Seborg et al., 2010). The PID controller parameters were estimated with the Internal Model Control (IMC) (Garcia and Morari, 1982). Because the pH (controlled variable), depends on the manipulation of the inlet cations and anions concentration (S_{cat_in} and S_{an_in} i.e,. base or acid addition), which are complementary, it is proposed to implement a override controller to exploit this particular system characteristic. Manipulated variables can be switched according to a specified situation.

On the top of the control structure, a real-time optimization (RTO) layer is implemented. Considering the economic profit as target, the implementation of the RTO closed-loop aims to increase the daily revenue according to a positive or negative disturbance. The economic objective function used for process design is re-used (equation 4-1) which takes into account the sale price of the VFAs (Table **4-1**). Once again, Matlab® solver "fmincon" was used to solve the optimization problem. A step disturbance of the input variable X_{pr_in} of +10 % and -10 % was carried out in a time of 200 days.

4.3. Results and discussion

4.3.1. Implementation and validation of ADM1 model

The implemented model was used as an independent model to test a specific system to enhance VFAs production and inhibit biogas production. ADM1 consists of 35 components that are presented in the nomenclature along with their units (Batstone et al., 2002). The process operating conditions are also presented.

Model verification is important due to that it verifies that model results are reliable. The verifying was performed by comparing results from the model with results from Rosen and Jeppsson (2006) ADM1 implementation. Error absolute between the benchmark outputs and outputs derived from ADM1 simulation in this study for the same input values are presented in Figure **4-2**. As can be seen from the comparison between the benchmark data and steady-state results derived from the model simulation, there was a very close agreement for all values. The prediction errors were encountered in the range of 10^{-3}, where the variable $S_{gas,ch4}$ had the highest absolute error with 4.3x10^{-3}. Due to the small values encountered, the implementation is considered appropriate and the reasons for the differences could be attributed to potential updated in Matlab® numerical methods.

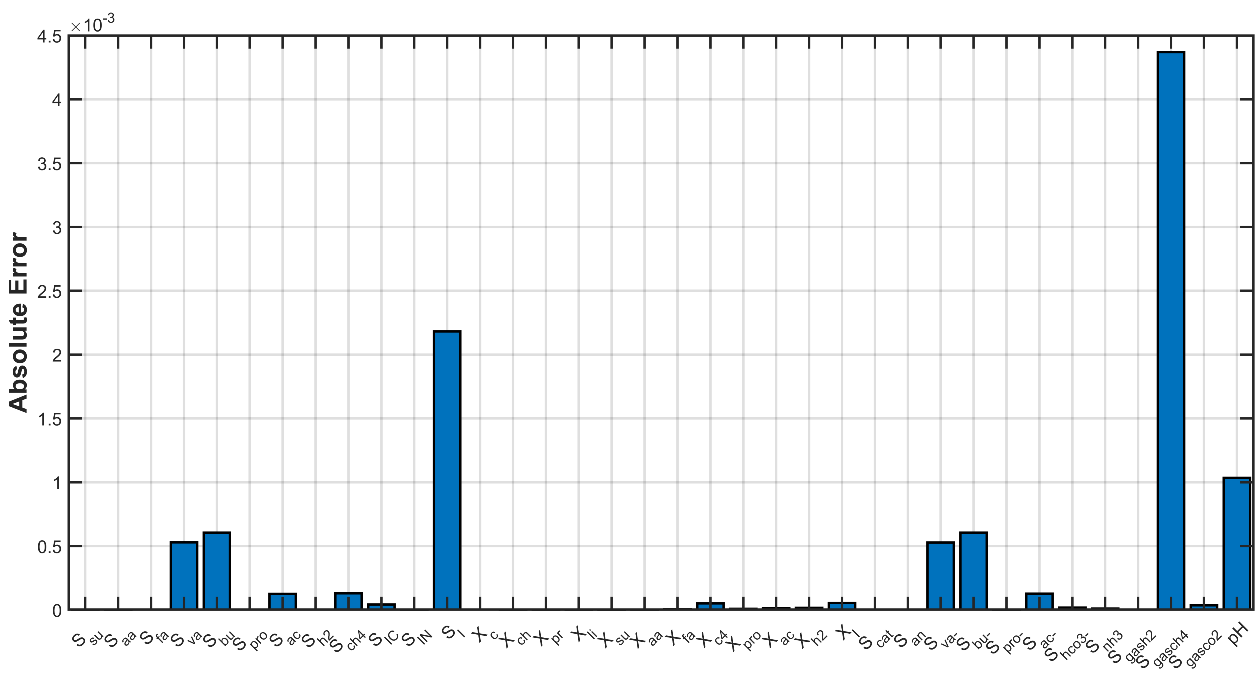

Figure. **4-2**: Steady-state output comparison between Rosen and Jeppsson (2006) and actual model implementation

4.3.2. Operating point: VFAs production enhance

Through a sensitivity analysis, ADM1 input variables were individually modified, without altering parameters, coefficients, and operational conditions stipulated by Rosen and Jeppsson (2006)). It was found that the input variable with the highest effect promoting the VFAs production was S_{an_in} (soluble components anion input) which defines the concentration addition of acidic anions. Figure 3 shows the behavior of the VFAs concentration, together with other key components, when S_{an_in} was modified.

