



Design of Biorefineries from Lignocellulosics Through The Use of Thermodynamic Concepts

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*“A mi mamá y mi hermana por todo su
apoyo y compañía durante todo este
camino”*

*“Hay una fuerza motriz más poderosa que
el vapor, la electricidad y la energía
atómica: LA VOLUNTAD”*

Albert Einstein

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Christian David Botero G., **Daissy Lorena Restrepo S.**, and Carlos Ariel Cardona A., “A comprehensive review on the implementation of the biorefinery concept in biodiesel

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Microalgae. In: United States. ISBN: 978-3-319-69093-3 Ed: Springer Publishing Company, pp. 181 - 200, 2018

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Daissy Lorena Restrepo Serna, Juan Carlos Higueta Vasquez, Carlos Ariel Cardona Alzate, "Energy and Economic Challenges in the Growth and Harvesting of Microalgae, the Chlorella vulgaris Case" Recent advances in renewable energy. Volume 1. Microalgae as a source of Bioenergy: Products, processes and economics. In: United Arab Emirates ISBN: 978-1-68108-523-4 Ed: Bentham Science Publishers pp. 332 - 351, 2017

Conference papers

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Jimmy Andres Martinez Ruano, **Daissy Lorena Restrepo S.**, Estefanny Carmona García, Carlos Ariel Cardona A. Effect of co-digestion of milk-whey and potato stem on heat and electricity generation using biogas as an energy vector. Event: NAXOS 6th International Conference on Sustainable Solid Waste Management, 2018.

Daissy Lorena Restrepo S., Jimmy Andres Martinez Ruano, Carlos Ariel Cardona A. Energy Efficiency of Biorefinery Schemes Using Sugarcane Bagasse as Raw Material. Event: NAXOS 6th International Conference on Sustainable Solid Waste Management, 2018.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Mariana Ortiz S., Carlos Ariel Cardona A. Determination of extraction kinetics of bioactive compounds from spent coffee grounds. Event: ATHENS 2017 5th International Conference on Sustainable Solid Waste Management, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Evaluation of metabolites extraction from lignocellulosic waste of tomato tree. Event: 10th World Congress of Chemical Engineering, 2017.

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Daissy Lorena Restrepo S., Ashley Sthefanía Caballero G., Mariana Ortíz S., Carlos Ariel Cardona A. Fermentación etanólica a partir de zoca, mucílago y borra de café. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017.

2. Poster

Daissy Lorena Restrepo Serna, Juan Camilo Solarte Toro, Juan Miguel Romero García, Encarnación Ruíz Ramos, Eulogio Castro, Carlos Ariel Cardona Alzate. Exergy analysis of different bioethanol production schemes using olive tree pruning as raw material. Event: Donostia – San Sebastian, Spain International Conference on Material & Energy. 2018

Daissy Lorena Restrepo S., Ashley Sthefanía Caballero G., Christian David Botero G., Carlos Ariel Cardona A. Energetic, techno-economic and environmental analysis of a biorefinery from sugarcane bagasse at different scales. Event: ATHENS 2017 5th International Conference on Sustainable Solid Waste Management, 2017.

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Jimmy Anderson Martinez R., Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Techno-Economic and environmental evaluation for the biogas production from banana peel in a biorefinery concept (*Musa paradisiaca*). Event: ATHENS 2017 5th International Conference on Sustainable Solid Waste Management, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Analysis of schemes of products of value-added products from naranjilla (*Solanum quitoense*): Colombia case. Event: 10th World Congress of Chemical Engineering, 2017.

Daissy Lorena Restrepo S., Ashley Sthefanía Caballero G., Carlos Ariel Cardona A. Análisis de exergía en esquemas de biorrefinerías basadas en el bagazo de caña de azúcar y zoca de café. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Evaluación de esquemas de biorrefinerías a partir de borra de café. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Aprovechamiento de residuos cítricos para la obtención de pectina: caso stand alone y caso biorrefinerías a diferentes escalas. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Carlos Ariel Cardona A. Cinética de extracción de metabolitos a partir de cáscara de lulo. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017.

Ashley Sthefanía Caballero G., **Daissy Lorena Restrepo S.**, Mariana S., Carlos Ariel Cardona A. Influencia de tecnologías convencionales y no convencionales en la producción de biodiesel. Event: Congreso Colombiano de Ingeniería Química y Profesiones Afines, 2017

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Universidad Nacional de Colombia, Manizales campus. “*Biorefinería para el tratamiento de residuos cítricos – CPW Biorefinery*” 2017. Eranet Lac Project

Universidad Nacional de Colombia, Manizales campus “Modelo de Plataforma de Aprovechamiento Integral, Adición de Valor y Competitividad de Frutales Comerciales Andinos” 2016. Proyecto Fontagro BID

Resumen

Las biorefinerías son procesos que involucran un alto número de etapas de procesamiento con el objetivo de obtener tanto un producto químico o un producto energético. En muchos casos, las biorefinerías solo son analizadas desde los ámbitos técnico, económico, ambiental y social, dejando de lado la parte energética del proceso. Sin embargo, a partir de un análisis energético del proceso es posible conocer el fenómeno que involucra cada etapa de procesamiento unidad por unidad. Así, es posible conocer el aprovechamiento energético que presenta una determinada materia prima en función de los productos obtenidos a partir de esta. Mostrando así que el aprovechamiento del potencial energético de una materia prima va a estar relacionado con la ruta de transformación seguida.

Mediante el empleo de conceptos termodinámicos tales como la exergía es posible identificar los principales cambios energéticos que ocurren etapa por etapa. La exergía involucra dentro de su cálculo el análisis de los cambios tanto físicos como químicos a los cuales es sometida una materia prima en un proceso. Permitiendo identificar de este modo las causas de los cambios presentados, así como su ubicación dentro del proceso.

El objetivo del presente trabajo es aplicar el cálculo de la exergía a diferentes procesos, principalmente biorefinerías. Permitiendo de este modo identificar la influencia que presenta la ruta de transformación seleccionada en un proceso complejo como las biorefinerías, así como la influencia tanto de la tecnología como de la materia prima empleada. Para esto fueron planteados diferentes casos de estudio a partir de procesos de simulación: en primer lugar, fue analizada la influencia de la tecnología de extracción de compuestos polifenólicos a partir de cascara de tomate de árbol. Para este caso fueron

consideradas la extracción con solvente y la extracción con fluidos supercríticos. En segundo lugar, fue analizada la obtención de etanol a partir de yuca (material amiláceo) y bagazo de caña de azúcar (material lignocelulósico). Por último, fueron evaluados diferentes escenarios de biorefinerías las cuales emplearon el bagazo de caña de azúcar como materia prima.

Palabras clave: *Biorefinería, Análisis exergético, Análisis energético, Bagazo de caña de azúcar*

Abstract

Biorefineries are processes that involve a variety of processing steps to obtain both a chemical and an energy product. In many cases, biorefineries are only analyzed from a technical, economic, environmental and social point of view, while the energy part of the process is not taken into account. However, from an energy analysis of the process it is possible to know the phenomenon that involves each stage of processing unit by unit. Thus, it is possible to know the energy use of a given raw material according to the products obtained from it. Thus showing that the exploitation of the energy potential of a raw material will be related to the transformation route followed.

Through the use of thermodynamic concepts such as exergy it is possible to identify the main energy changes that occur step by step. The exergy involves in its calculation the analysis of both physical and chemical changes to which a raw material is subjected in a process. In this way, the causes of the changes presented can be identified, as well as their location inside the process.

The purpose of this work is to apply the exergy calculation to different processes, mainly biorefineries. In this way, the influence of the selected transformation route on a complex process such as biorefineries can be identified, as well as the influence of both the technology and the raw material used. For this purpose, different case studies were presented from simulation processes: first of all, the influence of the technology of extraction of polyphenolic compounds from tree tomato peel is analyzed. Solvent extraction

and supercritical fluid extraction were considered in this case. Second, ethanol production from cassava (starchy material) and sugarcane bagasse (lignocellulosic material) are analyzed. Finally, different biorefinery scenarios are evaluated using sugar cane bagasse as raw material.

Keywords: *Biorefinery, Exergy assessment, Energy assessment, Sugarcane bagasse*

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Nomenclature

C_p	Heat capacity	Ex_Q	Exergy flow associated with a heat flow
Ex^{ch}	Chemical exergy	$Ex_{raw\ material}$	Exergy associated with the raw material
ex_i^{ch}	Specific chemical exergy	$Ex_{reagents}$	Exergy associated with the reagents
Ex_{des}	Exergy destroyed	Ex_W	Exergy flow associated with a work
Ex_{flow}	Exergy associated with a mass flow	Ex_{wastes}	Exergy associated with the wastes
Ex_{in}	Exergy input	Gf°	Standard Gibbs free energy
Ex^{ki}	Kinetic exergy	h_i	Enthalpy flow
Ex_{loss}	Exergy loss	h_o	Enthalpy flow of reference
Ex_{out}	Exergy output	n_i	Molar flow for the component i
Ex^{ph}	Physical exergy	P	Pressure
ex_i^{ph}	Specific physical exergy	P_o	Reference pressure
Ex^{po}	Potential exergy	R	Ideal gas constant
$Ex_{product}$	Exergy associated with the product	s_i	Entropy flow

s_o	Entropy flow of reference	$\Psi_{pro/RM}$	Exergy efficiency between products and raw material
T_j	Operation temperature		
T_o	Reference temperature	$\Psi_{prod/RM+rea}$	Exergy efficiency between products and the sum of raw material and reagents
x_i	Molar fraction		
W	Work into state 1 to 2	$\Psi_{prod+w/RM+rea}$	Exergy efficiency between products and wastes and the sum of raw material and reagents

Hypothesis

From the analysis of energy efficiency and, more precisely, from the calculation of exergy, it is possible to establish the best transformation routes for complex processes such as biorefineries.

Objectives

General objective

Evaluate through thermodynamic concepts making emphasis in the exergy and the energetic efficiency of a biorefinery based on lignocellulosic materials.

Specific objectives

1. To design biorefineries for the use of lignocellulosic materials derived from sugar cane (sugar cane bagasse) using different technologies.
2. To implement an exergy calculation methodology based on the balances of mass and energy developed in Aspen plus software.
3. To evaluate the exergetic yield of the process
4. To evaluate the exergetic efficiency step by step of the biorefineries.
5. To evaluate and compare the proposed biorefineries exergetically, energetically, technically, economically and environmentally.

Introduction

The continuous study of science through time has made possible for man to understand the universe through the application of principles or laws, which allow him to understand concepts such as energy. In the course of time, the man has developed processes in which transformations of the material into energy and other products are carried out. This has promoted industrial development without considering the repercussions of the irrational use of resources supplied by the planet. Nowadays, man is thinking about the design of efficient processes not only from the point of view of design, but also from the energy point of view.

One of the variables to be considered in process design is energy, especially when considering large-scale processes such as biorefineries in which different raw material transformations are carried out. Considering the great impact that biorefineries have on the environment, especially in the use of waste, it is of great interest to carry out studies that allow to know and identify the different areas of the process in which the main energy changes are carried out (Sadhukhan, Siew Bg, & Martinez Hernandez, 2014).

Through thermodynamics it is possible to derive about the phenomenon that involves each process unit. In processes involving a large number of units, it allows to establish what happens step by step. For this purpose, it is necessary to know the energy input and output characteristics or, given the case of generation in each of the equipment involved in the production process (Nishio, Itoh, Shirolu, & Umeda, 1980). Not only is it important to analyze energy, but also to establish strategies that allow to identify the changes that have occurred besides energy, such as exergy (Ojeda & Kafarov, 2009; Soheli & Jack, 2011). This last analysis is based on the Second Law of Thermodynamics, providing more information in comparison with the energetic analysis. Being that energy is conserved or transformed, while the exergy can be destroyed, and this destruction is quantifiable (irreversibilities).

On the basis of these energy analyses and especially of exergy, it is possible to identify the process areas in which the main energy changes occur. This allows to take measures in order to obtain the maximum yield in terms of conversion or separation processes and above all, the energy efficiency involved in each step. Among these measures, changing the technology being used is an option (Emets, Hoo, & Mann, 2006). For this purpose, impact assessments of each technology must be carried out, consequently, comparisons

must be made between obtained yields, environmental impacts (Ruiz-Mercado, Smith, & Gonzalez, 2012; D. M. Young & Cabezas, 1999) and economic impacts.

Thus, from a thermodynamic analysis, it is possible to determine: the yield that can be obtained in a process, the residence times and the volume of each reactor, therefore obtaining a total process time (Sin, Woodley, & Gernaey, 2009). Another factor that can be obtained from these analyses is the amount of energy involved in the process, and as by means of knowledge of properties such as the energy of a stream, it is possible to determine a method that allows the use of this as maximum as possible, thus allowing a reduction in the energy costs of the process.

Therefore, this paper proposes the inclusion of an energy and exergetic analysis, in addition to the traditional (technical, economic and environmental) analysis of processes. For this purpose, the transformation of a lignocellulosic residue such as sugar cane bagasse into different products was studied under stand-alone processes and under the concept of biorefinery. In stand-alone processes, the influence of both processing technology and separation technology for ethanol and polyphenolic compounds was evaluated. For the biorefineries, the differences associated with the implementation of a transformation route were studied.

1. Chapter 1: Theoretical context

Thermodynamics is understood as the science assigned to the study of energy, the processes in which it takes place, in other words, to study the changes of energy that can occur or more precisely, the transformations that energy is subjected to in a process (M.A. Rosen & Dincer, 2003). On the other hand, thermodynamics is also attributed to the study of how energy can be used to improve the quality of life of people. The efficient use of natural and renewable energy sources is one of the most important topics for the technical, political and environmental sectors in the 21st century (Balmer & Balmer, 2011).

In a most general sense, thermodynamics can be defined as the science of energy and exergy that includes a series of concepts such as temperature, pressure, enthalpy, heat, work, energy and entropy. Under this definition, only the first and second laws of thermodynamics are considered, in which the first law of thermodynamics is responsible for the analysis of energy, the identification of energy changes and losses. For an analysis of efficient use of resources, the second law is the most useful in this sense, given that this law is formulated in terms of exergy, taking into consideration entropy by including irreversibilities (M.A. Rosen & Dincer, 2003).

1.1. Energy concept

The creation of energy as a concept has its origins in the "*vis viva*" of Huygens, which was introduced in 1669, but only until the beginning of the XX century, was when a concept of energy was established (Solbes & Tarín, 2008).

The concept of energy will depend on the field in which it is applied. Namely, whether it is the term for everyday use or a term referring to a science such as physics. Thus in the physical sense, energy can be defined as a scalar quantity, which cannot be directly observed. However, this can be evaluated from measurements in which an energy change is registered. This indicates the capacity of a body or system to carry out transformations, regardless of whether they occur or not (Ibrahim Dincer & Rosen, 2013; Moran & Shapiro, 2004).

Among the lessons that can be learned from thermodynamics and more precisely its relationship with energy is that, as more processing steps are involved in carrying out a transformation, the amount of energy consumption in the process will increase. In this

sense, dividing a step into several sub-steps tends to be ineffective from the energetic point of view, but from the organizational point of view, it can be very effective (Valero & Martínez, 2003).

1.2. Exergy concept

From the point of view of thermodynamics, exergy can be understood as the maximum amount of work that can be produced by a system or a flow of mass or energy, when it achieves a thermodynamic equilibrium with the environment (Ibrahim Dincer, 2002; Tsatsaronis, 2007). Unlike energy, exergy is not subject to a conservation law, that is, with the exception of ideal or reversible processes. Hence, exergy can be consumed or destroyed, due to the irreversibilities that occur in whichever real process. The consumption of exergy during a process is proportional to the entropy generated by the irreversibilities associated with the process (Ibrahim Dincer, 2002). The total exergy of a system consists of kinetic, potential, physical and chemical exergy (Tsatsaronis, 2007). The kinetic term is attributed to the speed of the system measured in relation to the environment. The potential exergy depends on the height of the system measured in relation to its environment. The physical exergy be subject to on the deviation of temperature and pressure of the system from its environment. Physical exergy is composed of mechanical exergy, which is associated with system pressure and thermal exergy, which is related to the system temperature. (Tsatsaronis, 2007). The chemical exergy correlated the deviation of the chemical composition of the system from its environment. This can be divided into reactive and non-reactive exergy. The first bases the calculation on the chemical reactions, while the second one is associated with reactive processes such as expansion, compression, mixing and separation (Tsatsaronis, 2007).

The division of physical and chemical exergy into its components could be useful in defining exergetic efficiency more precisely and, on the other hand, in improving the costing approach (Tsatsaronis, 2007).

1.2. Relationship between energy and exergy

From the point of view of thermodynamics, exergy can be understood as the maximum amount of work that can be produced by a system or a flow of matter or energy, since it

reaches a balance with a reference environment (Marc A. Rosen, Dincer, & Kanoglu, 2008). The main difference in respect to energy is that energy is subject to a conservation law, whereas exergy is consumed or destroyed in relation to the creation of entropy due to the irreversibilities of the process (A. K. Pandey, Chandra Pant, Sastry, Kumar, & Tyagi, 2015; M. a Rosen & Dincer, 2001). **Table 1-1** lists the main differences between energy and exergy.

Table 1-1. Differences between Energy and Exergy (Ibrahim Dincer & Rosen, 2013; Moran & Shapiro, 2004; Göran Wall, 2010)

Energy	Exergy
Depends only on parameters such as the material or energy flow in question, whereas it is independent of the environment parameters	Depends on both material and energy flow parameters and environment parameters
It has values different from zero. It can be calculated from the Einstein equation $E=mc^2$	It is equal to zero in a dead state by equilibrium with the environment
All processes are based on the first law of thermodynamics	For reversible processes it is based on the first law of thermodynamics. For irreversible processes it is partially or totally destroyed
For all processes it is limited by the second law of thermodynamics	Due to the second law of thermodynamics it is not limited only to reversible processes
It is defined as movement or the ability to produce it	It is a measure of work or the ability to generate it
In a process it is always conserved, so it cannot be created or destroyed	In reversible processes it is always conserved, unlike irreversible processes in which it is always consumed
It is a measure of quantity	It is a measure of quantity and quality due to entropy

1.3. Energetic and exergetic efficiency

Energy analysis is a method that combines the principles of mass and energy conservation with the second law of thermodynamics, for the analysis, design and improvement of the energy of the systems analyzed. The exergy method is a useful tool for achieving the objective of more efficient use of energy resources, since it allows the determination of the location, identification of the types and magnitudes of waste or losses that may occur in a process (Molina, Vidal, & Gonzalez, 2017). In general, efficiency can be evaluated from the concept of exergy, since it allows a more realistic view of what really happens with energy within a process. Therefore, the exergy analysis can show if it is possible to design a more efficient process by reducing the inefficiencies that can occur.

Comparing these two types of analyses, it is found that exergetic analysis provides more realistic results. Therefore, it provides more relevant information in evaluating system yields (Marc A. Rosen, 2002a, 2002c). The advantages of exergetic analysis include (Marc A. Rosen, 2002b):

- Exergetic analyses provide information about the loss of exergy, while providing information about the location, cause and sources of deviations from idealism that may occur.
- In systems in which more than one product is presented, this type of analysis helps to evaluate the thermodynamic values of each product.
- Methods based on the analysis of exergy have been developed which can become a useful tool in the design of processes.

The exergetic yield analysis not only determine magnitudes, location and causes of process irreversibilities, but also provides a more significant assessment of the efficiency of individual plant components. These points of exergetic analysis are the basic differences of energy analysis. Therefore, it can be considered that exergetic analysis and energy analysis together can provide a complete idea of system characteristics. Such a large analysis will be a more practical method of evaluation of performance and determining the steps towards improvement (Ganapathy, Alagumurthi, Gakkhar, & Murugesan, 2009; Rose, 2001).

Energy efficiency refers to the search for minimum energy use to produce the same amount of services (Patterson, 1996). Efficiency is one of the terms most commonly used in thermodynamics, and indicates just how well an energy conversion or process is performed. Efficiency is also one of the most frequently used terms in thermodynamics and it is frequently a source of confusion. This is because efficiency is frequently used without being adequately defined in the first place (Cengel & Boles, 2006). For an engineering system, efficiency can generally be defined as the desired input output ratio. Although this definition provides a simple general understanding of efficiency, a variety of specific efficiency ratios have been developed for different systems and engineering operations. Some researchers have acknowledged some of the difficulties associated with energy system efficiency definitions (Bisio & Rubatto, 2001; Brookes, 2004; Kano, 2001; Marc A. Rosen, Le, & Dincer, 2005; Struchtrup & Rosen, 2002).