As previously mentioned, S_{cat_in} and S_{an_in} are complementary variables. However, S_{cat_in} still does not modify the system significantly. A disturbance affects the results in Figure **4-3**, however, this variable remained constant and S_{an_in} varied. Lower S_{an_in} values than 0.15 kmol m^{-3} did not affect the system behavior. On the other hand, for higher values, the VFAs concentration increased and methane production decreased. The S_{an_in} value that maximizes the VFAs output concentration was 0.16 kmol m^{-3}, but notice that the system does not stabilize. The fact of increasing the S_{an_in} concentration implies that the H^+ ions concentration increase, causing a decrease in the pH. Besides, as can be seen in Figure **4-3**, and according to the chemical reaction: $H^+ + NH_3 \leftrightarrow NH_4^+$, the increase in H^+ ions causes the charge balance to destabilize, generating ammonium production ($S_{NH_4^+}$), resulting in a decrease in pH. According to the literature, pH has been identified as a the one of the main variables that can modify the behavior, being a critical factor that controls the VFAs production during acidogenic fermentation of the process (Zhou et al., 2018a). Wang et al. (2014) found that butyric acid was the main product under pH 5.0 with the percentage of butyrate above 80 % under anaerobic conditions. Jiang et al. (2013) found that when the pH decreases to 5 in an anaerobic digestion process, acetic acid was the dominant product, followed by butyrate, propionate, and valerate. Likewise, Min et al. (2005) observed in anaerobic digestion a maximum fraction of propionic acid (80 %) at a pH of 6.5.

According to Fukuzaki et al. (1990), methane production from propionic acid is an important intermediate step in the bioconversion of organic matter to biogas. This step is inhibited by the accumulation of H_2. The partial pressure of H_2 must be kept below 10^{-6} to 10^{-4} bar for methane production. If this step is inhibited, it would be expected that propionate and perhaps acetate would accumulate. Figure **4-3** shows an increase in the partial pressure of H_2 (P_{gash2}) above the range stipulated by Fukuzaki et al. (1990) (maximum value of 0.43 bar for S_{an_in}=0.16 kmol m^{-3}), thus being an important factor for the accumulation of VFAs. Also, due to this accumulation of propionic acid, a significant inhibition is generated, causing the concentration of methanogenic bacteria to decrease, and therefore the decrease in methane production (Wang et al., 2009). The accumulation of VFAs is also due to the decrease of the growth of the degrading microorganisms of the VFAs (X_{c4}, X_{pro}, X_{ac}). This is due to an inhibition by pH since micro-organisms are intolerable to acidic conditions.

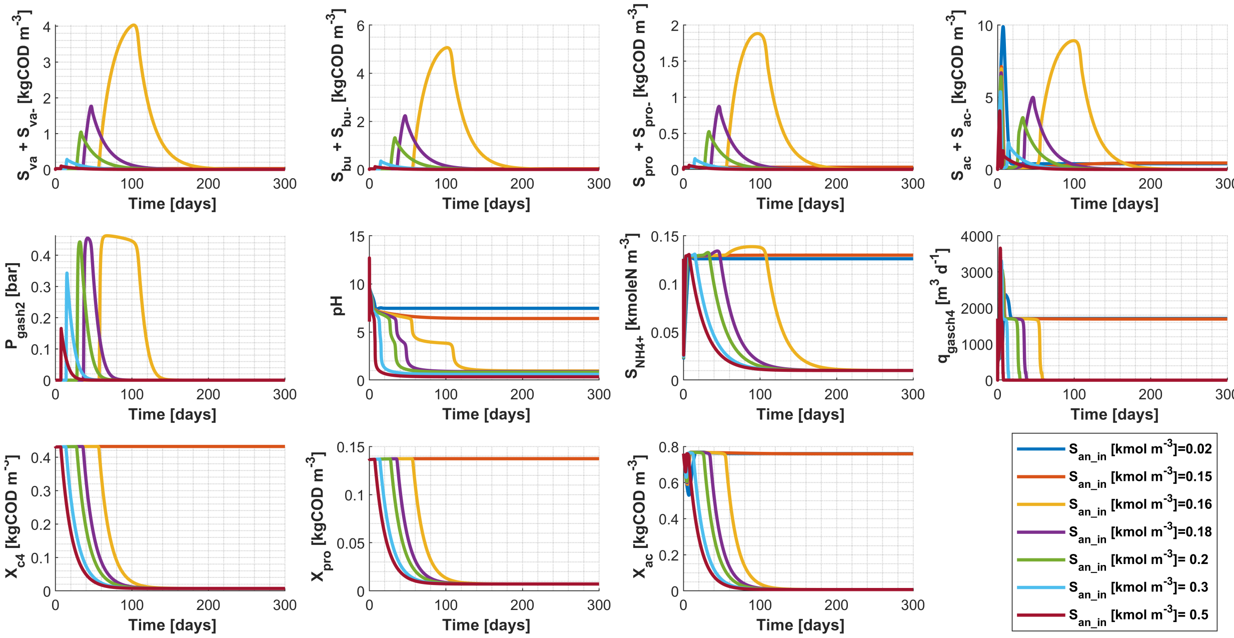

Figure. **4-3**: Sensitivity analysis of the input variable S_{an_in}. Where S_{an_in}=0.02 kmol m^{-3} (nominal value)

As previously mentioned, although an improvement in the VFAs production is observed, the system does not stabilize since it is completely inhibited, mainly due to the dropping pH with ranges from 0.96 to 0.34. That is the reason to implement an open-loop control an stabilize the VFAs production, during the economic optimization, where the manipulated variables were S_{an_in} and S_{cat_in}, are critical variables for the production of VFAs. For this, ADM1 was simulated by changing S_{an_in} from 0.02 to 0.16 kmol m^{-3}. Then, the economic optimizer manipulates S_{an_in} and S_{cat_in} to avoid a drastic pH drop, guarantee the stability of the system and generate the highest economic income from sales of VFAs.