Efficiency has been traditionally defined primarily based on the first law (i.e. energy). In recent decades, the analysis of exergy has found a greater acceptance as a useful tool in the design, evaluation, optimization and improvement of energy systems. The determination of the exergy efficiencies for a general system and/or the individual components that make up the system is an important part of the exergy analysis. An exhaustive analysis of a thermodynamic system includes both energy and exergy analysis in order to obtain a more complete overview of system behavior.

In the analysis of an energy conversion system, it is important to understand the difference between energy efficiency and exergy. This is essential to review the quality and quantity of energy used to achieve a given objective, and indeed to achieve efficient and effective use of energy resources (I Dincer, Hussain, & Al-Zaharnah, 2004). The improvement of the yield of energy systems is a major challenge to meeting energy policy objectives. Reductions in energy consumption can help achieve energy security objectives. In addition, efficient use of energy and the introduction of renewable energy technologies can significantly help to solve environmental problems. Increased energy efficiency benefits the environment by reducing energy use and resource consumption and associated pollution. From an economic as well as an environmental perspective, improving energy efficiency has great potential.

Wall (1993) (G. Wall, 1993) noted that "the concept of exergy is crucial not only for efficiency studies, but also for economic analysis. Costs should reflect value, as value is not in energy, but in exergy, allocation of costs to energy results in inappropriate appropriation, which are common and often severe. Using an exergy content as a basis for cost accounting is important for the management of products and prices for profit assessment. It is also useful for engineering operational and design decisions, including design optimization. Therefore, exergy is the only rational basis for evaluating: fuels and resources, processes, the device and system efficiency, dissipations and their costs, and the value and cost of system products".

1.4. Exergy in economic and environmental aspects

Exergy is strongly related to sustainability and environmental impact. Consequently, there is a relationship in which when the exergy decreases, sustainability and environmental impact increase, on the contrary, these two parameters decrease as the exergetic efficiency of a process increases. In other words, when the exergetic efficiency is around 100%, the environmental impact associated with the operation of the process is near zero, since the exergy is only converted from one form to another without a loss occurring (either through consumption or internal waste emissions). The process also approaches sustainability as it approaches reversibility. On the other hand, as it approaches zero per cent efficiency, the process is deviated out of sustainability because the resources it contains (fuel, minerals, steam, etc.) are used, but nothing is obtained. There is also a significant increase in the environmental impact of providing a fixed service, due to the fact that an increasing amount of resources is required and a larger amount of waste that even contains useful energy is emitted (Cornelissen & Hirs, 2002; Ibrahim Dincer & Rosen, 2005; Lombardi, 2003; Marc A. Rosen et al., 2008).

Exergy is also a useful concept in economics. In macroeconomics, it offers a way of assessing resource reduction and environmental destruction through an exergy tax. In microeconomics, it has been beneficially combined with cost-benefit analysis to improve designs. By reducing the life cycle cost to a minimum, the best system has been found because of the predominant economic conditions, and by minimizing exergy losses, it is also possible to minimize environmental effects (Ibrahim Dincer, 2002; M.A. Rosen & Dincer, 2003). Among the challenges confronting the engineers today is the design of

efficient and cost-effective systems that satisfy environmental conditions. The latter is due to the fact that it is a world with finite resources, but at the same time presents great energy demands. For this reason, there is a growing need to understand the mechanisms in which energy is degraded and in itself, the available resources. In conclusion, the combination of exergy with the economic context provides a tool for systematic study and optimization of processes (Ibrahim Dincer, 2002).

1.5. Biorefineries: Design and evaluation

1.6.1. Biorefinery concept

The indiscriminate use of non-renewable resources in the last decades has been a subject of discussion, due to its possible exhaustion in future years, and the great environmental impact that is caused in the extraction and subsequent processing (Woldeyohannes, Woldemichael, & Baheta, 2016). Until this date, the international market is dependent on oil, both in the production of fuels and in the production of different chemical synthesis products (Moncada B., Aristizábal M., & Cardona A., 2016). In oil refining, a broad spectrum of fuels such as kerosene, gasoline, and natural gas can be obtained, just to name a few (Xie, Shao, & Lin, 2016). It is estimated that energy use will have a steep increase in future years due to factors such as population growth, increased transportation, and the use of high amounts of energy in industrial processes (Meher, Sagar, & Naik, 2006). Despite the fact that in recent years oil production has increased thanks to emerging technologies such as fracking, the lack of certainty about of the actual exploitable amount of this resource has become a matter of concern (Christenson, Goldfarb, & Kriner, 2017). On the other hand, it has been evidenced that in some cases the world's oil reserves are located in places with political instability (Daza, Solarte, Serna, Chacón, & Cardona, 2016).

For these reasons, the search for new alternatives for the production of biofuels, electricity, and chemicals from renewable raw materials is an objective to the order of day in the roadmap of the global research (Chew et al., 2017). Since the end of the nineteenth century, it was emphasized that one of the main objectives for the future would be to obtain an economy and processes based on the use of renewable resources, such as biomass, to achieve a sustainable development (Ghatak, 2011). In order to fulfill these objectives, different definitions have been given to the word sustainable development. The World

Commission on Environment and Development (WCDE) defines sustainable development as *“development that meets the needs of the present without compromising the ability of future generations to meet their own needs”* (Ghatak, 2011). For its part, the UN in 1992 stressed the importance of sustainable development and promulgated that *“the right to development must be fulfilled so as to equitably meet developmental and environmental needs of present and future generations”* (Ghatak, 2011).

In order to comply with the implementation of renewable processes and resources, the World Summit on Sustainable Development in 2002 set the goal of sustainable development (Ghatak, 2011). This goal is based on the *“access to reliable, affordable, economically viable, socially acceptable and environmentally sound energy services and resources”* (Ghatak, 2011). The integral use of biomass for the production of value-added compounds such as biomaterials and chemical compounds is of great importance in the chemical industry in general (Cherubini, 2010). However, biomass has been used mostly for the production of biofuels that can replace highly polluting fuels (Cherubini, 2010). With the integral use of biomass for the production of a broad spectrum of added-value products such as biomaterials, fine chemicals, biopolymers, biofuels and others that can replace petroleum products (Cherubini, 2010). The existing oil-based economy is expected to be gradually replaced by a biomass-based economy (Cherubini, 2010).

The first uses of biomass were inefficient since the obtainment of the different products involved the low conversion of the raw material and the high generation of residues (Moncada B. et al., 2016). An example of this was the production of essential oils, where only 1-2% of the raw material was used, while the remaining 98% was treated as process waste (Moncada B. et al., 2016). This idea of exploitation of biomass is contrary to what was sought by process designers, as the pollution in the transformation of biomass was very high and the economic benefits limited. At this point, the integral use of biomass becomes a fundamental part of the biotechnological processes, because through the integral use of the raw material, it is pretended to reduce environmental impacts, increase economic benefits and generate a positive social impact on rural communities (Moncada B. et al., 2016).

In the search to generate an integral use of biomass, the concept of biorefinery emerges as the best alternative (Moncada B. et al., 2016), (Ghatak, 2011), (Cherubini, 2010). Briefly, biorefineries are a network of facilities and equipment arranged for the transformation of

the different components present in biomass into added-value products such as food, biofuels, energy, biomaterials and marketable chemicals (Cherubini, 2010). A large number of definitions have been given to the concept of biorefinery since this constitutes a fundamental part of the integral exploitation of biomass. International Energy and Bioenergy Agency (IEA) task 42 defines a biorefinery as the “*sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, and chemicals) and energy (fuels, power, and heat)*” (Ghatak, 2011). Some authors have tried to further break down this definition and have established their own definition of biorefinery. One of the most cited definitions is given by Cherubini (Cherubini, 2010), where he defines a biorefinery as being “*able to separate biomass resources (wood, grasses, corn. . .) into their building blocks (carbohydrates, proteins, triglycerides. . .) which can be converted to value added products, biofuels and chemicals. A biorefinery is a facility (or network of facilities) that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass*”.

From the above definitions, it can be understood that a biorefinery is a system in which the constituents of biomass must be harnessed as much as possible to produce a palette of products, an analogous concept to oil refineries (Moncada B. et al., 2016), (Cherubini, 2010). Although the concept of biorefinery is an adaptation of the concept of refinery, biorefineries and refineries have large differences (Moncada B. et al., 2016). First, the raw materials are completely different, because although biomass and oil are rich in carbon, biomass is obtained from living or recently living materials and crude oil is a compound that is obtained after millions of years of biodegradation (Moncada B. et al., 2016). The fact that the biomass is a renewable resource and that is produced in different amounts in the whole planet earth presents alternatives of use at different scales, contrary to the crude oil (Cherubini, 2010). The second difference is based on complexity, since biorefineries apply and integrate a large number of mature and emerging technologies for the production of different products (Moncada B. et al., 2016). The third difference lies in the broad spectrum of products obtained in biorefineries, in addition to products that cannot be obtained from petroleum, such as food (Moncada B. et al., 2016). This offers a great advantage for biorefineries, since with the use of the same raw material, specialized products can be obtained depending on the technology used in the transformation (Moncada B. et al., 2016).

Due to their advantages, biorefineries are very versatile and can be adapted according to the desired needs or objectives. In most cases, biorefineries are designed to meet three main objectives. The first objective is based on the energy security of the developed and underdeveloped countries that have a large amount of biomass (Martinez-hernandez, Sadhukhan, & Campbell, 2013). Since through the production of biofuels and the generation of energy by mean thermochemical processes, part of the energy needs can be covered, reducing dependence on energy products derived from crude oil (Moncada B. et al., 2016). The second objective is based on the reduction of environmental impacts associated with the production of chemical products, using renewable raw materials and processes that generate less waste and greenhouse gases (Cherubini & Ulgiati, 2009). Third, the rural development and an increase in the quality of life of people involved in the supply chain is an important objective of the biorefineries (Cherubini, 2010).

However, for the development of the three objectives mentioned in a biorefinery, it must be conceptualized. Some authors in the last days assert that in order to be able to identify a sum of processes and technologies as a biorefinery, it must be designed as such from a beginning (Moncada B. et al., 2016). That is, if a stand-alone process is added to a process to obtain an added-value product, this should at no time be considered as a biorefinery, since it is only an association of stand-alone processes and was not designed under the concept of biorefinery (Moncada B. et al., 2016). For the design of a biorefinery, different approaches are presented in the literature. Among the most widely described approaches for the design of biorefineries are superstructures, conceptual design and optimization (Zondervan, Nawaz, de Haan, Woodley, & Gani, 2011). These approaches can interact with each other.

In order to clarify the design process, some authors have tried to develop a design strategy that can be followed step by step to obtain the biorefinery with better economic, environmental and social characteristics (C. A. Cardona, Aristizábal, & Solarte, 2016). The methodology proposed by Cardona et al. (C. A. Cardona et al., 2016) for the design of a biorefinery takes into account three essential factors which are hierarchy, sequencing and energy and mass integration. These concepts are presented below.

1.6.1.1. Hierarchy

The hierarchy is the stage of the design of a biorefinery in which the hierarchical decomposition of the raw materials, products and technologies is performed (C. A. Cardona et al., 2016). Any biorefinery in the first instance is obliged to select the raw material to obtain the products (C. A. Cardona et al., 2016). This selection is not a simple process as this depends on the availability, political situations, geographic features and other factors that were previously described in this chapter (C. A. Cardona et al., 2016). For this reason, the selection of the raw material implies a direct relation with the products, since each raw material can be decomposed into different buildings blocks (e.g. sugars) that will later be transformed into added-value products through a series of technologies (Moncada B. et al., 2016). In addition, the raw materials selected for use in biorefineries can be separated according to their generation, where each generation has specific characteristics (Naik, Goud, Rout, & Dalai, 2010). In this sense, many authors describe that the selection of feedstocks generation can be an important part of the biorefinery design since the economic, social and environmental aspects are severely affected (Naik et al., 2010).

Limiting the process to a generation of raw material does not obey the objective of a biorefinery, on the contrary the possible combination of generations can cause a biorefinery to use in an integral way all the raw material (Ghatak, 2011). An example of this is the production of biodiesel from oil palm. In this process, oil is produced for edible use and biodiesel by means of a transesterification process, in which oil reacts with monohydric alcohol in presence of a catalyst (Meher et al., 2006), (Luis E Rincón, Moncada, & Cardona, 2014). But if the lignocellulosic material present in the seeds after the extraction would be used for the production of ethanol, the combination of first and second generation feedstocks can provide better economic and environmental alternatives to the process (Luis E Rincón et al., 2014).

With the raw material defined, the next step in the design of the biorefinery and to understand which technologies will be applied in the transformation of biomass. For the transformation of biomass, (Moncada B. et al., 2016) there are four main transformation pathways which are thermochemical, biochemical, chemical and physical. **Figure 1-1** presents the conceptual scheme of the hierarchy in a biorefinery.

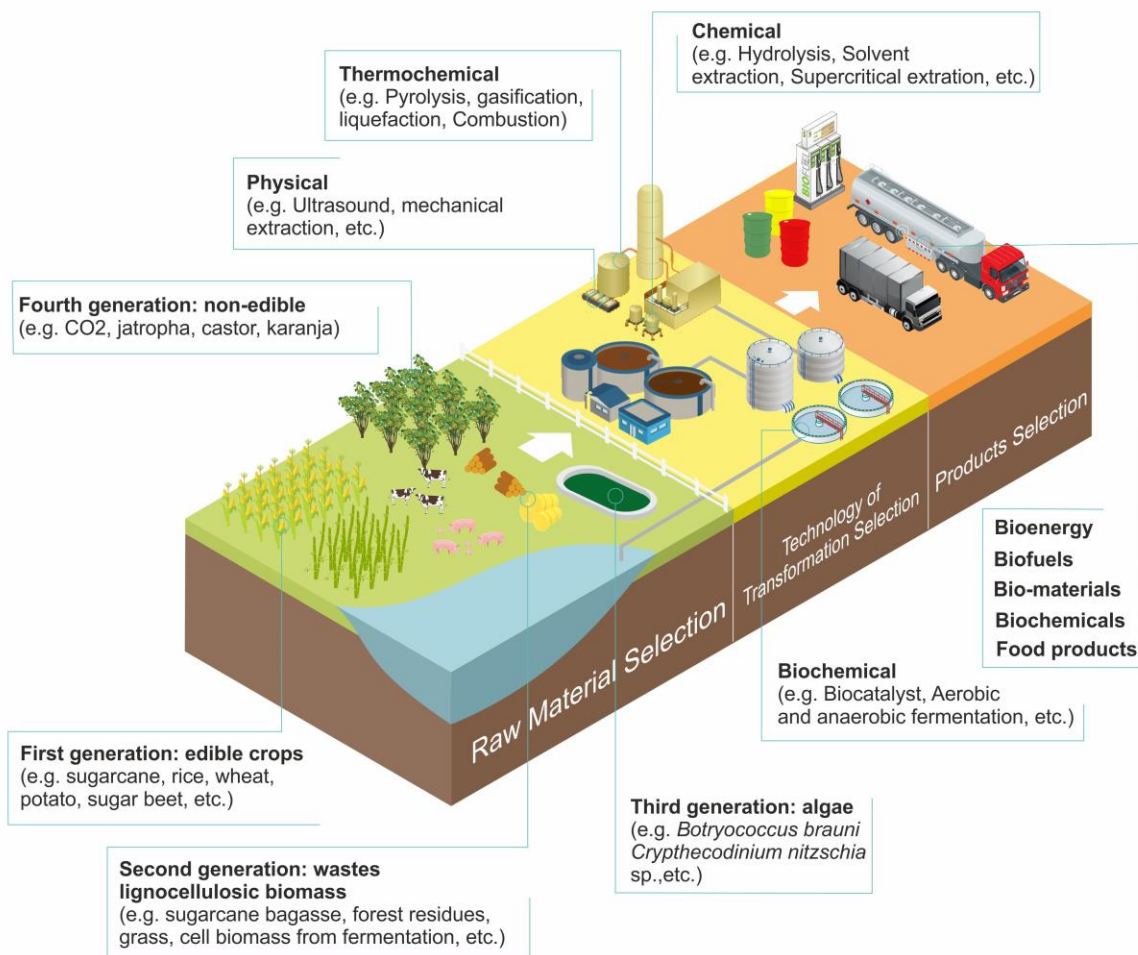


Figure 1-1. Scheme of the hierarchy of a biorefinery

Finally, hierarchy involves the selection of products as an essential part of the design of a biorefinery (C. A. Cardona et al., 2016). In a biorefinery, high-volume but low-cost products such as biofuels can be obtained, or on the other hand, low-volume products can be obtained but with a very high added value (pharmaceutical products and fine chemicals) (C. A. Cardona et al., 2016). The selection of products depends on the decision of the designer and the available technologies and raw materials (C. A. Cardona et al., 2016). It is clear that all the steps of the hierarchy must be interconnected in order to obtain a sustainable biorefinery.

1.6.1.2. Sequencing

Sequencing is the stage where a logical sequence is given to the technologies used and products to be obtained (Moncada, Tamayo, & Cardona, 2014b). That is to say, if what is wanted in the biorefinery is to obtain energy products, this implies that some technologies are discarded, reducing the options of possible sequences (C. A. Cardona et al., 2016), (Moncada et al., 2014b). Finding the optimal sequence for the biorefinery is not an easy case, since the possibilities of sequences can be multiple. Therefore, it is important to define the most interesting products (Moncada B. et al., 2016).

In sequencing, it is also implied that certain distribution rates are given to raw materials and buildings blocks products, in order to give priority to specific products (Moncada B. et al., 2016), (C. A. Cardona et al., 2016), (Moncada et al., 2014b). In the same sense, it is a golden rule that when designing a biorefinery, food products must be in the first steps of the biorefinery sequence; this will avoid possible contamination with substances used in the synthesis of other products (Moncada B. et al., 2016). In addition, the products must be obtained with the highest purity possible, to generate less wastes and consequently a lower environmental impact (Moncada B. et al., 2016), (C. A. Cardona et al., 2016), (Moncada et al., 2014b).

1.6.1.3. Integration

The integration aims to an integral use of the mass, energy and in general of the resources present inside the plant. In this sense, the integration of a biorefinery is decomposed into three levels (Moncada B. et al., 2016), (C. A. Cardona et al., 2016). (i) Integration of feedstocks, (ii) integration of technologies, and (iii) integration of products.

Mass integration is based on the integral use of materials. That is to say, the residues coming from a process in the biorefinery will be again used as raw material in a following process (Moncada, Tamayo, & Cardona, 2014a). As an example, in the palm oil extraction process a lignocellulosic residue is obtained called the empty fruit bunches. This residue can be transformed by different technologies into ethanol, butanol, or electricity, just to name a few products (Daza et al., 2016). In turn, the ethanol produced can be used for the production of biodiesel, or the oil product of the extraction can be used in part for the production of antioxidants and the remaining part in the production of biodiesel (C. A.

Cardona et al., 2016). All this type of integration of raw materials allows decreasing to the minimum the produced wastes.

The integration of technologies is based on the use of technologies to exploit energy resources, seeking to improve environmental and economic aspects of the biorefinery (Zondervan et al., 2011). The integration of heat, through pinch technologies, allows using the energy that is released in a process and exploited in the preheating of raw materials or other processes that require heat (Martinez-hernandez et al., 2013). This gives great economic benefits to biorefineries, since the high consumption of energy resources is one of the weaknesses of biorefineries (Martinez-hernandez et al., 2013). The recycling of water resources that were used to wash equipment, or other functions that do not involve a significant contamination allow these resources to be treated and reused in the process. The integration of technologies is also related to the intensification of processes, so that a biorefinery will be as compact and efficient as the design allows (Nhien, Van Duc Long, Kim, & Lee, 2016).

1.6.2. Types of biorefineries

As mentioned above, there is a direct relationship between the raw material, products and technologies in a biorefinery. Consequently, the definition of the types of biorefineries is linked to these concepts, since a biorefinery can be defined according to the type of raw material and the production scale (Naik et al., 2010). As for raw materials, a biorefinery can be classified in first, second, third and fourth generation, which will be explained as follows.