Solving equation 4-1 (economic objective function), the optimal inlet concentration of soluble component cations ($S_{scat\_in\_op}$) was 0.04 kmol m^{-3} (value equal to nominal) while for soluble component anions ($S_{an\_in\_op}$) was 0.0495 kmol m^{-3}. The simulation time to solve the economic optimizer was 28.19 seconds. Finally, ADM1 was simulated with t_{span}=300 days again, by performing a step disturbance from S_{an_in} to $S_{an\_in\_op}$ in a time of 80 days. The disturbance time corresponds to a range of 55 to 108 days (time where the VFAs accumulate), and the choice of the disturbance time within this range did not influence the results. Figure **4-4** shows a comparison between the results of the nominal ADM1 simulation (so called nominal process (S_{an_in}=0.02 kmol m^{-3})), ADM1 simulation when VFAs production is maximum (so called unstable process (S_{an_in}=0.16 kmol m^{-3})), and ADM1 simulation when open-loop control with economic optimizer was implemented (so called optimal process ($S_{an\_in\_op}$= 0.0495 kmol m^{-3})). The implementation of the open-loop control coupled with the economic optimization stabilized the system due to the pH control, avoiding the process inhibition. In both the unstable process and in the optimal process, degraders of VFAs showed the same behavior, suggesting that the inhibition of the system was due to the pH dropping and the accumulation of VFA was caused by the low growth rate of VFAs degraders. The ammonia concentration also stabilized because the generation of H^+ ions is smaller, stabilizing the charges of the aforementioned reaction.

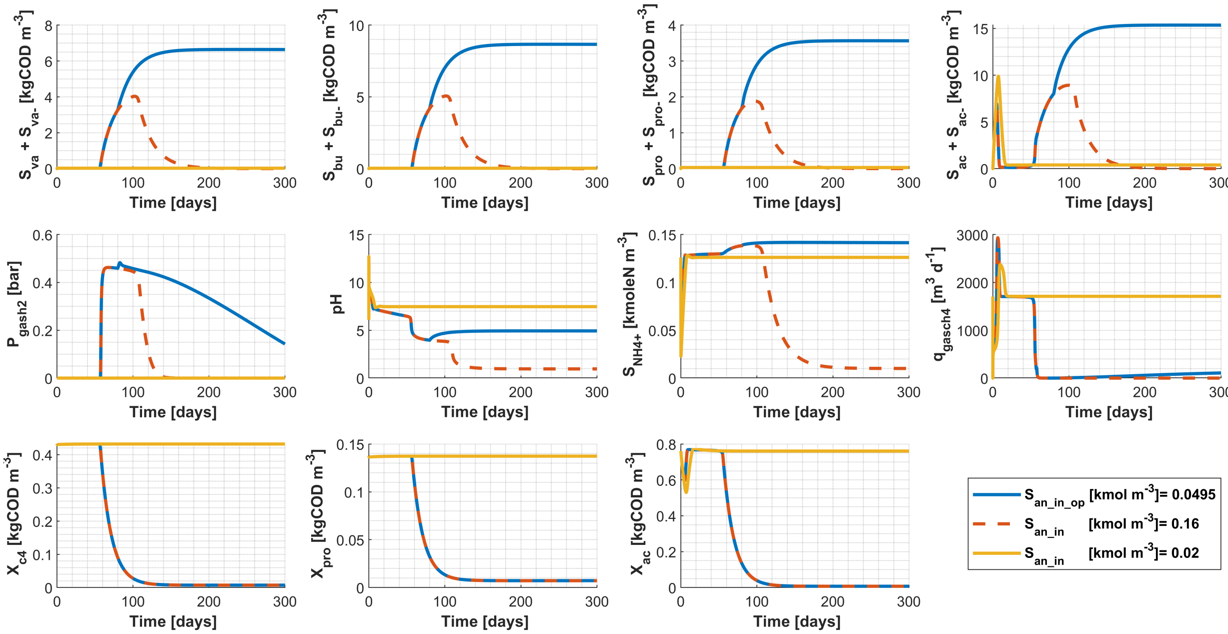

Figure. **4-4**: ADM1 simulations: Nominal (S_{an_in}=0.02 kmol m^{-3}, maximum VFAs production (S_{an_in}=0.16 kmol m^{-3}) and open-loop control with economic optimizer ($S_{an\_in\_op}$= 0.0495 kmol m^{-3}).

In comparison with the simulation with the unstable process, the optimal process obtained a concentration of 34 times larger of total sum of VFAs, which generated a profit of 8800 USD day^{-1} per sale of VFAs. This results was expected since the unstable process is completely inhibited at the steady-state. Regarding the nominal process, the methane production of the nominal process is 16 times greater than that of the optimal process, logical result since the nominal ADM1 model was developed to reproduce biomethane production. Table **4-2** presents the relevant comparisons of results obtained for the nominal process, the unstable process, and the nominal process for the steady-state at a t_{span} of 300 days. Finally, the optimal process was simulated with a t_{span} of 2000 days (steady-state) to obtain the operating point to implement closed-loop control.