1.6.2.1. Raw material

Each raw material gives a feature to a biorefinery. For a biorefinery to be reliable and comparable to the oil refinery, it must have a constant and assured supply of raw material (Ghatak, 2011). The availability of biomass is related to geographical, political, social and, above all, economic and logistical aspects (Ghatak, 2011). In this sense, the biomass has been differentiated in generations to give clarity to the factors related to each of the raw materials. The first generation feedstocks are those that are involved with food safety, which means that are those crops used for human consumption, which has high amounts of triglycerides, sugars or starch (Moncada, El-Halwagi, & Cardona, 2013). The use of first generation feedstocks can threaten food secure by increasing the cost of edible crops and

competing for land use. For this reason, doubts arise with respect to the sustainable use of these raw materials in long term (Moncada, El-Halwagi, et al., 2013).

Second generation feedstocks are those that are generated as waste in the agro-industry, agriculture, forestry, and cooking oil wastes, among others (Mathioudakis, Gerbens-leenes, Van Der Meer, & Hoekstra, 2017). Second generation feedstocks give biorefineries great advantages because of their low cost, since in a typical biorefinery the costs of the raw material are 40 to 60% of the total cost (Ghatak, 2011). Additionally, the use of second generation feedstocks produces environmental improvements to the process, since the production of greenhouse gases are minimal compared to oil-based processes (Mata, Martins, & Caetano, 2010). Another important aspect related to second generation feedstocks is the development of rural areas (Mata et al., 2010). **Table 1-2** shows some examples of the different raw materials for each of the generations.

Table 1-2. Feedstock classification into the different generations. Taken from: [52]

First generation Feedstocks: Edible crops	Second generation feedstocks: Wastes lignocellulosic biomass	Third generation feedstocks: Algae	Fourth generation feedstocks: Non-edible	References
Sugarcane, rice, wheat, potato, sugar beet, barley, corn, peanut, soybean, rapeseed, sunflower, olive, oil palm etc.	Sugarcane bagasse, forest residues, grass, cell biomass from fermentation, wood, wood waste, glycerol, black liquor, crops residues, waste cooking oil, animals fats, etc.	<i>Botryococcus brauni</i> , <i>Cryptocodinium Nitzschia sp.</i> , <i>Phaeodactylum Schizochytrium sp.</i> , <i>Tetraselmis suecia Pavlovalutheri</i> , <i>Scenedesmus ob.</i> , <i>Spirulina maxima</i> . <i>Ankistrodesmus sp.</i> <i>Chaetoceros cal.</i> <i>Chlorella vulgaris</i> . <i>Dunaliella tertiolecta</i>	CO ₂ , Jatropha, Castor, Karanja	(Azad, Rasul, Khan, Sharma, & Hazrat, 2015; Cherubini & Ulgiati, 2009; Feyzi, Hosseini, Yaghobi, & Ezzati, 2017; Gonzáles-Delgado & Kafarov, 2011; Haider et al., 2017; Keeffe, Schulte, Sanders, & Struik, 2012; Lu, Sheahanb, & Fu, 2011; Mansoornejad, Chambost, & Stuart, 2010; Martinez-hernandez et al., 2013; Moncada, El-Halwagi, et al., 2013; Naik et al., 2010; Negm, Sayed, Yehia, Habib, & Mohamed, 2017; Patel & Sankhavara, 2017; Posada, Rincón, & Cardona, 2012; Luis E Rincón et al., 2014; Sacramento-Rivero, Romero, Cortés-Rodríguez, Pech, & Blanco-Rosete, 2010)

Third generation feedstocks are related to the use of algae for the production of added-value products. Some species of algae are sources of high amounts of oils, which can later be used in the production of biofuels such as biodiesel (Mata et al., 2010). It has also been demonstrated that in the oil obtained from these organisms, a number of products with high cost in the market are present that can be isolated, such as docosahexanoic acid (Trivedi, Aila, Bangwal, Kaul, & Garg, 2015). However, microalgae crops require large extension of land for sustainable oil production, which creates a clear disadvantage because of the high cost and competition for land use (Moncada B. et al., 2016). As a final element, in this classification of raw materials, it is called fourth generation feedstocks to those crops that are not used for human consumption and that can be used for industrial use.

Fourth generation feedstocks include carbon dioxide that is a pollutant residue and that being used as a feedstock could be interesting from the environmental and economic point of view (Mata et al., 2010). The crops that are denominated like fourth generation feedstocks grow in lands with low availability of water offering alternatives of use to arid soils (Moncada B. et al., 2016).

1.7. Raw materials in Colombia

Colombia is a country with a wide variety of climates, which makes it an ideal place to grow a wide range of agricultural products. Depending on the geographical region analyzed, it is possible to find different crops. However, this predisposition to the cultivation of a large quantity of products means that during their harvest and processing large quantities of waste are generated. In many cases these residues are used as fertilizers of the same farmland, employed for animal feed, or in a few cases are used in combustion processes for power generation (Angel Siles López, Li, & Thompson, 2010; King et al., 2010; Manochio, Andrade, Rodriguez, & Moraes, 2017; Mayer, 1997; Murthy & Madhava Naidu, 2012). Nevertheless, a large part of this waste will be disposed of in the form of municipal solid waste or will simply not be properly processed. This can lead to contamination of farmland or areas near it. To prevent this situation, many of these wastes have been a source of study to be used in transformation processes which allow the obtaining of a great variety of value-added products (Aristizábal M., Gómez P., & Cardona A., 2015; Cai, Zhang, Kumar, & Wyman, 2014; Isikgor & Becer, 2015; Jong & Jungmeier, 2015; Lange, van der Heide, van Buijtenen, & Price, 2012; Mariscal, Maireles-Torres, Ojeda, Sádaba, & López Granados, 2016). In addition, these processes are giving benefit to waste that has a wide

potential for generating more profits for both farmers and the country. At the same time, the generation of new jobs will be promoted both in the collection processes of this waste and in the corresponding transformation processes.

Agroindustrial waste is one of the main sources of lignocellulosic biomass; this waste is rich in cellulose and hemicellulose polymers (around 75 - 80%); these components can be used to obtain value-added products through transformation processes (Muñoz-Muñoz, Pantoja-Matta, & Cuatin-Guarin, 2014). Thus, this type of waste is exploited allow to obtain useful compounds, which can be employed as inputs for other industrial processes (Saval, 2012). Among the advantages of processes that use an agro-industrial waste as raw material, is that its implementation does not represent a risk for food safety (Julian, Carlos, Erika, Jonathan, & Juan, 2015; Kristensen, Birch-Thomsen, Rasmussen, Rasmussen, & Traoré, 2014; Nuwamanya, Chiwona-Karlton, Kawuki, & Baguma, 2012). **Figure 1-2**, presents a scheme of processing lignocellulosic biomass, from which different transformation processes are presented to finally obtain a wide range of products including ethanol, furfural, phenols, electricity, fuels, acetone and lactic acid, among others. Some of the lignocellulosic residues include sugarcane bagasse (SCB) and tree tomato peel.

Not only waste can be used in processing processes, agricultural products with a high production rate can also be used in processing processes. This is the case of cassava, a starchy material which, due to its composition, has been widely studied for the production of ethanol (Atthasampunna, Somchai, Eur-aree, & Artjariyasripong, 1987; Chacón Perez, Restrepo Serna, & Cardona Alzate, 2017; Dai, Hu, Pu, Li, & Wang, 2006; Production, Cassava, Using, Process, & Saccharification-fermentation, 2008; Julian A. Quintero & Cardona, 2009). In order for this agricultural product to be used in transformation processes, food safety policies must be implemented. These policies would allow the correct distribution of the agricultural product both for human consumption and for processing processes (Chacón Perez et al., 2017).

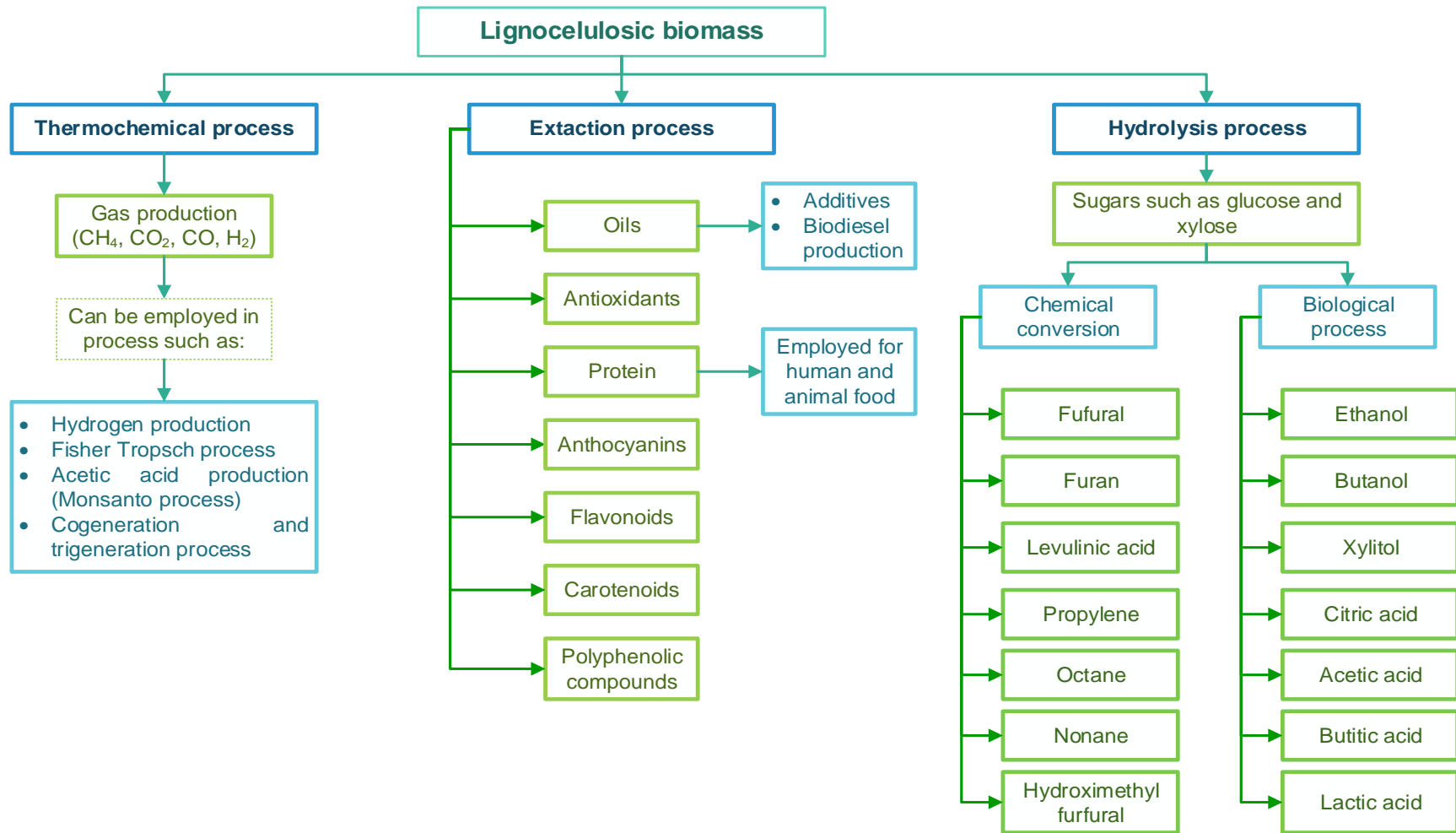


Figure 1-2. Products that can be obtained from lignocellulosic biomass through some transformation processes (Botero, Restrepo, & Cardona, 2017; Cherubini, 2010; King et al., 2010; Machado et al., 2016; Mikkola, Sklavounos, King, & Virtanen, 2015; Moncada, Matallana, & Cardona, 2013; Muñoz-Muñoz et al., 2014; Julián A. Quintero, Moncada, & Cardona, 2013a; L.E. Rincón, Jaramillo, & Cardona, 2014; Saval, 2012)

1.7.1. Sugarcane bagasse (SCB)

Sugarcane bagasse is a waste generated during the extraction of sugarcane juice. For each ton of sugarcane processed, approximately 280 kg of bagasse are generated (C. A. A. Cardona, Quintero, & Paz, 2010). This waste is generated in large quantities in countries such as Brazil, India, China, Thailand, Pakistan, Mexico, Colombia, Indonesia, the Philippines and the United States (“Top Sugarcane Producing Countries,” 2017). Between 2014 and 2015, world sugarcane production was 175.1 million metric tons (The Statistics Portal, n.d.). In countries such as Colombia, production in 2016 was 24.4 million tonnes. When these are processed, around 6.8 million tons of sugarcane bagasse are produced. As shown in the **Figure 1-3**, sugarcane production in Colombia has shown similar values in recent years. This makes the production of SCB stable, allowing for the availability of this raw material when it is used in transformation processes.

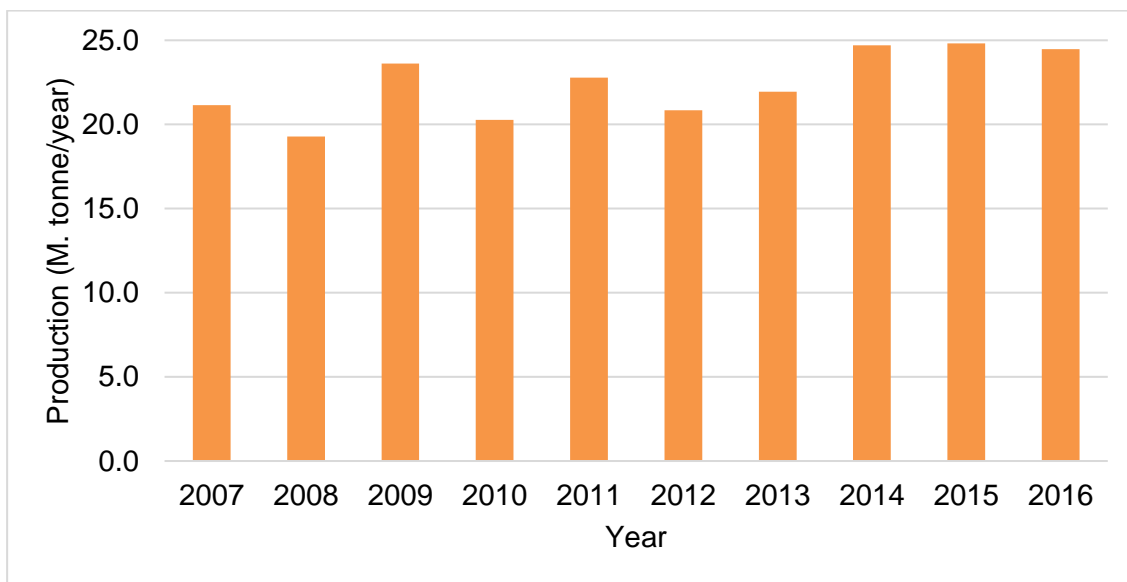


Figure 1-3. Annual sugarcane production in Colombia [78]

1.7.2. Cassava

Cassava (*Manihot esculenta*) is a tuber of American origin of the family *Euphorbiaceae* of the genus *Manihot*. It is one of the main foods in food-deficit regions. This is due to its high protein and energy content. In countries such as Colombia, it has an approximate annual

production of 2.00 million tons (see Figure 1-4). The pulp of the cassava is around the 16% of the fruit total weight (Ratnadewi, Santoso, Sulistyaningsih, & Handayani, 2016)

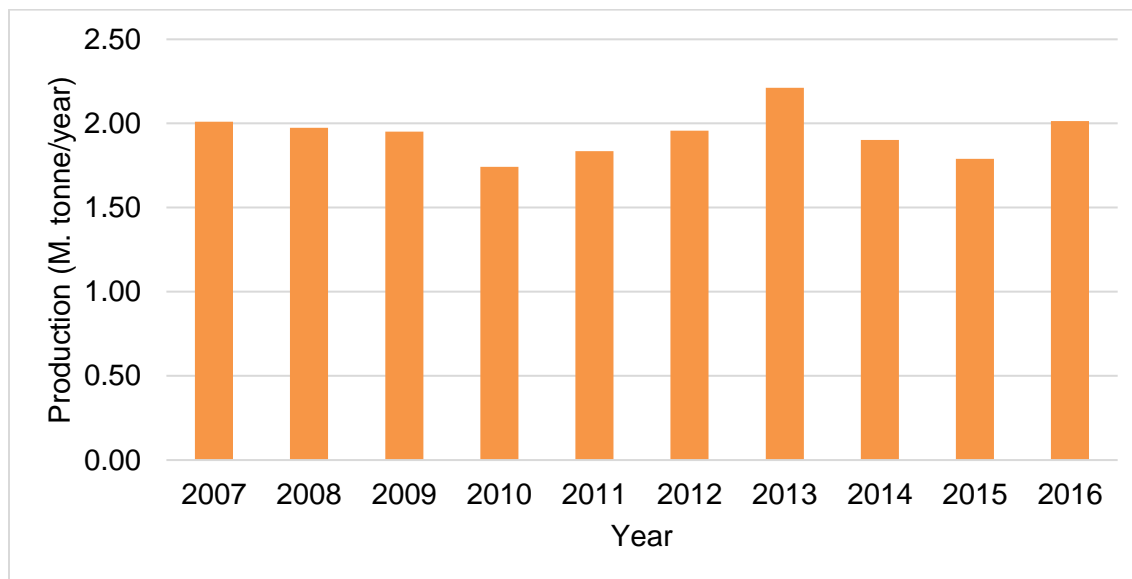


Figure 1-4. Annual cassava production in Colombia (MinAgricultura, 2018)

1.7.3. Tree tomato peel

The tamarillo or tree tomato (*Cyphomandra betacea*) is a *Solanacea* native to South and Central America. Commercial growing started in New Zealand. It is a tree species that grows 3-3.6 m high. The fruits are ovoid and smooth-skinned, are yellow (yellow tamarillo) or red (red tamarillo), and contain many small seeds. The pulp is also yellow or red, with a slightly acid taste, reminiscent of tomato (Romero-Rodriguez, Vazquez-Oderiz, Lopez-Hernandez, & Simal-Lozano, 1994). The tomato tree production in Colombia is shown in the **Figure 1-5**.

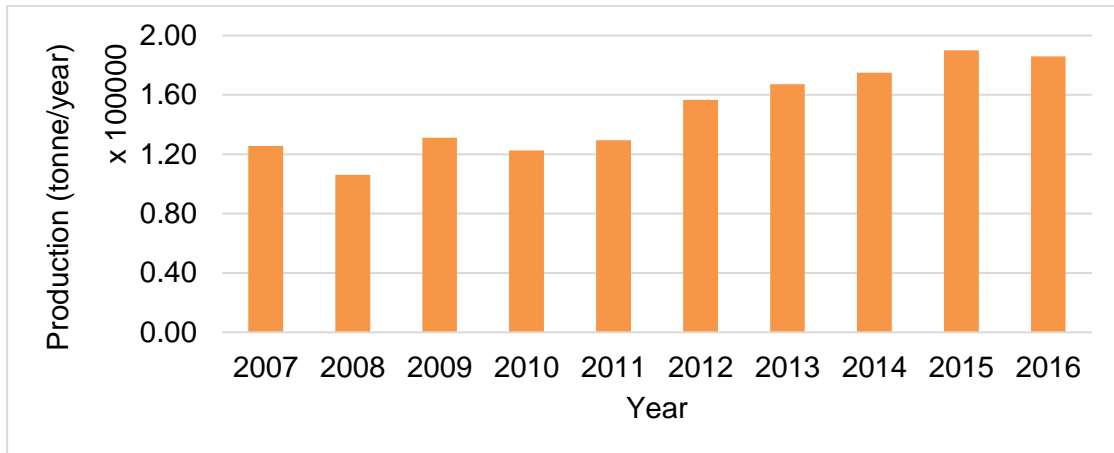


Figure 1-5. Annual tomato tree production in Colombia (MinAgricultura, 2018)

1.8. Final remarks

The design of processes based on the different raw materials that are presented in Colombia depends both on their availability and on their potential for obtaining specific products. Among the raw materials with the greatest advantages are the different agro-industrial wastes. Where one of the advantages is the low costs and the fact that it does not compromise food security.

The analysis of complex production processes such as biorefineries involves in many cases the technical, economic and environmental fields. In few cases are the energy aspects of the process considered. By calculating properties such as exergy it is possible to determine not only the energy changes throughout the process, but also to identify the energy content of a raw material.