Table. **4-2**: Steady-state results comparisons from ADM1 simulations

Parameter	Unit	Nominal process	Unstable process	Optimal process	% Enhancement
S_{an_in}	kmol m^{-3}	0.02	0.16	0.0495	-
S_{cat_in}	kmol m^{-3}	0.04	0.04	0.04	-
Total VFAs	kgCOD m^{-3}	0.478	0.0051	34.217	7058.37
Total VFAs sale	USD day^{-1}	82.317	1.4834	8853.72	10655.64
q_{gasCh4}	m^3 d^{-1}	1709.23	0.000618	107.144	-
pH	-	7.466	0.958	4.929	-

4.3.3. Control structure design

To calculate the state-space model, 35 states (35 ADM1 components from table 3), 36 inputs (35 ADM1 components + q_{in}), and 36 outputs (35 components + pH) were considered. On the other hand, flow rate acts as a disturbance to the system and, as mentioned earlier, the pH as a variable to control due to this is a critical factor that controls the VFAs production during acidogenic fermentation of the process. Through the sensitivity analysis, the pH was corroborated as the critical parameter for the production of VFAs. Based on that, the RGA was limited to 5 input variables that can control pH. From the linear approximation, it is validated that the system is stable and controllable. For this case the RGA is interpreted as the gains of each manipulated input towards the pH, and using the linear system, the RGA matrix obtained is depicted in Table **4-3**.

Table. **4-3**: The relative gain array for ADM1

Controlled variable	Manipulated variables				
	S_{IC_in}	S_{IN_in}	S_{cat_in}	S_{an_in}	q_{in}
pH	1.625x10^{-6}	0.0548	0.481	0.463	1.518x10^{-11}

From Table **4-3** only S_{cat_in} and S_{an_in} present values close to 0.5, while the other variables present a value close to zero, which indicates that the later manipulated variables do not affect the variable to be controlled. Thus, S_{cat_in} and S_{an_in} present a high degree of interaction, having the same effect on the variable to control. This was to be expected since the addition of soluble component anions and cations directly influence the pH in opposite directions. With this, the selected variable to control to maintain the production of VFAs was pH and the manipulated variables were S_{cat_in} and S_{an_in}, two complementary variables that be controlled according to the override control strategy. This strategy involving one constraint variable implemented using a control selector, two PID and one associated input and output.

Once the controlled variable and manipulated variables were identified, disturbances that modify the operating point were determined using a sensitivity analysis. Figure **4-5** shows the accumulated RMSE results for each of the 36 input variables. The variables that presented the highest accumulated RMSEs were X_{pr_in} and X_{ch_in}, indicating disturbances in those variables, have the highest impact on the system pH, thus represent the most difficult control scenario to be further investigated.

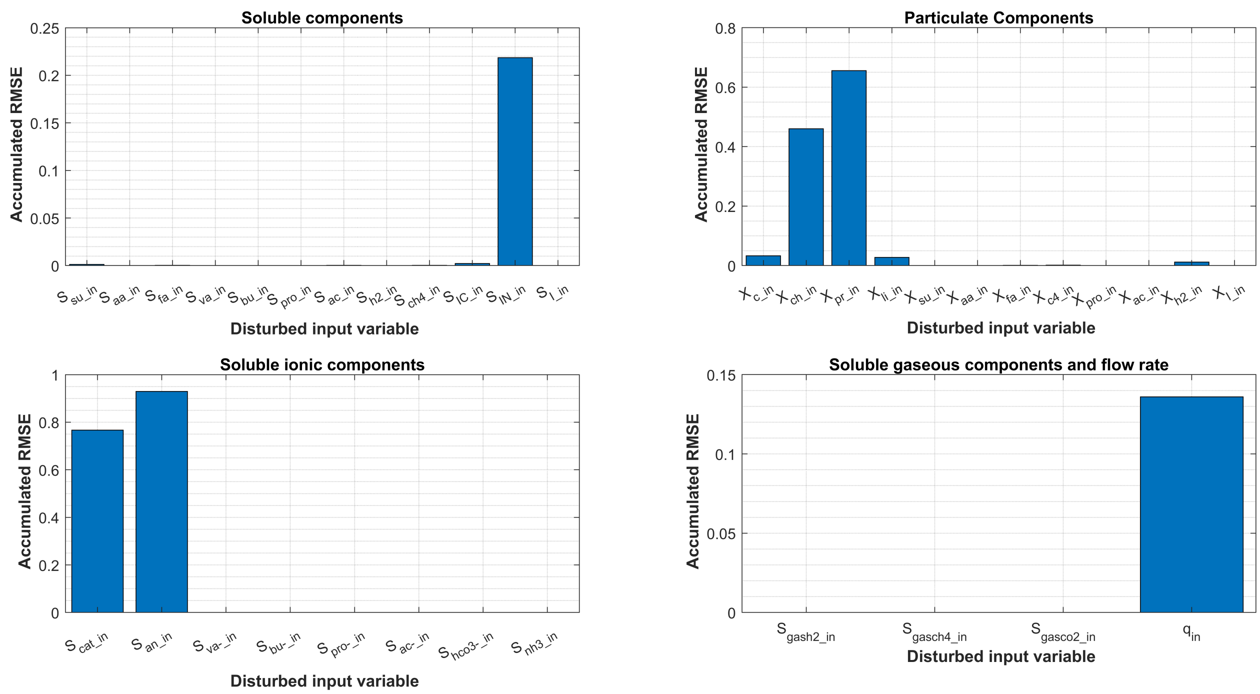

Figure. **4-5**: Accumulated RMSE of disturbance of input variables concerning the pH of the operating point

4.3.4. Hierarchical control structure: real-time optimization layer for closed-loop control

The FOPTD model obtained from the sensitivity analysis is shown in Table **4-4**. The system requires controlling the pH using S_{cat_in} and S_{an_in}, These variables are complementary and to stabilize the system, it is only necessary to add them. Thus, to increase the pH, adding S_{cat_in} is necessary, and to decrease the pH, adding S_{an_in} is necessary. The time constant for the two variables is similar, therefore, the response speed of the process is also similar. With K and t defined, the PID controller settings were estimated. The results are shown in Table **4-5**.

Through the override control strategy, also called selective control, it was possible to implement two controllers (PID1 and PID2) that manipulated the same process. The selection of the controller was determined by the difference between the signal of the variable to control (pH) and the value of the set-point, for which the following constraint was established:

if(set-point pH - signal pH)>1x10^{-10} $\Rightarrow$ PID1 on $\wedge$ PID2 off, else PID1 off $\wedge$ PID2 on

Table. **4-4**: Parameters for FOPTD function

Manipulated variable	K (m^3 $kmol^{-1}$)	τ (day)
S_{cat_in}	6.447	15.99
S_{an_in}	-6.591	16.61

Table. **4-5**: PID controllers settings

Controller	Manipulated variable	P	I	D	α	N
PID1	S_{cat_in}	0.4653	0.0291	0.4653	0.05	20
PID2	S_{an_in}	-0.4552	-0.0274	-0.4552	0.05	20

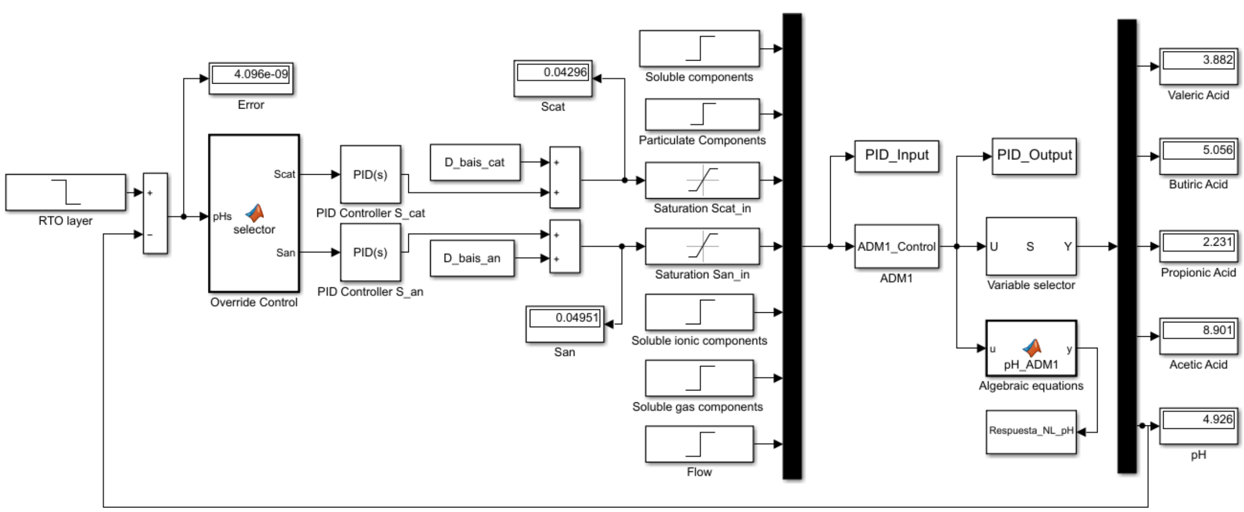

Figure. **4-6**: Simulink® implementation scheme of closed-loop for real-time optimization implementation that enhances VFAs production in anaerobic digestion

The implementation of RTO in the process should ensure maximum profit from the sale of VFAs produced when the system under disturbances. RTO collects the pH measurement from the process, updates the model data, and performs economic optimization using Equation 4-1. As a result, the RTO layer sends new set-points to the control layer to achieve the optimal operating point. A control scheme implemented in Matlab/simulink® of the closed-loop control with the RTO layer can be seen in Figure **4-6**.