2. Chapter 2: Methodology

2.1. Raw materials

The raw materials selected for the development of this work were sugarcane bagasse, tree tomato peel and cassava. Where the first two are residues obtained from the processing of sugar cane and tree tomato, respectively, being both raw materials of second generation. Due to its composition, both SCB and tree tomato peel can be used in different transformation processes, both stand-alone and biorefineries. Tree tomato peel is evaluated as a raw material for obtaining polyphenolic compounds from extraction technologies such as solvent extraction (conventional technology) and extraction with supercritical fluids (non-conventional technology). SCB is studied to obtain ethanol and as a raw material for the formulation of different transformation scenarios using the biorefinery concept. Cassava, a first-generation raw material, is selected as the object of comparison for ethanol production.

For this work, the compositions of raw materials reported in the literature were used. The composition of the all raw materials used in this work are presented in the **Table 2-1. Table 2-1.** Composition in percentage by weight in wet basis of raw material used in this work. The same SCB composition is used for the design of the biorefineries.

Table 2-1. Composition in percentage by weight in wet basis of raw material used in this work.

Component	Cassava ^a	Sugarcane bagasse ^b	Tree tomato peel ^c
Moisture	71.40	50.00	-
Extractives	-	-	38.12
Cellulose	0.26	23.70	21.58
Hemicellulose	0.33	12.05	17.15
Lignin	0.01	11.70	18.51
Protein	0.80	2,40	-
Starch	26.50	-	-
Ash	0.70	1.15	4.34

Source: ^a (Julian et al., 2015), ^b(C. A. Cardona Alzate, Posada Duque, & Quintero Suarez, 2010), ^c(Caballero Galván, 2017).

Experimental data are used for the evaluation of the extraction of polyphenolic compounds. A description of the process of obtaining is presented in the **section 2.2**, the process of quantification and determination of some compounds is presented in the **section 2.2.1**. The experimental data obtained are employed as a basis for the SE and SFE simulation processes presented in the **section 2.4.1**. The evaluation of the production of ethanol from SCB and cassava, as well as the use of SCB as raw material for the design of biorefineries are based on the use of information reported in the literature.

2.2. Experimental component: Polyphenolic compounds extraction

In order to compare the influence of extraction technology on the processes of obtaining polyphenolic compounds, two technologies were selected: one conventional such as solvent extraction (SE) and another non-conventional such as supercritical fluid extraction (SFE). The SE was performed using a 60% ethanol solution and a solid-liquid ratio of 1:20 (w/v). Extraction conditions were 300 rpm and 25°C for 8 hours. Subsequently the solid was separated by means of combined processes of filtration and centrifugation. The SFE used carbon dioxide as a solvent and 60% ethanol in a solid-liquid ratio of 1:3 (w/v) as a co-solvent. The process is carried out in a extractor of stainless steel at 300 bar and 50°C during a period of 60 min. The selected conditions were based on data reported in literature in pre-experimental work (Mertz et al., 2009; Mutalib, Ali, Othman, Ramasamy, & Rahmat, 2016).

2.2.1. Quantification of polyphenolic compounds

The Total content of phenolic compounds (TPC) was determined through the implementation of the Folin-Ciocalteu method (Rover & Brown, 2013). The procedure is performed in the absence of light, taking 100 µL of extract and adding 1600 µL of distilled water. Before, 100 µL of Folin-Ciocalteu reagent (1N) is added, mixing the solution and letting it equilibrate for 5 minutes. Lastly, sodium carbonate 20% (200 µL) is added, measuring the solution two hours later in a spectrophotometer to 765 nm.

For the determination of the antioxidant activity of the extracts was used the DPPH method (Brand-Williams, Cuvelier, & Berset, 1995). For the determination of the antioxidant activity of the extracts was used the DPPH method (Brand-Williams, Cuvelier, and Berset 1995).

Five dilution factors are prepared for each extract. From this 150 μL were taken and 2,850 μL of DPPH reagent is added. The solution is mixed during 60 minutes. This solution is stored in a dark place and the absorbance is measured at 515 nm, using an UV-Vis spectrophotometer.

The High Performance Liquid Chromatography (HPLC) is used for the quantification of polyphenolic compounds in the extracts. The HPLC used a C18 column (dimensions of 150 mm x 4.6 mm and a particle diameter of 5 μm) with UV-visible detector. Calibration curves of compounds such as chlorogenic acid, ferulic acid and quercetin are developed for each method. For the calibration method of chlorogenic acid and ferulic acid was used the methodology proposed by Zhang and Li, respectively (Li, Wang, Li, Xu, & Xue, 2007; Q. Zhang et al., 2007). While for the determination of the other compounds the proposed method by Chen was carried out (Chen, Zuo, & Deng, 2001).

2.3. Process simulation

The design of this process was carried out in the Aspen Plus software. For the simulation of the different separation areas, the DSTWU module was used, which uses an approximate method based on Winn-Underwood-Gilliland equations and correlations. This module is built into the Aspen Plus software. With this module an initial estimate of the number of theoretical stages, the reflux relation, the location of the feed stage, and the distribution of the components can be obtained. The rigorous calculation of the separation units was carried out in the RadFrac module. This module is based on the inside-out equilibrium method that uses the MESH equations, which involves the simultaneous solution of the mass balance, phase equilibrium, summation expressions, and equations of heat balance of all components in all stages of the distillation column (Cerón-Salazar & Cardona-Alzate, 2011).

Simulation of the presented processes is based on investigations from different authors. Aspen Plus commercial software presents a wide content of physico-chemical properties, thermodynamic models and equipment that allow handling solids, liquids and gases allowing to design the process in terms of material and energy balances. Due to the lack of certain compounds it is necessary to involve the thermodynamic properties of organic and inorganic compounds present in biomass like proteins (lysine), hemicellulose, lignin and

ash presented by the National Renewable Energy Laboratory (NREL) (Wooley & Putsche, 1996). During simulation procedure, the thermodynamic models used to represent the behavior of vapor and liquid phase were NRTL and Hayden O'Connell to obtain the activity coefficient and fugacity, respectively.

2.4. Comparison of stand-alone processes

2.4.1. Comparison of technologies for the polyphenolic compounds extraction

2.4.1.1. Solvent extraction

For the SE, first the raw material is dried at 40°C and milling until size particle of 2 mm. Subsequently is sent to the extractor, which is also feed with an ethanol solution at 60%. The ratio employed is 1:20 (w/v) solid - liquid. The extraction process is carried out at 50°C. The liquid fraction is submitted to a purification process, which allow to obtain a stream rich in polyphenolic compounds and in the other stream the ethanol employed. The ethanol recovered is recirculated at the process. The process is shown in the **Figure 2-1**.

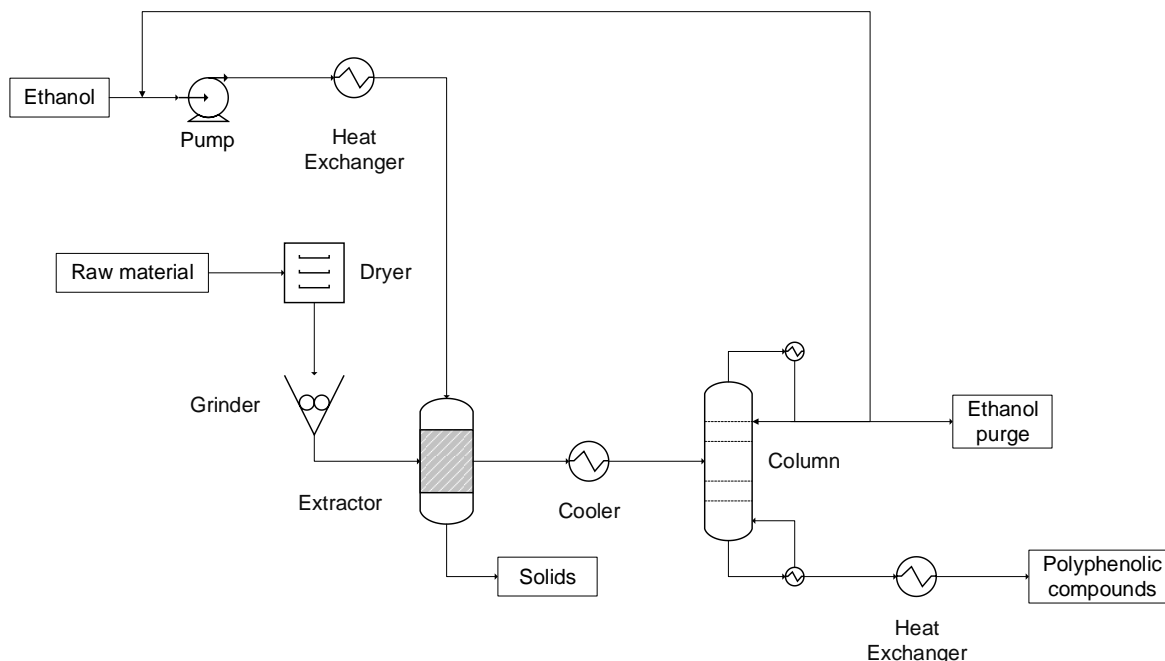


Figure 2-1. Flow diagram for solvent extraction of polyphenolic compounds from tomato tree

2.4.1.2. Supercritical fluid extraction

In the first step of the SFE, the raw material is dried at 40°C. After, the raw material is milled until a size particle of 2 mm and sent to the extractor. This equipment is feed CO₂ at supercritical conditions (300 bar and 50°C). To achieve these conditions, the CO₂ is cooled at -19°C and pressurized at 300 bar. This process allows obtaining a CO₂ in liquid state, which is heated until 50°C and sent to the extractor. Also, the extractor has a feed of an ethanol solution (co-solvent) at 60%, in a ratio 1:3 solid - co-solvent. After the extraction process, the system is depressurized through the use of a valve. A collector is employed for the recuperated CO₂. The liquid stream is submitted at an evaporation process, which allow to obtain a stream rich in polyphenolic compounds and in another stream the recovered ethanol employed in the process. Both the CO₂ and the ethanol are recirculated at the beginning of the process. **Figure 2-2** presents the supercritical fluids extraction scheme.

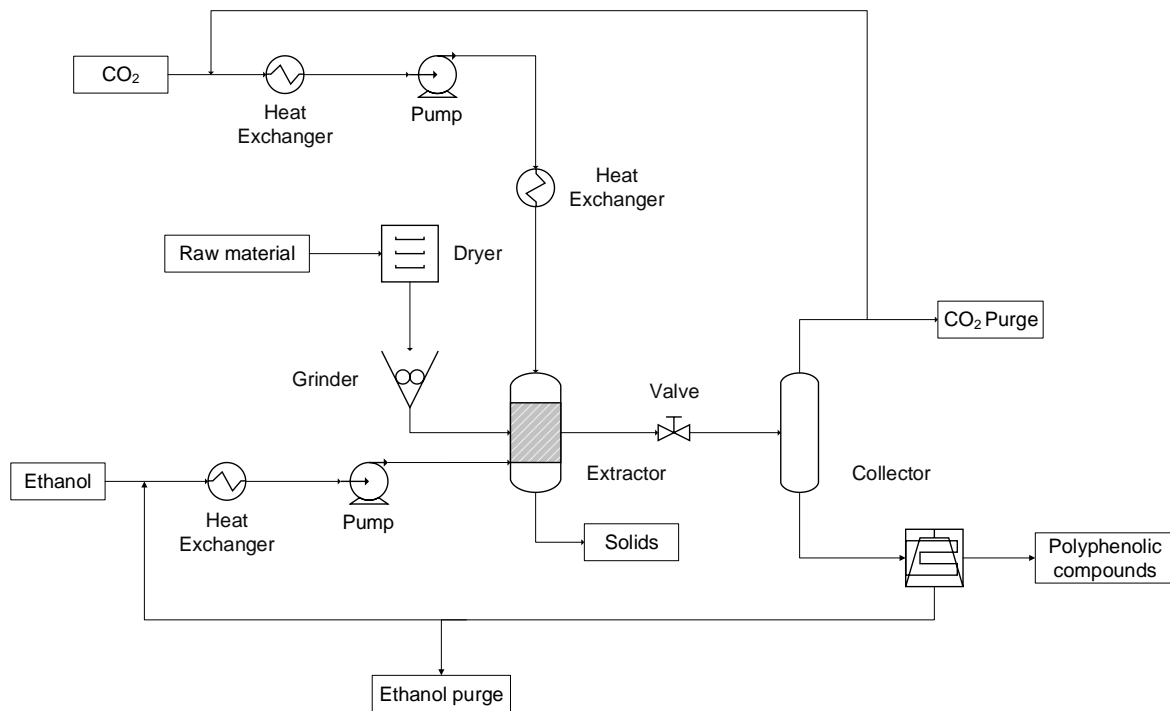


Figure 2-2. Flow diagram employed SFE of polyphenolic compounds from tomato tree.

2.4.2. Influence of raw material in the ethanol production

Ethanol is a biofuel obtained from the sugar fermentation processes. This biofuel has a potential for energy security and environmental security with respect to fossil fuels (Sarkar, Ghosh, Bannerjee, & Aikat, 2012). To obtain the sugars used in the fermentation process, different raw materials have been studied (Sánchez & Cardona, 2012). These can be classified into sugars, starch and lignocellulosic biomass (C. A. A. Cardona Alzate, Sánchez Toro, & Sanchez Toro, 2006; Carlos Ariel Cardona, Sánchez, & Gutiérrez, 2010; Mekala, Potumarthi, Baadhe, & Gupta, 2014). However, both the starchy and the lignocellulosic materials must be subjected to transformation processes that allow to obtain the sugar monomers for fermentation process (Zabed, Sahu, Suely, Boyce, & Faruq, 2017). Since the two materials have different compositions, it is necessary to use a different treatment in both cases (Chacón Perez et al., 2017). Once the sugars are obtained, microorganisms such as *Saccharomyces cerevisiae* and *Zymomonas mobilis* can be used for the fermentation process (Zabed et al., 2017). Where the first microorganism has the ability to synthesize C6 sugars as glucose, while the second can synthesize both C5 and C6 sugars (Rogers, Jeon, Lee, & Lawford, 2007; Zabed et al., 2017).

Materials such as sugarcane bagasse and cassava have been studied as raw materials for obtaining ethanol (ADO, S. A. OLUKOTUN, G. B. AMEH, J. B. & YABAYA, 2009; C. A. A. Cardona et al., 2010; Carlos A Cardona & Sánchez, 2007; Kosugi et al., 2009; Liscano Martínez, 2014; Julián A. Quintero et al., 2013a; Julián A. Quintero, Moncada, & Cardona, 2013b; Sánchez, Cardona, Sanchez, & Cardona, 2008). To obtain sugars from lignocellulosic materials it is necessary to use combined processes of hydrolysis of hemicellulose and hydrolysis of cellulose. There are several hydrolysis, however the most commonly used are acid hydrolysis and enzymatic hydrolysis (Julián A. Quintero et al., 2013a). Acid hydrolysis allows the breakdown of the hemicellulose chain into xylose monomers (C5 sugar), while enzymatic hydrolysis allows the production of glucose monomers (C6 sugar) from cellulose.

On the other hand, the process of obtaining fermentable sugars from starchy materials is based on the processes of liquefaction and saccharification of the starch present in these materials. This process results in a solution rich in glucose, which can be used in fermentation processes such as the production of ethanol (Julian et al., 2015; Pervez, Aman, Iqbal, Siddiqui, & Ul Qader, 2014; Sánchez et al., 2008).

Due to the technological difference presented by the composition of the raw material, the yields obtained in each case may present some differences. Similarly, differences in economic, environmental and energy aspects are also possible. For this reason, this paper studies the production of ethanol using two different raw materials: first, a starchy material such as cassava is analyzed, secondly, sugarcane bagasse is considered, which is a lignocellulosic material. The **sections 2.4.2.1** and **2.4.2.2** describe the process of obtaining ethanol from each of the raw materials under consideration.

2.4.2.1. Ethanol from starchy materials: case cassava

The fuel ethanol production process consists of the following steps: Conditioning and pretreatment, biotransformation, separation and purification. The design of the ethanol production process is based on the developed process by Cardona and Quintero et al. (Carlos Ariel Cardona et al., 2010; Julian et al., 2015), which it is presented in **Figure 2-3**. The fresh cassava is subjected to a process of cut and sieve, to reduce its size up to 4 mm. Then, a gelatinization process to dissolve polysaccharides is applied, aiming to improve the enzymatic hydrolysis. This process is carried out at temperatures higher than gelatinization (i.e. 63 °C) with continuous agitation to slow down viscosity and prevent the formation of gel when it is cooled (Aristizábal & Sánchez, 2007). To obtain a partial starch hydrolysate (liquefied starch), cooked starch is subjected to a treatment with α -amylase. This treatment takes place in a bioreactor at 88 °C, obtaining a hydrolysate of cassava. The hydrolysate is then sent to a bioreactor where amyloglucosidase is added to convert starch fragments into glucose. The glucose solution is sent to another bioreactor in which the sugar is converted into ethanol using *Saccharomyces cerevisiae* at 31 °C. The yeast biomass is separated by conventional sedimentation. The liquor obtained contains a concentration of 8 – 10 % in weight of ethanol. This is destined to a conventional separation process identified for first generation fuel ethanol process. This process begins with distillation followed by rectification. The distillation was realized at 1 bar of pressure obtaining a concentration of ethanol of 56.7 % and with the rectification process this concentration is increased at 86.7 %. In order to increase the concentration of ethanol, the ethanol solution obtained in the rectification is sent to preheating at 116 °C and then a stage of adsorption with molecular sieves. The adsorption process is carried out in vapor phase and with the help of two columns. The operating cycle of the two adsorption columns comprises the pressurization of the column (that was carried out using the distillate preheated from rectification column),

adsorption of water (in this period the product is removed), and desorption of water (that was carried out with a fraction of the vapors of the product). Desorption of water was simulated at 0.14 atmospheres of pressure (Julián Andrés Quintero, Montoya, Sanchez, & Cardona, 2007). Vapors resulting from the desorption process were recycled back to the rectification column where the used ethanol was recovered. While one of the adsorption columns operates under pressure obtaining 99.5 %v/v of ethanol, the other one is regenerated.

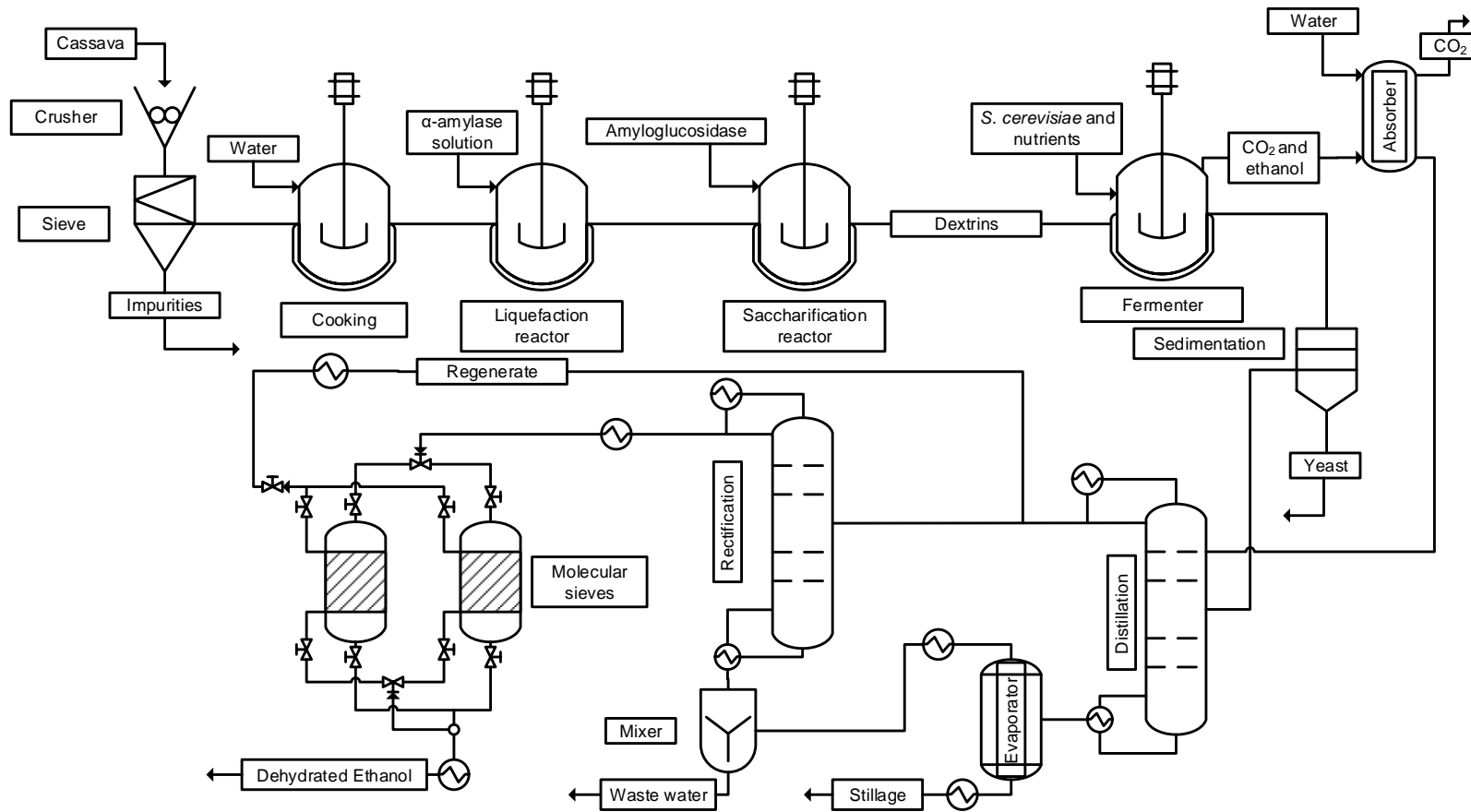


Figure 2-3. Flowsheet of ethanol production for the Cassava case.