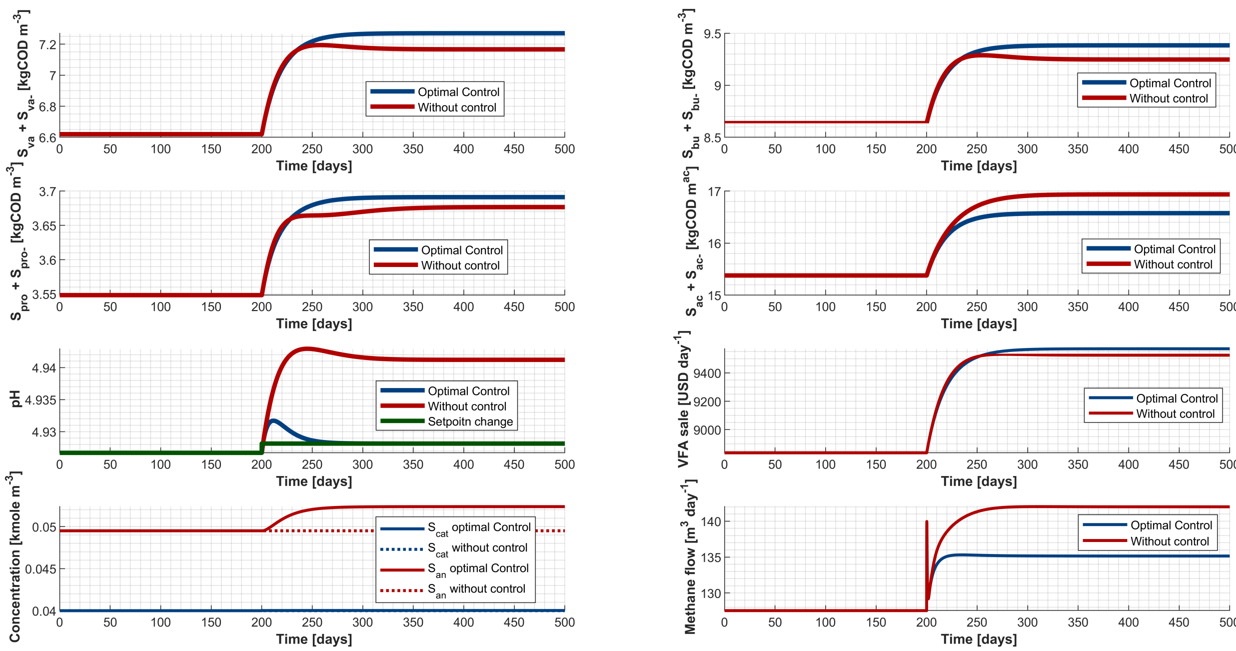

Figure. **4-7**: ADM1 simulation results with and without closed-loop real-time optimization when a step disturbance of 10 % X_{pr_in} was performed

Figures **4-7** and **4-8** show the system response when the optimal control (RTO) was implemented and when it was not. For the positive disturbance, it can be seen that the system benefits from the increase in the concentration of X_{pr_in} since more VFAs are produced and therefore, greater profits concerning the initial operating point. Due to the control structure, process inhibition and unstability are avoided. The results indicate that when the disturbance was performed and the optimal control is not implemented, more total VFAs were produced (37.02 kgCOD m^{-3}) but fewer gains (9524.5 USD day^{-1}) concerning the optimal process (36.92 kgCOD m^{-3} total VFAs and 9569.9 USD day^{-1}). This is because, in the uncontrolled process, more acetic acid is produced, which has the lowest price of the 4 potential VFAs. Acetic acid is the main intermediate of VFAs for the conversion into methane, which also explains the increase in methane flow by 7 m^3 day^{-1} when the control is not applied in the process. The system presented acidification in response to the positive disturbance of X_{pr_in}, with a pH value of 4.941, which decreases 34 % with respect to the nominal value (7,466). To control this, the optimizer determined an optimal operating point where the pH should be kept at 4.928. Thus, according to the override control constraint, the variable to manipulate was S_{an_in} (PID2 on), and an increase in S_{an_in} of 0.0029 kmol m^{-3} was needed to guarantee the highest profit from the sale of VFAs. On the other hand, when the process was disturbed with X_{pr_in} of -10 %, PID1 (manipulated variable S_{cat_in}) was the controller that acted. Although the disturbance did not destabilize or inhibit the process, the response variables decreased. For this case, the optimizer determined the best possible operating point under these conditions. Regarding the uncontrolled process, losses of 783.98 USD day^{-1} were generated, while for the optimal process, losses of 733.14 USD day^{-1} were generated after the system was disturbed.

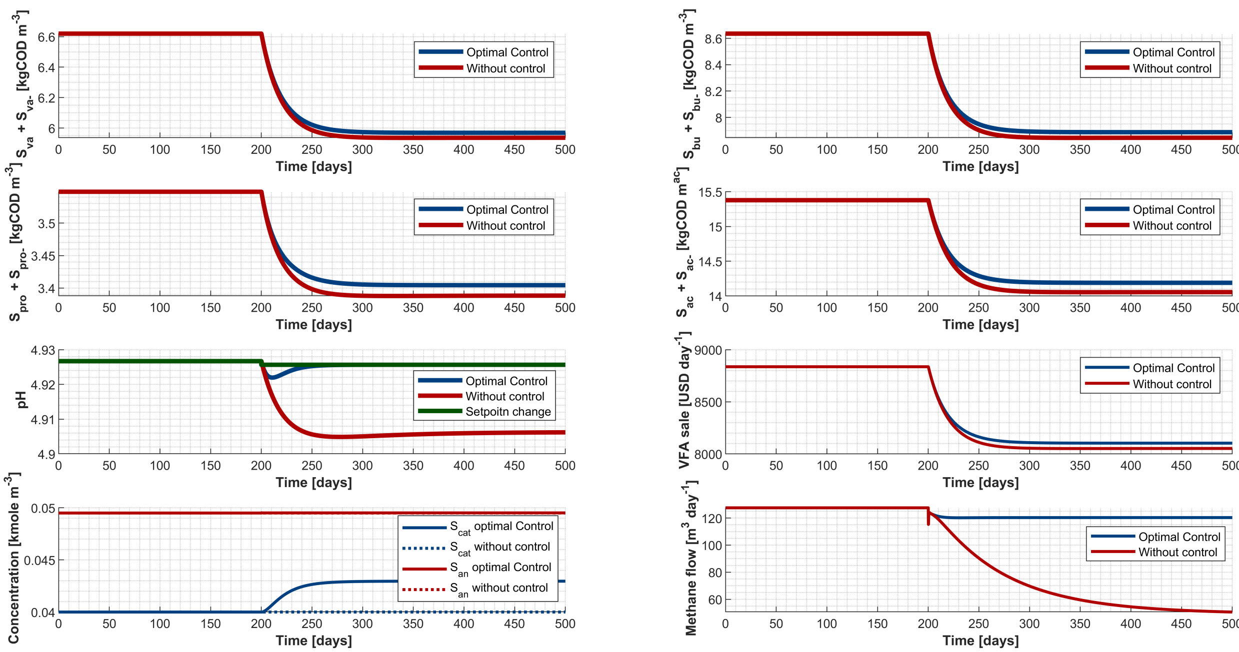

Figure. **4-8**: ADM1 simulation results with and without closed-loop real-time optimization when a step disturbance of -10 % X_{pr_in} was performed