2.4.2.2. Ethanol from lignocellulosic biomass: case sugarcane bagasse

The process implemented in the simulation for this case is shown in **Figure 2-4** and is based on previous work (Daza Serna, Solarte Toro, Serna Loaiza, Chacón Perez, & Cardona Alzate, 2016; Moncada, Hernández, Chacón, Betancourt, & Cardona, 2015; Julián A. Quintero et al., 2013a). First, the particle size reduction to a 16 mesh screen with the assistance of milling and sieving equipments is carried out. Then, pretreatment step is carried out with chemical agent for the solubilization of hemicellulose to better accessibility of the enzyme to cellulose (Jung & Kim, 2014; Sun, Sun, Cao, & Sun, 2016). Pretreatment with dilute acid was selected based on Esteghlalian (Esteghlalian, Hashimoto, Fenske, & Penner, 1997), using a load of solids of 10 % wt at 160 °C and sulfuric acid concentration of 0.9 %wt. After, it is necessary to perform a wash for complete recovery of sugars hydrolyzed and neutralize the fraction solid. Separating the solid and liquid fractions was done with a filter, the liquid fraction has toxic compounds formed in the pretreatment step as furfural, HMF and acetic acid which are fermentation inhibitors (da Silva Martins, Rabelo, & da Costa, 2015; Guo, Cavka, Jönsson, & Hong, 2013). For this reason is necessary to carry out an evaporation to concentrate and a detoxification for removal of inhibitors with help of temperature and chemical agent. Operating condition of detoxification with overliming are based on Purwadi *et. al.* for calcium hydroxide at 60 °C and then neutralized to pH 7 of co-fermentation process (Purwadi, Niklasson, & Taherzadeh, 2004). During neutralization, calcium sulfate is obtained and precipitated by the pH change and it is removed by filtration. Thus, it is obtained a xylose liquor that was used in the co-fermentation. The solid fraction obtained above can be denominated as cellulignin (i.e. fiber without hemicellulose) and is an intermediary in the global process, this is easily digested by cellulase and β -glucosidase in a citrate buffer. The enzymes hydrolyze the glycosidic bonds of cellulose to obtain glucose and cellobiose units, a disaccharide composed of two glucose molecules linked by (1-4)- β bonds, which subsequently are broken to obtain monosaccharides. The saccharification reactor is operated at 50 °C with a solids loading of 10% and then, the temperature is increase to 90 °C during five minutes for enzyme denaturalization. The remaining solid, composed mainly of lignin, is removed with the aid of a filter and the liquid phase is concentrated to obtain the glucose liquor mixed with xylose liquor to carry out co-fermentation. The co-fermentation process used a recombinant bacterium *Z. moibilis* with a plasmid pZB5. The plasmid is responsible for gene expression of xylose isomerase, xylulokinase, transketolase involved in the metabolic pathway to

digest xylose and produce ethanol at a temperature of 30 °C (Leksawasdi, Joachimsthal, & Rogers, 2001). Separation and purification steps are consider the same of the **section 2.4.2.1.**

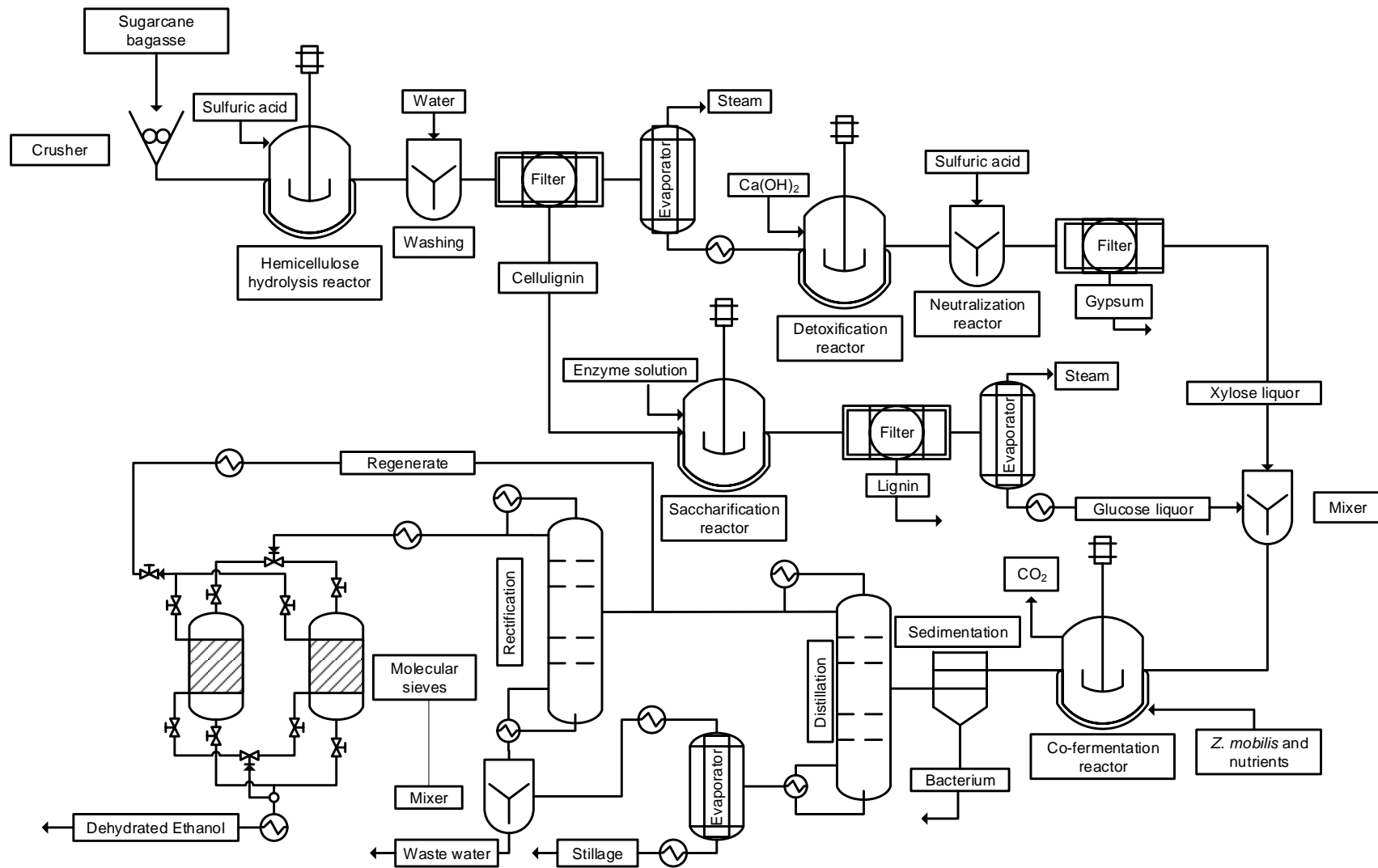


Figure 2-4. Flowsheet of ethanol production for the cane bagasse case.

2.5. Products obtained through the use of the biorefinery concept using SCB as raw material

The products to be obtained in this work are based on the use of SCB as a source of sugar, which will be used as a platform. First, the SCB must be subjected to processes that allow the release of sugars. In order to obtain glucose from SCB, it is necessary to use pre-treatment, which allows the enzyme to have greater accessibility to cellulose (glucose polymer). The pre-treatment used in this case is presented in the **section 2.5.1**. While the enzymatic hydrolysis process is described in the **section 2.5.2**. As object of study were selected the products which are obtained from the **section 2.5.3**.

2.5.1. Pretreatment of the raw material

The raw material (SCB) was subjected to a grinding process, reaching a particle size of 1 mm in diameter. The sugars contained in the lignocellulosic residues were released by using a dilute sulfuric acid treatment (2% v/v). The kinetics employed were those previously reported by Aguilar et al. (2002) (Aguilar, Ramírez, Garrote, & Vázquez, 2002). The resulting solution was filtered, obtaining a liquid fraction (xylose liquor) and solid fraction (cellulose and lignin). The **Figure 2-5** shows the process described previously.

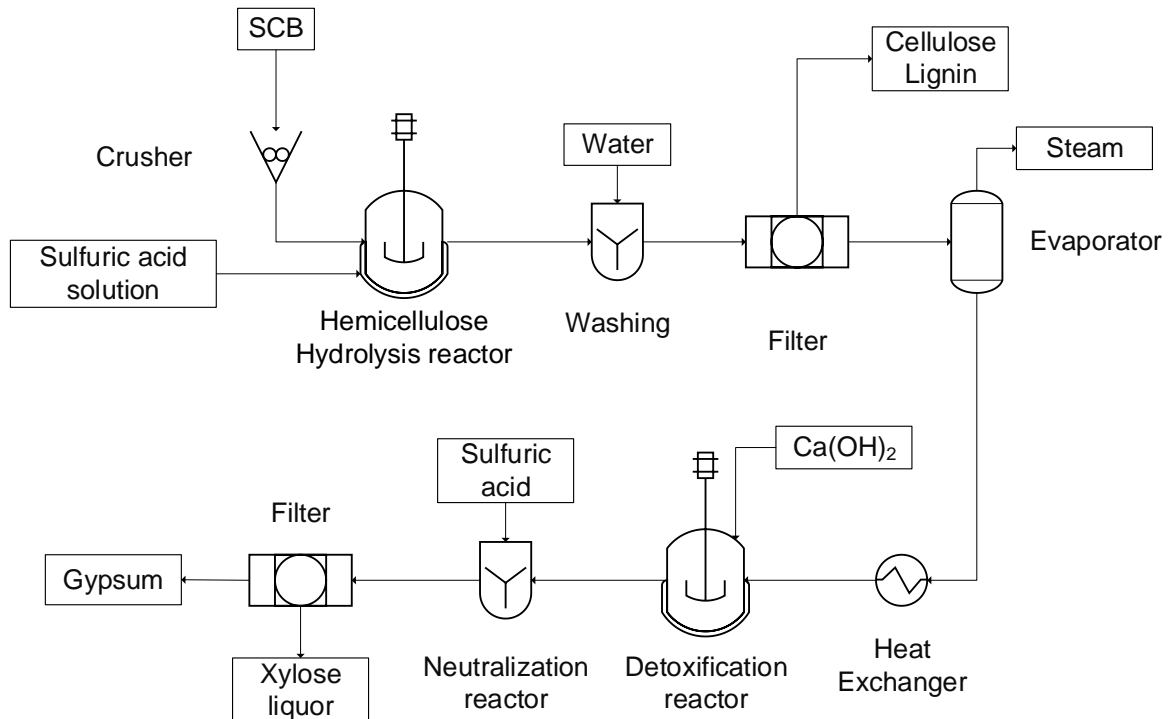


Figure 2-5. Flowsheet for the pretreatment of the SCB

2.5.2. Enzymatic hydrolysis

The solid fraction obtained in the pretreatment (cellulose/lignin) was sent to enzymatic hydrolysis process to release the glucose contained within the pulp. For this, the kinetics reported by Philippidis et al. (1993) (Philippidis, Smith, & Wyman, 1993) was employed. The obtained liquor was subjected to a separation process in which a solution rich in glucose was obtained while lignin was remained as solid fraction. The **Figure 2-6** shows the process described previously.

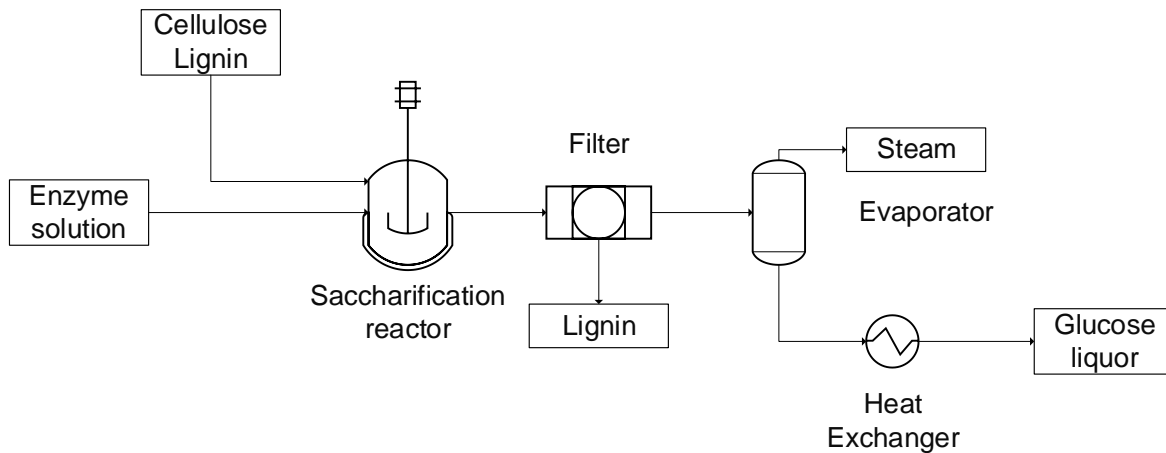


Figure 2-6. Flowsheet for enzymatic hydrolysis of cellulose obtained from SCB

2.5.3. Ethanol production

For the transformation of glucose into ethanol, it is first carried out a sterilization step at 121 °C so that the biological activity is neutralized. Then, *Saccharomyces cerevisiae* is employed for the ethanolic fermentation at a temperature of 37 °C, according to the kinetics reported by *Rivera et al. (2006)* (Rivera et al., 2006). After the fermentation process, the culture medium contains approximately 5-10% concentration in ethanol. In order to increase its concentration, the broth undergoes a distillation, rectification and a dehydration process with molecular sieves. Where the distillation process is based in a beer column, which separates the biomass and a high quantity of water (Aden et al., 2002; Kazi et al., 2010). This process allows that in the rectification process, the ethanol concentration achieved is the azeotropic. Also was employed molecular sieves, which allow to reach an ethanol concentration of 99.6%wt (Pitt, Haag, & Lee, 1983). The **Figure 2-7** shows the process described previously.

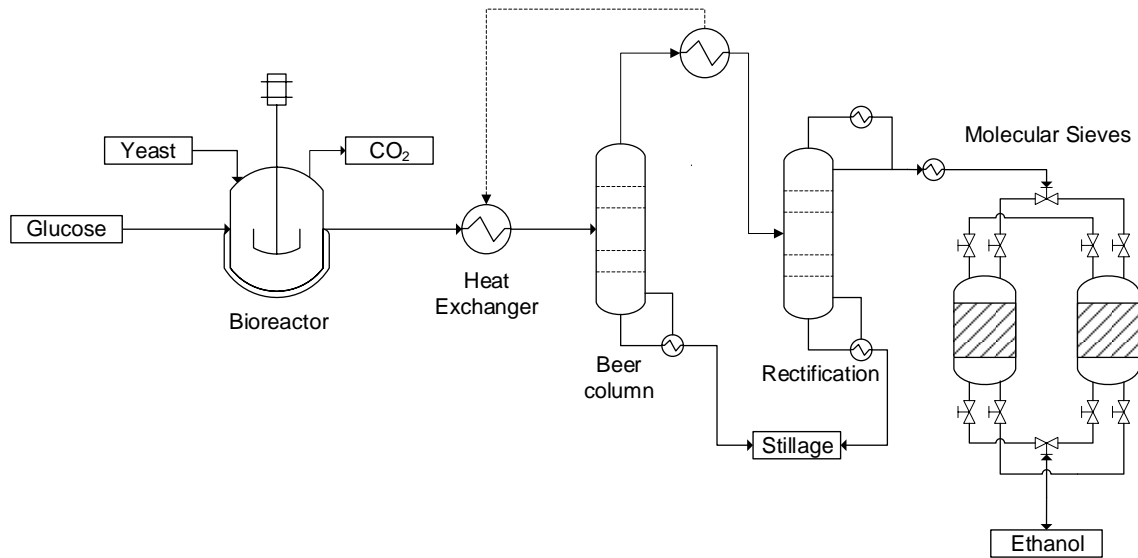


Figure 2-7. Flowsheet for ethanol production from glucose

2.5.4. Xylitol production

The xylose obtained in the pretreatment step is used for the production of xylitol. The fermentation microorganism employed is *Candida parapsilosis* at a temperature of 30 °C. The kinetics used for this case is that reported by Aranda B, J. S. *et al* (2000) (Aranda-Barradas, Delia, & Riba, 2000). After the fermentation, the biomass obtained is separated by means of a filtration process. The obtained liquid fraction is mixed with ethanol in a 1:1 (v/v) ratio in order to precipitate the xylitol (Mussatto, Santos, Filho, & Silva, 2014). Once precipitated the xylitol, it is separated by means of a filtration process. The liquid fraction, is recirculated at the precipitator, with the purpose to increase the yield of precipitation. The **Figure 2-8** shows the process described previously.

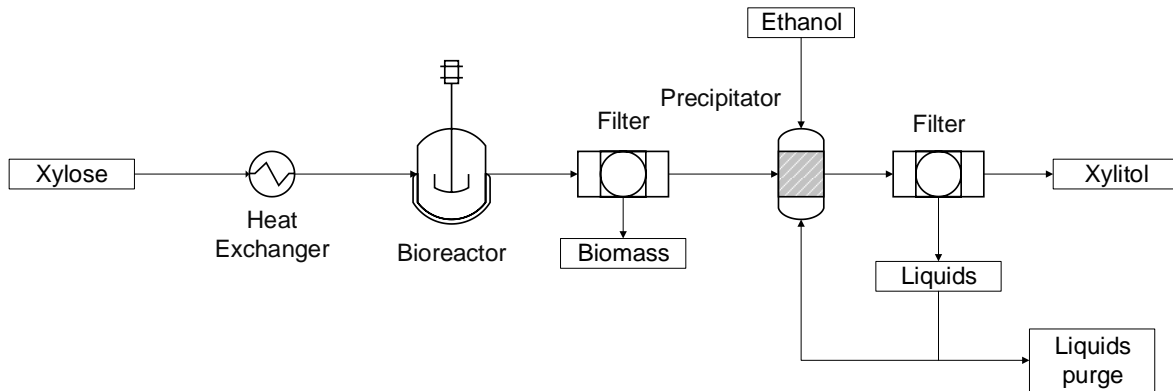


Figure 2-8. Flowsheet for xylitol production

2.5.5. Furfural production

The furfural is produced from the dehydration of the xylose previously obtained. This procedure is based on the work of Cortés, W. (2013) (Cortés, Departamento, Básicas, Jorge, & Lozano, 2013). A reactor operating at 170°C and 10 bar is used for this purpose. The reactor is fed with aluminium and hafnium clays, which are used as catalysts. In order to extract the furfural as it is produced, the reactor is fed air which functions as a recovery agent. For the furfural recovery and purification process, the mixture is depressurized and taken to a distillation tower followed by a decanter. This equipment takes advantage of the low solubility of furfural in water to carry out its recovery (Montastruc et al., 2011). The **Figure 2-9** shows the process described previously.

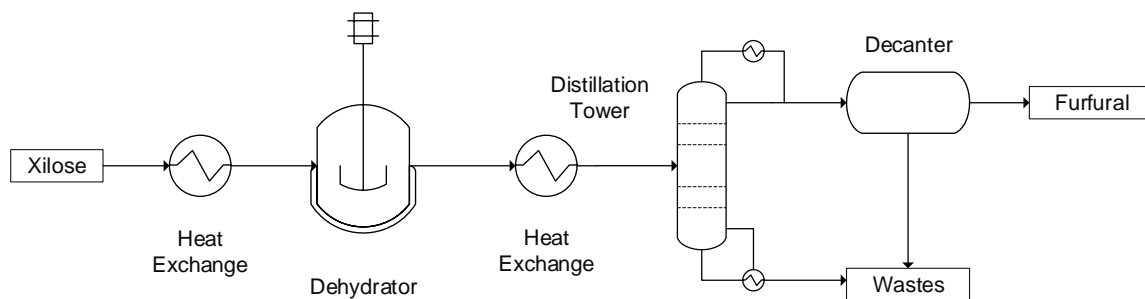


Figure 2-9. Flowsheet for furfural production

2.5.6. Octane production

From the reactions of aldol condensation, hydrogenation and deshydration/hydrogenation the octane is obtained. In a first step, furfural and acetone was mixed in a ratio 1:2, NaOH at 0.03 mol/L was used as catalyst. The reaction was carried out in a solution of ethanol - water (Faba, Díaz, & Ordóñez, 2012), the kinetic of Fakhfakh, N. et al (2008) (Fakhfakh, Cognet, Cabassud, Lucchese, & Días de Los Ríos, 2008). In this process was obtained the 4-(2-furyl)-3-buten-2-one (FAc), which is a precursor of octane. The FAc was hydrogenated at 198°C and 4.05 MPA, using platinum supported over alumina as catalyst, the medium of reaction was hexane (0.25 L of hexane per 0.42 g of FAc). The catalyst was selected based on the high selectivity that present in the octane production (Faba, Díaz, & Ordóñez, 2014). The purification of the octane was carried out using a distillation train, where a purity of 81.72% was achieved. The **Figure 2-10** shows the process described previously.

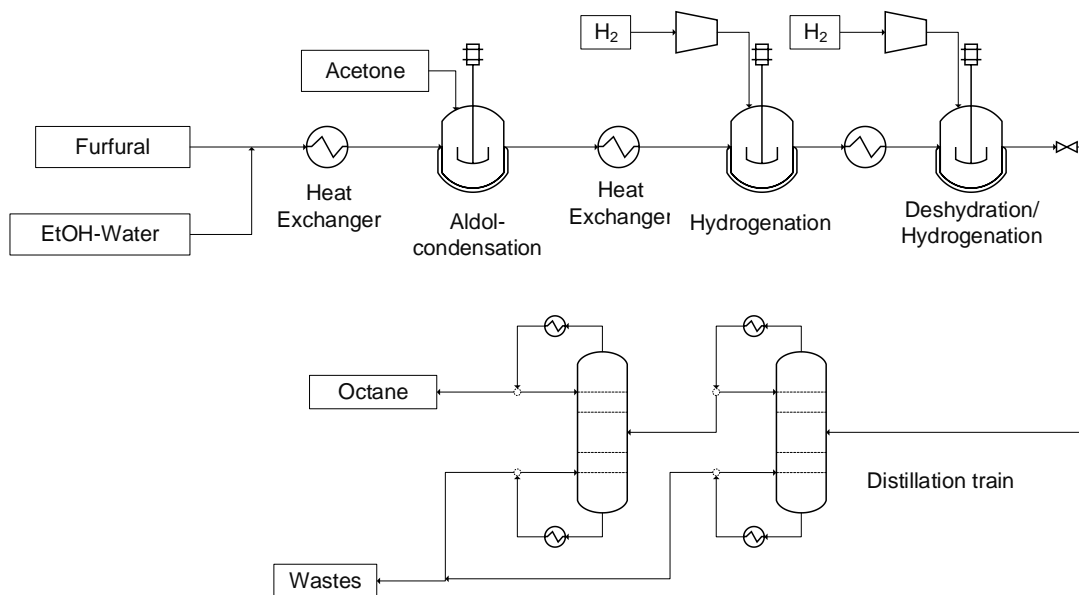


Figure 2-10. Flowsheet for octane production

2.5.7. Gasification process

The lignin obtained from the filtration process of the glucose enters into a gasification process in which it generates a synthesis gas. This gas is passed through a turbine to obtain

electricity, taking advantage of the energy content of the gas obtained in the gasification process. The synthesis gas is composed mainly of H_2 , CO , CH_4 and CO_2 (Manatura, Lu, Wu, & Hsu, 2017). The **Figure 2-11** shows the process described previously. The conditions of the gasification was 60 bar and 850 °C. The syngas obtained was sent to a turbine, where the power was generated.

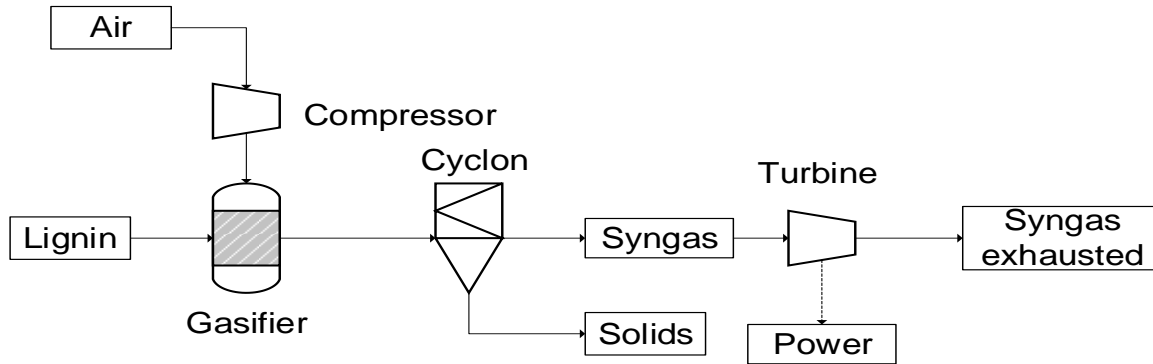


Figure 2-11. Flowsheet for syngas production

2.5.8. Cogeneration process

The syngas obtained in the gasification process has a high caloric power which can be used for steam generation. For this purpose, the process is fed a flow of water which is pressurized to 20 bar. A heat exchanger is then used to completely vaporize the water flow. A flash separator is then used to provide that the liquid phase water is not present in the later stages. Two heat exchangers are used to adjust the temperature to 212°C. The syngas is used as the heating fluid in each heat exchanger. The **Figure 2-12** shows the process described previously.

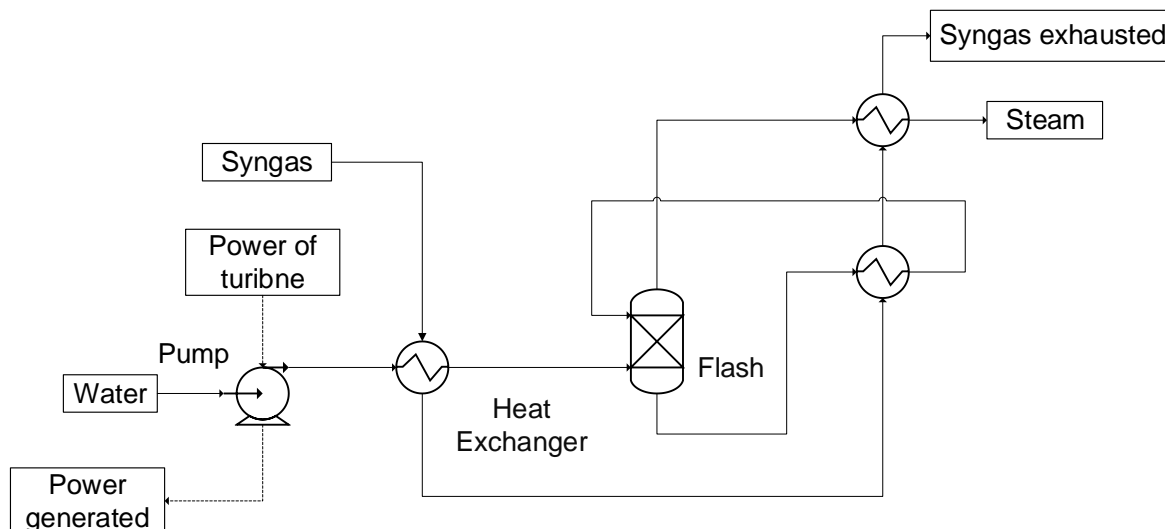


Figure 2-12. Flowsheet for the cogeneration process employed syngas as heating fluid

2.5.9. Poly-hydroxybutyrate (PHB) production

The production of PHB is carried out through a fermentation process using as microorganism *Bacillus subtilis*. The fermentation was carried out according to the methodology and kinetics proposed by Panda, I. (2017) (Panda, Balabantaray, Sahoo, & Patra, 2017). After the fermentation process was carried out a filtration in which recovered the biomass generated in order to undergo an extraction process that allow to obtain the PHB content inside the microorganism.

For the extraction of the PHB content in the biomass of the microorganism, was employed the methodology proposed by Ramsay, J.A. (1994) (Ramsay, Berger, Voyer, Chavarie, & Ramsay, 1994). This methodology apply a pretreatment with acetone in order to facilitate the PHB extraction process. At the stage of pretreatment with acetone, the biomass obtained was mixed with 10 volumes of acetone for 24 h at 25 °C. Acetone was recovered through a filtration process. The pretreated biomass was then mixed with the solvent (chloroform) in a ratio 1:10 solid - liquid. After 12 hours the residual biomass was removed through a filtration process. The solvent was recovered through an evaporation process. PHB solution was concentrated by evaporation then added 2.5 volumes of ethanol cold (4 °C). The suspension was kept cold (0 °C) during 15 min. The precipitate was removed through a filtration process, pressed to remove ethanol and dried at 60 °C for 24 h. The **Figure 2-13** shows the process described previously.

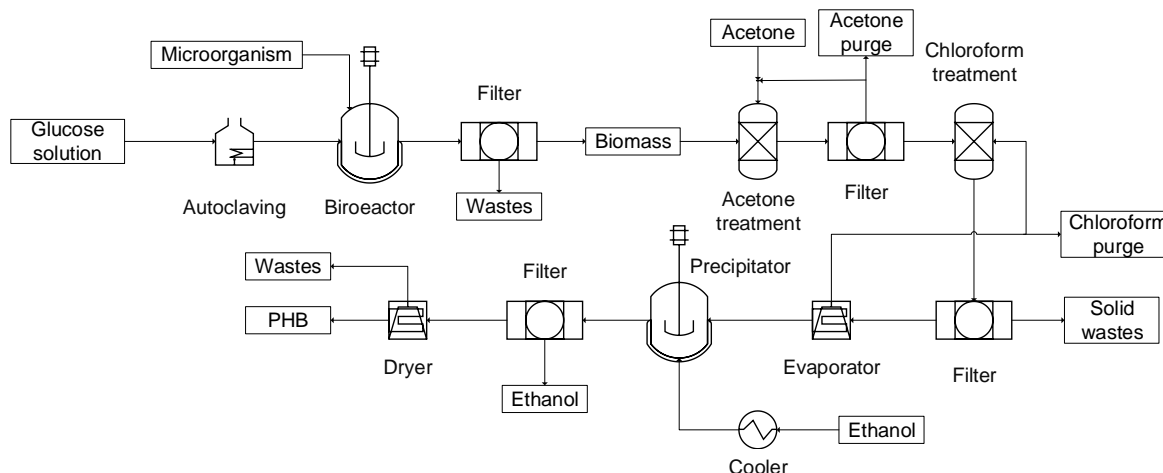


Figure 2-13. Flowsheet for the PHB production

2.5.10. Methanol production

The production of methanol was carried out using syngas as raw material. The process is based on the work of De María, et al (2013) (De María, Díaz, Rodríguez, & Sáiz, 2013). First, the syngas is sent to a compressor and heat exchanger to achieve the operating conditions of the reactor (76.98 bar and 503K). The reactor used is a tubular reactor. The reactor output stream is cooled and then sent to a separator. Where the non-reactive gases are recovered, which are recirculated at the beginning of the process. The mixture composed mainly of methanol and water is sent to a distillation tower. In the bottom flow, the water present in the process is recovered, while methanol is obtained from the distillate. The **Figure 2-14** shows the process described previously.

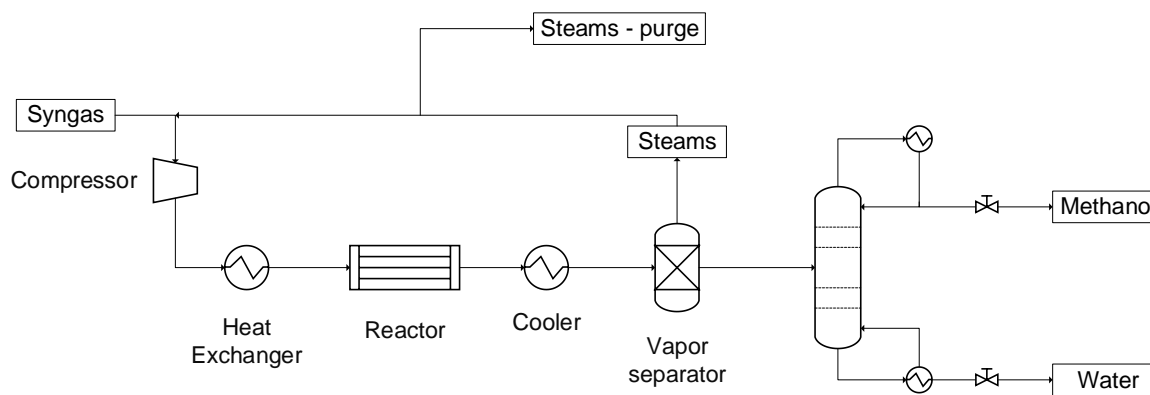


Figure 2-14. Flowsheet for the methanol production from syngas

2.6. Scenarios to be analyzed under biorefinery concept

Based on the different processes described in the **section 2.5**, it is possible to formulate a wide range of transformation processes. For the present work, 4 scenarios presented in the **Table 2-2** are considered. In all the scenarios, three basic processes are considered (pretreatment, detoxification and enzymatic hydrolysis), which allow the obtaining of sugars which are going to be used in the later stages (glucose and xylose). From these sugars, different processing routes are proposed.

Scenario 1 considers the processes of sugar production, PHB production, xylitol, gasification, cogeneration and methanol production. In the gasification process, syngas is generated which presents a high pressure, which makes it attractive to be used in cogeneration processes, in which both electricity and water steam are obtained. In addition, due to its composition (high content of CO, CO₂ and H₂) it can be used as a raw material for obtaining methanol. For this process, the synthesis gas can be used both before and after being subjected to a cogeneration process. In order to evaluate the influence of the implementation of a cogeneration stage, scenarios 1 and 2 are evaluated. Where the first scenario considers the cogeneration process as an intermediate stage between the gasification process and the process of obtaining methanol. While in scenario 2, this stage is not carried out, i.e. the syngas obtained from the gasification process is sent directly to the production of methanol. In scenario 3, the influence of a process change is evaluated. For this purpose, PHB production is replaced by ethanol production, because it is used in the process of purification of xylitol. In scenario 4, the production of xylitol is replaced by the production of furfural. In the scenario 5, the furfural is employed for the octane production. It allows to identify in the transformation process of a raw material how these changes influence at technical, energy, economic and environmental aspects.

Table 2-2. Process involved in each scenario

Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Acid retreatment				
Detoxification				
Enzymatic hydrolysis				
PHB	PHB	Ethanol	Ethanol	Ethanol
Xylitol	Xylitol	Xylitol	Furfural	Octane

Gasification	Gasification	Gasification	Gasification	Gasification
Cogeneration	Methanol	Methanol	Methanol	Methanol
Methanol				

2.7. Energetic assessment

The energy of a system is related to its transformation capacity. This relation is of great importance when is considering processes in which different transformations are carried out to obtain a range of value-added products (Ibrahim Dincer & Rosen, 2013; Moran & Shapiro, 2004). Due that this work is considering a biorefinery for obtaining different products was performed an energy analysis. The purpose of this analysis was to allow the identification of the different energy consumptions and what is the nature of these consumptions. For this analysis, the data corresponding to energy consumption were used, which were obtained from the Aspen Plus software. This information was used by carried out the energy balance for the biorefinery and step by step.

2.8. Exergetic assessment

From the analysis of energy and especially of the exergy, it is possible to identify the zones of the process in which the main energy changes occur. In this way, it is possible to take measures in order to obtain maximum yields in terms of conversion or separation processes and above all the energy yield involved in each stage (Emets et al., 2006; Ruiz-Mercado et al., 2012; D. M. Young & Cabezas, 1999).

The exergetic balance in non-stationary state can be written in a general way, as the exergy that inputs into the system equals the sum of the exergy that output, destroy and lose the system respectively. The exergy balance for a system in a non-stationary state is described by Equation 1. This considers the exergy transfer associated with the mass flows of the system, and the heat and work flows. In addition, it considers the exergy destroyed during the process, which is associated with the irreversibilities of the process (Ibrahim Dincer & Rosen, 2005; Mabrouk, Erdocia, Alriols, Jeday, & Labidi, 2016). Rearranging Equation 1 results in Equation 2, which represents the balance of exergy in a system in a non-stationary state.

$$Ex_{in} = Ex_{out} + Ex_{loss} + Ex_{des} \quad Eq. 1$$

$$\frac{dEx}{dt} = Ex_Q - Ex_W + Ex_{flow} - Ex_{dest} \quad Eq. 2$$

For a system in a stationary state, in which there are no variations in properties over time, Equation 3 (obtained by equating the Equation 2 to zero) represents the exergy balance. Where the terms associated with the flow of exergy by mass, heat and work can be calculated using Equations 5, 13 and 14, respectively. In this way, it is possible to determine the term of destroyed exergy (Equation 4) using Equation 3.

$$0 = Ex_Q - Ex_W + Ex_{flow} - Ex_{dest} \quad Eq. 3$$

$$Ex_{dest} = Ex_Q - Ex_W + Ex_{flow} \quad Eq. 4$$

The exergy change associated with mass flows is divided into four main components: physical, chemical, potential and kinetic exergy (Ibrahim Dincer & Rosen, 2005; Jaimes, Rocha, Vesga, & Kafarov, 2012; Y. Zhang, Li, Li, & Zhang, 2012):

$$Ex_{flow} = Ex^{ph} + Ex^{ch} + Ex^{ki} + Ex^{po} \quad Eq. 5$$

Some authors report that the contributions made by the terms of kinetic and potential exergy are very low compared to the contributions made by the terms of physical and chemical exergy, these can be ignored (Ibrahim Dincer & Rosen, 2005; Jaimes et al., 2012; Y. Zhang et al., 2012), so Equation 5 is reduced to:

$$Ex_{flow} = Ex^{ph} + Ex^{ch} \quad Eq. 6$$

Physical exergy is defined as:

$$Ex^{ph} = \sum_i n_i ex_i^{ph} \quad Eq. 7$$

$$ex_i^{ph} = (h_j - h_o) - T_o(s_j - s_o) \quad Eq. 8$$

The differences $(h_j - h_o)$ and $(s_j - s_o)$ can be calculated from Equations 9 and 10:

$$(h_j - h_o) = \int_{T_o}^{T_j} Cp \, dT \quad Eq. 9$$

$$(s_j - s_o) = \int_{T_o}^{T_j} \frac{Cp}{T} \, dT - R \ln\left(\frac{P}{P_o}\right) \quad Eq. 10$$

The chemical exergy (Equation 11) is calculated to take into account the standard exergy of each component (ex_i^{ch}) which can be found in the literature (see Equation 11). However, it can be determined although the use of Equation 12 (Rivero & Garfias, 2006; Song, Shen, & Xiao, 2011).

$$Ex^{ch} = \sum_i n_i \left(ex_i^{ch} + RT_o \ln\left(\frac{n_i}{\sum n_i}\right) \right) \quad Eq. 11$$

$$ex_i^{ch} = \Delta Gf^\circ + \sum x_i ex_i \quad Eq. 12$$

The exergy associated with the transfer of energy in the form of heat depends on the temperature at which it is produced in relation to the temperature of the reference stable environment. Thus, the heat exergy is determined by the Equation 13. The exergy transfer associated with the work, is determined equal to the mechanical work supplied per stage (Equation 14) (I Dincer et al., 2004).

$$Ex_Q = \int_{T_1}^{T_2} \left(1 - \frac{T_o}{T}\right) \delta Q \quad Eq. 13$$

$$Ex_W = W_{1,2} \quad Eq. 14$$

With Equations 4 - 14 was determined the flow of exergy destroyed in each of the equipment involved in each transformation process. These values were used to determine the amount

of exergy destroyed at each stage of the process. The reference conditions used were 25°C and 1 bar.