The implementation of the RTO allowed to obatin 0.48 % increase in process profit when the system was disturbed with X_{pr_in} +10 %. On the other hand, 7 % improvement was obtained when X_{pr_in} is disturbed by -10 %. % enhancement refers to the situation with control plus RTO, compared to the situation only with control. For the second disturbance, RTO increased profit by 0.51 % and 0.54 % for X_{ch_in} disturbances of +10 % and -10 %, respectively. From both scenarios, it can be seen that it is worth implementing RTO when the disturbance is negative, since the percentage of improvement is greater when it is positive, and generating the least possible loss of income. Significant results are observed when X_{pr_in} is disturbed, the disturbance of the other variables is negligible.

4.4. Conclusions

A real-time optimization closed-loop with ADM1 as a test platform to improve VFAs production was implemented. The ADM1 implementation was carried out in Matlab/Simulink®. ADM1 model results were verified with the results of Rosen and Jeppsson (2006). Through sensitivity analysis, S_{an_in} and S_{cat_in} were the most important variables that enhance VFAs production and inhibited methane production, obtaining a value of S_{an_in}=0.16 kmol m^{-3} (S_{cat_in} remained constant). To stabilize the system, an open-loop control was implemented with an economic optimizer. It was determined that a disturbance of $S_{an\_in\_op}$= 0.0495 kmol m^{-3} in 80 days, allowed VFAS production that generated maximum profit corresponding to de optimal operation condition. The results showed that the production of total VFAs about the nominal ADM1 model increased from 0.478 kgCOD m^{-3} to 34.217 kgCOD m^{-3}, generating economic incomes of 8853.72 USD day^{-1} from sales of VFAs.

To implement the closed-loop control at the operating point, the state-space model was calculated. Using the RGA, the variable to control was the pH and the manipulated variables were S_{an_in} and S_{cat_in}. Through a disturbance analysis, X_{pr_in} was the variable with the highest effect on the process behavior with an accumulated RMSE of 0.65. An override control strategy was implemented with two PID1 and PID2 controllers and a selector, where the first manipulates S_{cat_in} and the second manipulates S_{an_in}, to control the pH. Finally, RTO layer was implemented in the control process to find the optimum operating point (pH set-point) that maximizes the economic profit from the sale of VFAs, in response to disturbances step by $\pm 10\,\%$ of X_{pr_in}. The RTO layer allowed up to $7\,\%$ increase on process profit. This low value could decrease the interest to have a complex control structure, however, for a larger scale this value is significant. Other input disturbances should be investigated that could generate the need of an RTO on the top of the control structure. Finally, the implementation of this control system could provide theoretical guidance for practical applications and the development of control strategies that allow promoting the production of VFAs through the anaerobic digestion process.

Nomenclature

	No	Components	Descriptions	Unit
Soluble components	1	S_{su}	Monochaccharides (sugars)	kgCOD m^{-3}
	2	S_{aa}	Amino acids	kgCOD m^{-3}
	3	S_{fa}	Fatty acids	kgCOD m^{-3}
	4	S_{va}	Total valerates	kgCOD m^{-3}
	5	S_{bu}	Total butyrates	kgCOD m^{-3}
	6	S_{pro}	Total propionates	kgCOD m^{-3}
	7	S_{ac}	Total acetate	kgCOD m^{-3}
	8	S_{h2}	Hydrogen gas	kgCOD m^{-3}
	9	S_{ch4}	Methane gas	kgCOD m^{-3}
	10	S_{IC}	Inorganic carbon	KmolC m^{-3}
	11	S_{IN}	Inorganic nitrogen	kmolN m^{-3}
	12	S_{I}	Soluble inerts	kgCOD m^{-3}
Particulate Components	13	Xc	Composites	kgCOD m^{-3}
	14	X_{ch}	Carbohydrates	kgCOD m^{-3}
	15	X_{pr}	Protein	kgCOD m^{-3}
	16	X_{li}	Lipid	kgCOD m^{-3}
	17	X_{su}	Sugar degraders	kgCOD m^{-3}
	18	X_{aa}	Amino acids degraders	kgCOD m^{-3}
	19	X_{fa}	Fatty acids degraders	kgCOD m^{-3}
	20	X_{c4}	Valerate and Butyrate degraders	kgCOD m^{-3}
	21	X_{pro}	Propionate degraders	kgCOD m^{-3}
	22	X_{ac}	Acetate degraders	kgCOD m^{-3}
	23	X_{h2}	Hydrogen degraders	kgCOD m^{-3}
	24	X_{I}	Particulate inerts	kgCOD m^{-3}
Soluble ionic components	25	$_{cat}$	Soluble component cations	kmol m^{-3}
	25	S_{an}	Soluble component anions	kmol m^{-3}
	27	S_{va-}	Soluble component valerate ions	kgCOD m^{-3}
	28	S_{bu-}	Soluble component butyrate ions	kgCOD m^{-3}
	29	S_{pro-}	Soluble component propionate ions	kgCOD m^{-3}
	30	S_{ac-}	Soluble component acetate ions	kgCOD m^{-3}
	31	S_{hco3-}	Soluble component hydrogen carbonate	KmolC m^{-3}
	32	S_{nh3}	Soluble component ammonia ions	kmolN m^{-3}
Soluble gaseous components	33	$S_{gas,h2}$	Soluble component hydrogen gas	kgCOD m^{-3}
	34	$S_{gas,h2}$	Soluble component methane gas	kgCOD m^{-3}
	35	$S_{gas,co2}$	Soluble component carbon dioxide gas	KmolC m^{-3}