2.9. Economic assessment

In the analysis of the feasibility of the process were estimated the costs of utilities using mathematical models presented by Ulrich, G. and Vasudevan P. (2006) (Ulrich & Vasudevan, 2006). From the information reported by Peters M. and Timmerhaus K. (1991) it was possible to calculate labor costs (Peters & Timmerhaus, 1991). Depreciation was calculated using the straight line method. The costs of the equipment were obtained through the use of the Aspen Process Economic Analyzer (ASPEN TECHNOLOGY Inc.) software. Using this information was make the calculation of the net present value (NPV) of the project for the Colombian context for a period of 10 years. The costs of raw material, reagents and the parameters (under the Colombian context) used for the realization of the economic analysis are presented in **Table 2-3**.

Table 2-3. Prices and economic parameters used in the economic assessment

	Price	Reference
Raw material		
Sugarcane bagasse	70 USD/tonne	("Alibaba.com," 2017)
Cassava	38 USD/tonne	(Julian et al., 2015)
Reagents		
Carbon dioxide	1.55 USD/kg	(Cerón Salazar, 2013)
Ethanol	1.24 USD/kg	("ICIS," 2018)
Acetone	0.44 USD/lb	("ICIS," 2018)
Sulfuric acid	25 USD/tonne	("ICIS," 2018)
Hydrogen	1.7 USD/kg	("Alibaba.com," 2017)
Hexane	1,000 USD/tonne	("Alibaba.com," 2017)

Calcium hydroxide	80 USD/tonne	("Alibaba.com," 2017)
Chloroform	0.34 USD/lb	("ICIS," 2018)
Utilities		
Electricity	0.10 USD/kWh	(Dávila,
Fuel	7.21 USD/MMBTU	Hernández,
Water	1.25 USD/m ³	Castro, & Cardona, 2014)
LP steam	1.57 USD/tonne	(Moncada et al.,
MP steam	8.18 USD/tonne	2015)
HP steam	9.86 USD/tonne	
Operating cost		
Supervisor	4.29 USD/h	(Dávila et al.,
Operator	2.14 USD/h	2014)

2.10. Environmental assessment

In order to determine the environmental impact of a process, different methodologies have been developed, such as Greenhouse Gases (GHG), Potential Environmental Impact (PEI) and Life Cycle Assessment (LCA).

- ✓ The objective of the GHG is to calculate the greenhouse gas emissions generated in a process. The GHG calculation can be made taking into account the emissions generated by the production and production of raw materials, the emissions produced by the transformation of raw materials, as well as the emissions during the transport and distribution of the final products. It is therefore necessary to delimit the analysis of greenhouse gases, as this analysis can be carried out at all stages of the production of the final products (ISCC, 2011).
- ✓ The approach of assessment of environmental impacts throughout the life-cycle is called LCA (Reap, Roman, Duncan, & Bras, 2008). This assessment is a methodological tool used to estimate and measure the environmental impact of a product, process or system throughout its life cycle, from the moment the resource is obtained to its recycling or treatment as waste (Finnveden et al., 2009; Reap et al., 2008).

- ✓ The environmental assessment of a process can be performed using the PEI methodology (D. Young, Scharp, & Cabezas, 2000). This approach is related to the impacts of each one of the chemical, biochemical, and thermochemical processes involved in terms of their mass and energy consumptions (Douglas M. Young & Cabezas, 1999).

Both the performance of a GHG analysis and an LCA can be used for the complete evaluation of a process from the obtaining of raw material to the disposal of process wastes. While a PEI analysis is performed primarily on the process, considering only inputs and outputs of the process. In this work a comparison is presented for the obtaining of different products by means of different technologies (stand-alone processes) and different routes of transformation for the same raw material (biorefineries). So the main system to analyze in each case are the different processes of transformation, showing that among the possible environmental analyses the PEI is presented as an applicable tool.

By the determination of the PEI caused by the proposed process, the software developed by the Environmental Protection Agency (EPA): Waste Algorithm Reduction (WAR) is used. It allows to evaluate the environmental impact through eight categories: Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential Exposure (HTPE), Terrestrial Toxicity Potential (TTP), Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Smog Formation Potential (PCOP) and Acidification Potential (AP) (D. Young et al., 2000).

2.11. Exergetic efficiency evaluation

Based on the previously obtained data and with the help of relation reported in literature, exergetic efficiency was determined from the calculated exergy. This process was carried out step by step for each stand-alone process and the biorefineries analyzed. The main relation that can be found is between the exergy at the output, i. e. useful energy that still presents a stream and the exergy at the input (Equation 15) (Caliskan, 2015).

$$\Psi_{pro/RM} = \frac{Ex_{product}}{\sum Ex_{raw\ material}} \quad Eq. 15$$

In addition to Equation 14, it is also possible to find other correlations for exergetic efficiency (Marmolejo-Correa & Gundersen, 2012). One of them, Equation 16 correlates not only the exergy of the raw material with the products, but also the exergy of the other reagents used in the process. On the other hand, the Equation 17 consider the exergy of the products also considers the exergy of the waste obtained in the process.

$$\Psi_{prod/RM+rea} = \frac{Ex_{product}}{\sum Ex_{raw\ material} + \sum Ex_{reagents}} \quad Eq. 16$$

$$\Psi_{prod+w/RM+rea} = \frac{\sum Ex_{product} + \sum Ex_{wastes}}{\sum Ex_{raw\ material} + \sum Ex_{reagents}} \quad Eq. 17$$

**3. Chapter 3:
Technical results
stand-alone
processes and
biorefineries**

3.1. Stand-alone processes

3.1.1. Comparison of technologies for the polyphenolic compounds extraction

Polyphenolic compounds are part of secondary metabolites, being identified more than 8,000 compounds (Bravo, Sources, & Significance, 1998). These components have great benefits for the human health (Ozcan, Akpınar-Bayizit, Yilmaz-Ersan, & Delikanli, 2014), due to their anti-cancer (Cooper, Morr e, & Morr e, 2005; Liu, 2004), anti-diabetic (Gandhi, Ignacimuthu, & Paulraj, 2011), anti-microbial (An et al., 2004) and anti-allergic potential (YAMAMOTO et al., 2004). Cooper studied the health effects of green tea consumption, finding anti-carcinogenic properties associated with the polyphenolic compounds (Cooper et al., 2005). Blanch on the other hand conducted a study of the antioxidant properties and the reduction of degenerative diseases by the consumption of fruits and vegetables rich in polyphenolic compounds (Chiva-Blanch & Visioli, 2012). Different conventional and non-conventional technologies are employed for the extraction and purification of polyphenolic compounds. Among conventional technologies, solid-liquid extraction is the most widely studied (Baydar,  zkan, & Sagdic, 2004; Lapornik, Prošek, & Golc Wondra, 2005; Pekić, Kovač, Alonso, & Revilla, 1998; Tasioula-Margari & Tsabolatidou, 2015). This type of technology uses high amounts of solvent, causing that in the purification stage of the compounds requires greater amounts of energy to be used for recovery (Khaw, Parat, Shaw, & Falconer, 2017). In addition, these solvents can reduce the applicability of extracts since even at low concentrations it is harmful to humans, so it cannot be used in some industries (e. g. food and cosmetics) (Dick, 2006). In order to surpass this obstacle and improve performance in extraction processes, techniques as non-conventional and SFE have been developed based on the use of solvents that do not present such a high risk to humans. This process uses CO₂ as a solvent, which is a non-toxic, non-flammable compound with relatively low critical temperature and pressure (31.06°C and 7.386 MPa) (Shilpi, Shivhare, & Basu, 2013). These characteristics prevent thermal degradation of the compounds that are being extract. On the other hand, this process does not involve the generation of large quantities of waste, making it an environmentally friendly separation process. This characteristic is due to the fact that CO₂ can be recycled, thus reducing the acquisition costs of this compound (Ameer, Shahbaz, & Kwon, 2017; Chandrakant, Pravin, Bharat, Sachin, & Amol, 2011).

In this work, tree tomato peels were used as raw material for obtaining polyphenolic compounds. This is due to the high content of extractives present in this raw material (see **Table 2-1**) in comparison with raw materials such as SCB, coffee cut stems, empty fruit bunches and risk husk, which have less than 10% of their composition in extractives (Julián A. Quintero et al., 2013a). Presenting also a higher content of extractives than orange, lemon and mandarin peels, which have been studied for extraction processes (Mamma, Kourtoglou, & Christakopoulos, 2008; Marín, Soler-Rivas, Benavente-García, Castillo, & Pérez-Alvarez, 2007). In addition to having a high content of extractives, the tree tomato peels are a residue that is obtained when using the fruit in processes of elaboration of juices and other food products. Showing an advantage by not competing with food safety. On the other hand, this residue presents within its composition a considerable percentage of cellulose and hemicellulose, polysaccharides that by means of different processes can be hydrolyzed to obtain sugars. Where these sugars can be used in different transformation processes. In this way, the waste obtained from the extraction process could be used.

Both the pulp and the peels of tree tomato have been studied in extraction processes. Vasco (2009) reports that depending on the variety of tree tomato used (Purple-red or Golden-yellow); the content of phenolic compounds in the pulp will be different. Where the purple-red variety has a higher content of phenolic compounds (6.20 mg GAE/g), while the Golden-yellow variety has about half of this value (3.87 mg GAE/g) (Vasco, Avila, Ruales, Svanberg, & Kamal-Eldin, 2009). Variations in the extraction process such as the solvent used and its concentration have shown higher concentrations of phenolic compounds. An example of this is the studies conducted by Mutalib (2016), which used 80% ethanol for the extraction of phenolic compounds from tree tomato pulp (Mutalib et al., 2016). Under these conditions, Mutalib (2016) reports concentrations of 7.63 mg GAE/g. However, as reported by Torres (2012), as the concentration of methanol in the tomato pulp extraction process increases, the concentration of phenolic compounds obtained may decrease (Torres, 2012). Ali Hassan & Abu Bakar (2013) and Mandal & Ghosal (2012) report similar values for the concentration of phenolic compounds for tomato tree peel (4.89 and 4.11 mg GAE/g, respectively) (Ali Hassan & Abu Bakar, 2013; Mandal & Ghosal, 2012). Methanol was used as a solvent in both studies.

Comparing the results obtained by Ali Hassan & Abu Bakar (2013) and Mandal & Ghosal (2012) for tree tomato peel (Ali Hassan & Abu Bakar, 2013; Mandal & Ghosal, 2012), the concentrations of phenolic compounds obtained for both SE and SFE were higher in the

present study. First, a change from methanol to ethanol solvent was made. While Ali Hassan & Abu Bakar employed a 1:50 solid-liquid ratio for the SE, in the present paper the ratio employed was 1:20 solid-liquid. On the other hand, the value reported by Mandal & Ghosal corresponds to a Soxhlet extraction process. These modifications in the extraction processes lead to differences in the results obtained in each case. Comparing the present work with that reported by the authors mentioned above, it is observed that under the extraction conditions analyzed it is possible to obtain a higher concentration of phenolic compounds.

Comparing the results of the extraction processes presented in the

Table 3-1 it is observed that the use of SFE allows obtaining an extract with a higher antioxidant activity. However, the amount of polyphenolic compounds obtained is less than the concentration obtained by using SE. When using SFE as extraction technology the extraction efficiency decreases by 32.6%. Considering that the contact time between the raw material and the solvent is less in SFE than in SE, it is possible that the solvent does not penetrate completely into the lignocellulosic matrix to carry out the extraction process. On the other hand, when considering the extraction yield as a function of time, the use of SFE allows obtaining an extract with a high concentration of phenolic compounds in a less time.

Table 3-1. Concentration of polyphenolic compounds from SE and SFE employed tomato tree as raw material

	Units	Solvent extraction	Supercritical fluid extraction
TPC	(mg GAE/g)	10.95 ± 0.03	7.38 ± 0.29
Antioxidant Activity	(µg/mL)	413.52 ± 4.62	592.21 ± 5.19
Chlorogenic acid	(mg/g)	0.49 ± 0.04	1.35± 0.02
Ferulic acid	(mg/g)	0.14 ± 0.01	0.05± 0.01
Quercetin	(mg/g)	0.02 ± 0.00	0.04± 0.00

Analyzing the simulation process proposed in section 2.3.1. both for SE and SFE, the flows of phenolic compounds correspond to 324.04 and 310.01 kg/h, considering a raw material flow of 1,000 kg/h. Values corresponding to 84.75 and 81.08% of the total extractive content for SE and SFE, respectively. With respect to the total flow of raw material corresponds to extraction yields of 32.40 and 31.00%, respectively. Showing that with SE it is possible to obtain a higher flow of phenolic compounds than with the use of SFE.

3.1.2. Ethanol obtaining

According to the composition of raw material presented in the **Table 2-1**, the yields of ethanol per ton of feedstock expected were 190.13 L/ton of cassava and 258.7 L/ton sugarcane bagasse (considering the cellulose and hemicellulose). However the proposed process only achieve between 73 to 53% of the theoretical yield and even are lower than reported for stand-alone process presented in

Table 3-2. For SCB the difference can be attributed for physico-chemical composition in the raw material especially moisture content that reduces the quantity of cellulose and hemicellulose available for the information reported for Quintero et. al. (Julián A. Quintero et al., 2013a). In Cassava case the difference with respect to the yield obtained for Cardona et. al. (Carlos Ariel Cardona et al., 2008) can be attributed for the enzymes efficiency. This behavior reflects the influence of the different existing technologies for obtaining fermentable sugars from these biomass. For cassava can be consider technologies like simultaneous saccharification and fermentation (SSF) for improving yields and involves fewer equipment or even more innovative process known as simultaneous liquefaction, saccharification and fermentation (SLSF). Also, the behavior of process yield can be attributed to the microorganisms used because they have different metabolic pathways for consuming the substrates used.

In lignocellulosic biomass case, the results has to note because the fuel ethanol production was very close to the production obtained from cassava that corresponds of 32,654 liters of ethanol per day and 33,099 liters of ethanol per day, respectively. The use of this present a great opportunity for fuel ethanol production instead of Cassava that despite the great performance of production yield for the world and in Colombia (i.e. 102.26 tons cassava per ha in 257,621 ha (Food and Agriculture Organization of the United Nations (FAO), 2014)) its availability is limited for be a feedstock of food industry. This is reflected in the use of

60% of cassava world production for food, 33% animal feed and only 7% in the industry of textile, paper, food and fermentation (A. Pandey et al., 2000). Additionally, the amount generated from sugarcane bagasse in the world annually is close to 280 kg of sugarcane bagasse for 540 MMT of sugar cane dry processed (C. A. A. Cardona et al., 2010). In the case of based fuel ethanol production from cassava should be considered the use of bitter species for produce fuel ethanol to not affect the markets prices and food security especially in developing countries.

Table 3-2. Yields in the production the ethanol using as feedstock cassava and SCB.

Feedstock	Yield (L/ton)	Reference
Cassava		
Solid-state ethanol fermentation	361	(Sato, Nakamura, & Sato, 1985)
Liquefaction and SHF with yeast	164.47	(Julian et al., 2015)
Liquefaction and SSF with yeast	184.07	
Liquefaction and SSF with bacterium <i>Z. mobilis</i>	181.03	
Liquefaction and SHF with yeast	166.80	(Carlos Ariel Cardona et al., 2008)
Liquefaction and SHF with yeast	139.69	This work
Sugarcane bagasse		
<i>Stand-alone</i>	280	(Kim & Dale, 2004)

From cellulose and hemicellulose in co-fermentation	74.55	(Julián A. Quintero et al., 2013a)
From cellulose and hemicellulose fermented with different microorganisms	323.19	(Duque, Cardona, & Moncada, 2015)
From cellulose and hemicellulose in co-fermentation	137.81	This work
<i>Biorefinery context</i>		
(from cellulose)	56.37	(Aristizábal
(from hemicellulose)	92.78	M. et al., 2015)

3.2. Products obtained under biorefinery concept

3.2.1. Xylose and glucose production

The sugars obtained as a result of the use of SCB as raw material are the basis of the different scenarios proposed in **section 2.6**. Dilute acid pretreatment (**section 2.5.1**) followed by enzymatic hydrolysis (**section 2.5.2**) was used for this purpose. A xylose-rich solution can be obtained from pretreatment with dilute acid, while a glucose-rich solution can be obtained from enzymatic hydrolysis. Under the conditions analyzed, the concentrations of xylose and glucose obtained were 16.93 and 57.29 g/L, respectively. Values corresponding to yields of 0.0813 g of xylose and 0.2261 g of glucose per g of SCB processed. In the case of acid hydrolysis, the percentage of hydrolyzed hemicellulose was 89.93%. Besides xylose, other compounds were obtained such as glucose, acetic acid and furfural acid with concentrations of 2.28, 2.78 and 0.39 g/L, respectively. With yields of 10,964 mg of glucose, 13,364 mg of acetic acid and 1,887 mg of furfural per g of processed SCB. In the enzymatic cellulose hydrolysis process, the hydrolyzed percentage was 99.97%. Obtaining in the process a glucose solution with a concentration of 57.29 and a yield of 0.2261 g of glucose per gram of SCB processed. In addition to glucose, the

enzymatic hydrolysis process generated cellobiose with a concentration of 2.21 g/L and a yield of 8,713 mg of arabinose per g of processed SCB.

Aguilar et al (2002) report that for the same conditions of the acid hydrolysis process it is possible to obtain concentrations of 21.6 g of xylose/L , 3.65 g of acetic acid/L , 3 g of glucose/L and 0.5 g of furfural/L, with a hydrolyzed percentage of hemicellulose of approximately 90% (Aguilar et al., 2002). Rodrigues et al (2010) report that, for a dilute acid treatment, concentrations of 19.19 g of xylose/L, 3.49 g of acetic acid/L, 1.82 g of arabinose/L, 0.981 g of glucose/L, 0.082 g of furfural/L and 0.0071 g of 5-Hydroxymethylfurfural/L were obtained in the process (Rodrigues et al., 2010). Gámez et al (2006) report that using 4% phosphoric acid, concentrations of 17.6 g of xylose/L, 4.0 g of acetic acid/L, 3.0 g of glucose/L, 2.6 g of arabinose/L and 1.2 g of furfural/L were obtained (Gámez, González-Cabriales, Ramírez, Garrote, & Vázquez, 2006). The concentration of xylose obtained in this thesis is lower than that reported by Aguilar et al (2002) because the SCB used by him had a composition of 20.6% db, while the concentration used in this work was 12.05% w/w (see **Table 2-1**). In the case of Rodrigues et al (2010) the hemicellulose concentration was 24.1% w/w. Gámez et al (2006) used a SCB with a hemicellulose concentration of 20.6% w/w. Thus showing the influence of the initial concentration of hemicellulose on the acid hydrolysis process.

Enzymatic hydrolysis of SCB Adsul et al (2005) reports concentrations of 19.5 mg of reducing sugar per g SCB (Adsul et al., 2005). Compared to the results of this thesis, there are no significant differences. When analyzing other raw materials such as office paper, it is possible to observe that these present better yields in terms of sugar production by means of enzymatic hydrolysis. Kurakate et al (2007) report that from the enzymatic hydrolysis of office paper 241 mg of glucose per g of office paper can be obtained. However, with modifications in the process, more specific in the strain of the microorganism employed concentrations of 645 mg of glucose per gram of office paper can be achieved (Kurakake, Ide, & Komaki, 2007).

Comparing the results obtained in this thesis for SCB with the results reported by Moncada et al (2016) for *pinus patula* bark (Moncada et al., 2016), this last raw material presents a greater predisposition to obtaining xylose (concentrations of 20 g/L were obtained with a

yield of 15%) since it presents a higher concentration of hemicellulose. While the SCB used in this thesis presents higher yields in the production of reducing sugars from saccharification processes (from the *pinus patula* bark Moncada et al (2016) reports yields of 10 g per 100 g of dry feed). Compared to residues such as potato peels which are composed of 55.25%, 14.24%, 11.71%, 10.00% and 8.8% cellulose, lignin, hemicellulose, moisture and ash, respectively, lower yields were obtained in terms of xylose and glucose concentration. With the use of potato peel as raw material concentrations of 26.32 g xylose per 100 g dry potato peles and 53.8 g glucose per 100 g dry potato peel, was achieved (Moncada et al., 2016). In the case of wheat straw as raw material, yields of 0.21 g xylose/g dry matter straw and 0.40 g/g dry matter straw, was obtained. This raw material has a concentrations of cellulose and hemicellulose of 36.3 and 19%, respectively (Kootstra, Beeftink, Scott, & Sanders, 2009).