Nomenclature

	No	Components	Descriptions	Unit
Process operating conditions	36	T_{op}	Operation temperature	°C
	37	q_{in}	Flow rate	m3 day^{-1}
	38	P_{atm}	Atmospheric pressure	bar

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5 Conclusions and Recommendations

5.1. Conclusions

This thesis evaluated and analyzed the anaerobic digestion process from a techno-economic point of view under the circular economy philosophy. For this, experimental assays focused on the methane production of food waste from Colombia were carried out. A comparison of the economic viability of the process for the production of methane and platform products such as VFAs was performed. Finally, by using Anaerobic digestion model No 1 (ADM1), a closed-loop control system was implemented with a real-time optimization layer that enhances the production and the maximum possible economic profits from the sale of VFAs under input disturbances.

The experimental part of this thesis focused on characterization food waste from the department of Nariño-Colombia and the evaluation of the methane production through the anaerobic digestion process. The purpose of this study was to evaluate the potential for organic waste reuse for the renewable energy production, identifying properties of the substrate such as Carbon/Nitrogen ratio, Volatile Solids (VS) and Total Solids (TS), proximate analysis and ultimate analysis, which provide relevant information for waste management. Likewise, the experimental assays contributed to the understanding of the performance of the digestion process of these wastes by monitoring process variables such as VS/TS ratio, pH, temperature, removal of soluble COD, biogas production and methane concentration. The results obtained show that local food waste has great potential for the renewable energy production, suggesting that the application of this technology can contribute and encourage sustainable development, providing social, economic and environmental solutions.

The economic comparison of the production of biomethane and VFAs from the anaerobic digestion of food waste, found a different perspective of the digestion process, since it was proven that orienting the process towards the production of VFAs may be more economically viable than the process oriented to the generation of biogas. From this, the digestion process could be classified as a profitable and lucrative process. The results of this study identified that the main reason why VFAs production is economically viable was mainly due to the low hydraulic retention time (HRT), lower reactor volume and high sales price of VFAs. Additionally, by implementing this economic study in the Colombian context, a circular economy in underdeveloped countries is promoted, generating new business perspectives that in turn provide a response to current problems derived from non-renewable energies, such as environmental pollution and limited availability of resources.

The special focus of this thesis was the simulation and modeling of the anaerobic digestion process, towards on improving the production of VFAs. The implementation of ADM1 was a platform that allowed to understand the dynamic behavior of the anaerobic digestion process and, through its manipulation, scenarios to obtain products of interest could be estimated an evaluation of techno-economic viability incorporating a real-time optimization layer closed-loop control. The results of this investigation showed that it is possible to maximize the production of VFAs by controlling the pH of the process, being a variable governed by the concentrations of cations and anions in the system. The developed control computational platform brings good perspectives to simulate various scenarios, such as different control strategies, with and without the real-optimization layer as well, allowing the study of various scenarios of the anaerobic digestion process. The proposed control structure can help VFAs production investigations through anaerobic digestion, to operate optimally and to achieve the highest possible economic benefit.

5.2. Recommendations

Through the cases studied in this thesis, it was possible to identify problems and situations that can promote further research:

- In the Biochemical Methane Potential (BMP) assays, it was not possible to quantify the VFAs concentration. The monitoring of these properties can identify the phases of the digestion process, as well as the performance of these products can serve as an input variable for the implemented economic model.
- In the sacrifice bottle assay, methane production was not measured continuously. Factors such as access to the setup of the experiment prevented this activity from being carried out. Measurement of this variable can make the results from this assay comparable with the results of the on-line methane measurement assay.
- According to the experimental assays, it is recommend to degas the inoculum for 20 days and measure the gas production of the bottles every 5 hours for the first two days.
- The recommended method to determine the amount of nitrogen is the TKN method, because it measures biodegradable nitrogen, however, this measurement can be faster and more reliable using the methodology described in this research.
- It is suggested to validate the methane concentration measurement reported by the Yieldmaster equipment with a gas chromatography measurement of the same sample,

since values greater than 70 % v/v of methane are very unlikely.

- For the economic evaluation, methane production and VFAs production parameters from the literature were used. The economic study with local values could not be carried out, because the VFAs yield was not quantified (only the quality of the biogas was used) in the experimental assays. It is recommended to implement the economic model with these results to evaluate of the feasibility of these processes in Colombia.
- Substrate pretreatment costs, tools and equipment such as solid/liquid separator pipes, conduits, pumps, mixers, among others, were not taken into account in the economic model, because the study was a first approximation to give an overview of the process. The reason for this was due to the lack of information in the literature. It is suggested to carry out a process scheme with more equipment and tools to obtain more accurate results.
- In the techno-economic analysis, it is recommended to carry out a sensitivity analysis in terms of variability once the performance data of the anaerobic digestion products are available in the local context.
- In a more rigorous analysis of the comparison and economic evaluation of the products generated in the anaerobic digestion process, it is recommended to include unit processes and operations that contemplate the pretreatment of waste, such as: pumps, valves, compounds separation stage with low biodegradability, crushing stage, and stage of disposition of low biodegradability compounds and biol.
- An ideal separation of the interest products (biomethane and VFAs) was determined, in order to find the maximum economic profitability of the processes. It is recommended to use real values that determine the purification or separation of the products.