3.2.2. Ethanol production

Using a glucose flow of 1,346,759.06 kg/h (1,410.12 m³/h) with a concentration of 57.29 g/L (dissolved in water) an ethanol flow of 34,453.1 kg/h (26,167.7 m³/h) with a purity of 99.60% was obtained. Showing a yield of 42.65 g of ethanol per 100 g of glucose processed, which corresponds to a glucose conversion fraction of 92.22%, and a yield of 9.64 g of ethanol per 100 g of SCB. Obtaining a yield 16.60% lower than the theoretical yield (51.14 g of ethanol per 100 g of glucose (Kurakake et al., 2007)). With the ethanol purification and concentration system used, it was possible to recover 95.28% of the ethanol obtained in fermentation.

3.2.3. PHB production

From the glucose flow and concentration obtained in the enzymatic hydrolysis stage, a flow of 59,261.8 kg/h of PHB was obtained. These correspond to a recovery percentage of 97.90% of the PHB obtained in the first stage of extraction. Where the yield was 16.59 g PHB per 100 grams SCB. The percentage of glucose conversion in PHB was 73.36%.

3.2.4. Xylitol production

With the flow of xylose obtained 28,574.2 kg/h of xylitol (20,113 m³/h) were obtained with a purity of 88.41%. The conversion rate of xylose to xylitol was 98.42% and the yield was 7.99 g xylitol per 100 grams SCB.

3.2.5. Furfural production

Using a solution of xylose with a flow rate of 1,690,955.36 kg/h (15.72 g of xylose/L) 16,573.5 kg/h of furfural were obtained with a purity of 96.73%. A yield of 4.64 g of furfural per 100 grams of SCB is achieved.

3.2.6. Octane production

Using the furfural obtained in a previous stage, an octane flow of 10,135.3 kg/h (16.1966 m³/h) was obtained. With a purity of 94.03% which corresponds to a recovery rate of 82.49%. The furfural conversion was 90.28% and the yield of 2.84 g octane per 100 grams of SCB was obtained.

3.2.7. Gasification

Using 49,781.1 kg/h of solids (lignin, cellulose, hemicellulose and ash) (370,801 kmol/h) and an air flow of 43,275.6 (37,178 m³/h) (1,500 kmol/h) a syngas flow of 88,991.6 kg/h (17,277.1 m³/h) composed of 0.3316 CO₂, 0.3730 N₂, 0.2006 H₂, 0.0579 CO, 0.0368 CH₄ was obtained. A yield of 2.91 g syngas per 100 grams of SCB was obtained. The syngas obtained presented an energy flow of 10,522.8 MJ/h.

3.2.8. Cogeneration process

Through the use of the calorific value present in the syngas in cogeneration processes, both electricity and water vapour were obtained. With the process used in this thesis, 41,953.89 kW and 1,282 m³/h of water vapor (12,500 kg/h) were generated with a temperature and pressure of 212°C and 20 bar, respectively. The steam generated has an energy flow of 164,052 MJ/h.

3.2.9. Methanol production

Using the syngas obtained in the gasification stage both with and without an intermediate cogeneration stage, 21,447.5 kg/h of methanol are generated (29.38 m³/h), with a purity of 98.32%. A yield of 6.00 g methanol per 100 grams of SCB was achieved. The percentage of methanol recovery generated was 72.78%. The conversion rates of CO₂, CO and H₂ were 15.00%, 38.99% and 1.35%, respectively.

3.3. Final remarks

It was demonstrated that it is possible to obtain high quality polyphenolic compounds by means of the SFE technology. In addition, interesting yields were obtained to further study the potential of obtaining metabolites by means of the technology of supercritical extraction from residues of tomato tree.

The composition of the raw material and the technology used to obtain products such as ethanol lead to variations in the yields obtained in the process. However, when comparing raw materials from which it is possible to obtain similar yields, such as cassava and SCB, there are no significant variations in the process yield. This shows the technical feasibility of obtaining ethanol from both cassava and SCB. Where the selection of one raw material or another will depend on the availability of each raw material.

The selection of a raw material processing route can lead to a better use of the raw material. The change from PHB production to ethanol production causes a decrease in the use of SCB. While 9.64 g of ethanol are obtained per 100 g of SCB, with the production of PHB the yield is 16.59 g per 100 g of SCB. Showing that the production of PHB allows a better use of the raw material. A similar case is the one presented for the production of xylitol and furfural, which present yields of 7.99 and 4.64 g of product per 100 g of SCB, respectively. When furfural is used to obtain octane, a yield of 2.84 g per 100 g of SCB is obtained. The decrease in yield is due in part to the loss of product in the recovery process, as well as to the conversion from furfural to octane. In the case of syngas, the yield obtained was 24.91 g per 100 g of SCB. When used to obtain methanol, they yield 6.00 g of methanol per 100 g of SCB. From the yields presented it can be seen that SCB has greater potential for the combined production of PHB, xylitol and syngas than other combinations of the products analyzed.

**4. Chapter 4:
Energy and
exergy
assessment**

4.1. Stand-alone processes

4.1.1. Compounds extraction

The energy consumption in a process is distributed in its different stages. Where in each of these depending on the equipment used, a different energy requirement will be presented. Stages such as the pretreatment of the raw material, the reaction zone and the purification zone are of great interest when analyzing the energy consumption of a process. In addition, intermediate stages are to be considered in which the conditioning of a particular stream is carried out for further processing steps.

When analyzing the production of polyphenolic compounds from tomato tree peels, it is possible to find three main stages: pretreatment of raw materials and reagents, extraction and purification of the product. Comparing extraction technologies such as SE and SFE, there are differences both in the area of raw material pretreatment and in product purification. While with SE the conditioning zone is made up of drying, grinding and temperature adjustment processes, with the use of SFE pressure conditioning processes must be added. In the product purification zone with SE, a distillation tower is used, while with SFE a phase separator and evaporator are required. These differences mean that the energy consumption presented in each case is completely different. While with SE it is necessary to use 62.85 MJ per kg of tree tomato peel processed, with the use of SFE the energy consumption was 1.36 MJ per kg of tree tomato peel processed. In the case of SE, 94.73% of energy consumption was in the phenolic compounds purification zone. This is because this technology uses a large amount of solvent, which makes the separation process difficult. In the case of SFE, the areas of the process with the highest energy consumption are CO₂ conditioning and CO₂ recovery (55.80 and 43.65%, respectively). This is because CO₂ must pass from -19°C to 50°C before entering the process.

In the case of the exergy consumed by both processes was observed that SE and SFE presented 120,811.10 and 1,898.40 kW consumption, respectively. Where in a similar way to present in the energy consumption, for SE process the stage of purification which was contributed to increase this value. However, in the case of SFE distribution of exergy consumption was different in comparison with observed in energy consumption. As in the case of energy consumption, the CO₂ recovery was presented the greatest contribution to

the value of exergy (36.87 %). Another step that presents a greater participation in the exergy is the extraction process with a 26.12%. This is caused by the irreversibilities presented in the process of extraction due to the destruction of the structure of the raw material. Not only from the energy point of view, too from the point of view exergetic SFE had the lowest values in both cases. Thus showing the advantages of this process over the SE.

Table 4-1. Results energy and exergy for the polyphenolic compounds extraction from tree tomato peel

Technology	Energy (MJ/kg)		Exergy (MJ/kg)	
	SE	SFE	SE	SFE
Total process	62.55	1.36	434.92	6.83
Percent distribution				
Pretreatment	2.16	55.80	0.17	17.99
Extractor	0.61	0.13	0.04	26.12
Purification	94.73	0.06	99.75	13.81
Recovered ethanol	2.49	0.35	0.04	5.21
Recovered CO ₂	-	43.65	-	36.87

4.1.2. Ethanol production

In the **Table 4-2** are presented the energy consumption for each stage for ethanol production using as feedstock cassava and SCB. The stages considered are milling and pretreatment, hydrolysis and fermentation, separation and purification, and finally the concentration of stillage. In this sense it is observed that when cassava is used as a feedstock is required 40.52 MJ per liter of ethanol produced. An amount much lower than required with bagasse which is 241.10 MJ/L energy (Marcela & Montoya, 2012).

A comparison of both processes shows that the use of SCB as a raw material for ethanol production requires more energy in comparison with cassava as raw material. Where stages such as hydrolysis and fermentation and the stillage concentration have the highest

energy consumption in the case of SCB. In the case of cassava as a raw material, the stages that present the highest energy consumption are the separation and purification of ethanol and the stillage concentration. It shows the importance of evaluating new technologies to reduce the energy consumption caused by the concentration of the stillage in this process. On the other hand, analyzing the hydrolysis and fermentation stage for both raw materials it is observed that given the process conditions for SCB, the energy consumption is higher with this raw material. Showing the influence of the type of technology used, as well as the raw material. This is because in the case of SCB, the hydrolysis process is carried out at temperatures higher than those used in the cassava hydrolysis.

Table 4-2. Energy consumption per stage in the production of ethanol

Feedstock	Cassava			Sugarcane bagasse		
Stage	kW	MJ/L	Percentage	kW	MJ/L	Percentage
Milling and pretreatment	584.36	1.53	3.76	17,880.41	47.31	19.62
Hydrolysis and fermentation	2,433.63	6.35	15.68	34,490.33	91.26	37.85
Separation and purification	4,448.90	11.61	28.66	10,381.03	27.47	11.39
Stillage concentration	8,057.02	21.03	51.90	28,368.09	75.06	31.13
Total	15,523.91	40.52	100.00	91,119.85	241.10	100.00

Analyzing the exergy destroyed for the ethanol production, is observed that the use of SCB presents a higher value of exergy destroyed in the process compared to the value obtained with cassava (see **Table 4-3**). Stages such as the pre-treatment of raw materials and the hydrolysis and fermentation of sugars are the stages that make the most significant contribution to this value in the case of SCB. The use of cassava as a raw material contributes to reducing the destruction of exergy in pre-treatment processes. However, this raw material shows a high percentage of exergy destroyed in the process of stillage concentration. This is due to the difference in energy consumption between this process

and the other stages. For both cassava and SCB, the highest percentage of exergy destruction occurs in the hydrolysis and fermentation process. These stages of the process involve the transformation of polymer chains into sugar monomers. Where it is not possible to reconstruct the initial polymer from the processes used. On the other hand, inefficiencies in terms of the yield presented in each case are also associated. In both cases, the hydrolysis processes do not show 100% efficiency. Moreover, by using these sugars in fermentation processes, in which microorganisms are involved, it is not possible to recover them from the different products obtained. Both in terms of energy and in terms of exergy, it is evident that the production of ethanol from cassava as a raw material presents lower values than those obtained with the use of SCB as a raw material.

Table 4-3. Percentage distribution of destroyed exergy in ethanol production

Stage	Cassava	SCB
Total exergy destroyed (kW)	40,008	3,646,248
Percentage distribution		
Milling and pretreatment	1.07	45.98
Hydrolysis and fermentation	60.08	53.78
Separation and purification	4.66	0.05
Stillage concentration	34.18	0.19
Total exergy destroyed (MJ/ton raw material)	14,592.62	1,329,938.50
Total exergy destroyed (MJ/L ethanol)	104.43	9,647.65

4.2. Biorefineries

4.2.1. Energy efficiency of the products

A raw material such as SCB has a HHV of 19.81 MJ/kg. By using this material as a raw material in a production process, this energy will be distributed in the different products obtained in the process. Considering the HHV of each of the products obtained in the

different scenarios as well as the flow of each of them, the energy flow present in each product is presented in the **Table 4-4**. The percentage of energy of the SCB present in each product is also shown. This table shows that both PHB and synthesis gas have the highest percentages of the energy content of SCB. This is due to the high flow rate compared to other products.

Table 4-4. Distribution of the energy flow

Product	HHV (MJ/kg)	Energy flow (MJ/h)	Energy percent (%)
Ethanol	48.03	1,654,806.51	23.37
Furfural	49.14	814,428.42	11.50
Octane	48.41	490,656.97	6.93
Syngas	31.11	2,768,377.39	39.10
Xylitol	44.92	1,283,553.06	18.13
Methanol	23.52	504,443.06	7.13
PHB	47.65	2,823,753.66	39.89

The production of methanol from the synthesis gas obtained by the gasification of SCB, the lignin presents the lowest percentage of the energy of this raw material. This is due to the low energy content of methanol. On the other hand, the production of furfural, the product with the highest HHV, does not present a high percentage of the energy content of SCB. Therefore, the energy content of octane, which is obtained from furfural, did not present a high percentage of the energy present in the SCB. These values are due to the fact that the composition of both hemicellulose and lignin in SCB is lower compared to other raw materials.

Compared PHB with ethanol, where both products are obtained from the glucose of SCB, it is observed that PHB presents a higher percentage of the energy content of SCB. This is because, under the conditions analyzed, it is possible to obtain a higher flow of PHB compared to that obtained for ethanol. Even though ethanol has a higher HHV than PHB. Showing that it is more energetically feasible to obtain PHB than to obtain ethanol. This is based on PHB presenting a higher percentage of the energy power of SCB than ethanol.

4.2.2. Energy efficiency of the scenarios

Analyzing each of the scenarios, the first two present an energy flow of 4,611,749.78 MJ/h, which represents 65.14% of the energy contained in the SCB. Scenarios 3, 4 and 5 present energy flows of 3,442,802.63, 2,973,677.98 and 2,649,906.53 MJ/h, respectively. Energy flows corresponding to SCB energy percentages of 48.63, 42.00 and 37.43%, respectively. These results show that from scenario 1 and 2 the best use is made of the energy contained in the SCB. The selection of one scenario or another depends on the energy consumption presented in each case.

Scenarios 1 and 2 presented energy consumption of 61,627,899.56 MJ/h and 54,736,130.85 MJ/h, respectively. Thus showing a difference of 6,891,768.71 MJ/h. Energy that is reflected in the process of obtaining methanol. Considering that in the first scenario the synthesis gas is used in cogeneration processes and therefore its pressure and temperature decrease. This means that, for the methanol production process, it must be subjected again to a compression process, which implies an additional energy consumption. By changing from PHB production in scenario 2 to ethanol production, energy consumption decreases by 39,809,163.31 MJ/h. This decrease in energy consumption is due to the fact that in the process of obtaining ethanol the energy requirements are lower compared to those presented in obtaining PHB. When modifying scenario 3, that is, changing the production of xylitol by the production of furfural, an increase in energy consumption corresponding to 123,405.75 MJ/h is presented. This is because in the process of obtaining furfural it is necessary to use more energy in the process of purification. In this process, a joint distillation-decantation system is used, while the purification of methanol uses a precipitation-filtration system. Where the latter system has a lower energy consumption than the former. When using the furfural obtained in obtaining octane (scenario 5) an increase in energy consumption of 1,232,616.13 MJ/h was presented in comparison with scenario 4. This energy is invested in the different reaction processes involved in octane production, as well as in its purification process. Showing that energetically scenario 3 is the most viable with the lowest energy consumption.

4.2.3. Exergy analysis of the scenarios

The accumulated exergy in each process is presented in the **Table 4-5**. For this thesis, the cumulative exergy was considered to be the sum of the exergy destroyed in each of the processing stages involved in obtaining a given product. Comparing each of the products obtained in this thesis, those with the highest accumulated exergy values correspond to the production of octane, furfural and methanol, whether or not using a cogeneration process. In these processes, the values of destroyed exergy are caused mainly by the high energy consumption of these processes. As well as the irreversibilities, that occur in the reaction processes by not presenting 100% conversions. With respect to the production of methanol, the use of a cogeneration process leads to an increase in the accumulated energy. This is due to the fact that due to the decrease in syngas pressure in the cogeneration process, it is necessary to increase this value again for methanol production. However, when the cogeneration process is not considered, the amount of energy used in this process is smaller.

Table 4-5. Cumulative exergy for step

Process	Cumulative exergy (MJ/kg product)
Ethanol production	1,031.01
PHB production	821.36
Xylitol production	1,122.51
Furfural production	1,960.87
Octane production	4,497.21
Gasification	352.86
Methanol production with cogeneration	1,849.80
Methanol production without cogeneration	1,587.73

The flows of exergy destroyed in each scenario analyzed are presented in the **Table 4-6**. The differences presented between scenarios 1 and 2 are due to the energy differences in these scenarios. Considering that in both scenarios the same main products are obtained, yields are constant. However, when considering the cogeneration stage in scenario 1, a greater amount of energy needs to be used in the methanol production process to condition the syngas for the reaction process. By not considering this stage in the production process (scenario 2), it is possible to reduce the energy losses that occur in the process. This is

reflected in the difference in the value of destroyed energy between the two scenarios (5,620,837 MJ/h). When PHB production (scenario 2) is changed to ethanol (scenario 3), there is a decrease in the flow of exergy destroyed in the process (13,153,759 MJ/h). Although ethanol has a lower yield than that obtained with PHB, its production process involves a smaller number of equipment, which have lower energy requirements. However, by considering the exergetic efficiencies presented for both cases, PHB allows for a higher exergy efficiency of the raw material by presenting a higher yield. Obtaining PHB from SCB instead of ethanol allows an exergetic efficiency of 0.122 higher when correlating the exergy of the product with the exergy of the raw material (see **Table 4-7**). When considering the different reagents and residues of the process, the exergetic efficiency presents a difference of 0.296. When another modification is applied to the process (change from xylitol production to furfural production), an increase of 423.747 MJ/h occurs. This change in the value of the destroyed exergy is associated with the change in technology in the process of both the transformation of xylose and the purification of the product. While in the production of xylitol a fermentation process followed by precipitation and filtration processes is used, in the production of furfural, combined processes of dehydration - distillation - decantation are used. Where this last combination of processes presents a lower yield in terms of xylose conversion, as well as higher energy requirements. This is reflected in the fact that in each of the exergetic efficiencies analyzed, the production of xylitol presents higher values. In a process where the obtained furfural is used to obtain octane (scenario 5), the flow of destroyed energy presents an increase of 13,082,079 MJ/h. This increase is due to the low conversion from furfural to octane. In addition, a high amount of energy must be used in the purification process. These are the fundamental factors in increasing the value of the destroyed flow of energy. Analyzing the exergetic efficiencies that correlate the product with the raw material and the reagents, these present the lowest values in comparison with the other processes of transformation of raw material. While correlating the flow of exergy from both products and waste to raw material and reagents, there is an increase in comparison to obtaining furfural. This is because with this new process stage the amount of waste generated presents a considerable flow.

Table 4-6. Exergy destroyed in each scenario

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Exergy destroyed (MJ/h)	79,815,697	74,194,861	61,041,102	61,464,849	74,546,928

Table 4-7. Exergy efficiencies by product

Product	$\Psi_{prod/RM}$	$\Psi_{prod/RM+rea}$	$\Psi_{prod+w/RM+rea}$
Ethanol	0.072	0.071	0.129
PHB	0.194	0.155	0.425
Xylitol	0.043	0.033	0.078
Furfural	0.014	0.011	0.038
Octane	0.003	0.002	0.063
Gasification	0.203	0.199	0.222
MP steam	0.001	0.001	0.023
Methanol production with cogeneration	0.038	0.037	0.208
Methanol production without cogeneration	0.030	0.030	0.201

* w: wastes * RM: Raw Material * prod: Product * rea: Reagents

4.3. Final remarks

As it was demonstrated in the case of the tree tomato peel that the inefficiencies are mainly in the step of purification for SE case and the recovered CO₂ and extraction process for the SFE. In the case of the SE, this is due to the high-energy consumption at this stage. Where this energy is not used in other processes. In the case of SFE, in the extractor, the second highest percentage of the exergy of the process is presented by the destruction of the lignocellulosic matrix. This destruction is caused by the use of high pressures for the extraction process of polyphenolic compounds. An alternative to reduce the flow of exergy in the purification stage of solvent extraction processes is the evaluation of other purification techniques, which have lower energy requirements.

The production of ethanol from raw materials such as cassava presents better yields in exergetic terms compared to the value obtained by SCB. This shows that the use of cassava as a raw material allows both higher yields and lower energy requirements for the process. While with cassava, the flow of exergy destroyed is 104.43 MJ/L ethanol, with SCB this value corresponds to 9,647.65 MJ/L ethanol. Showing the energy and exergetic benefits of ethanol production from the cassava.

The determination of the exergetic efficiency in processes allows the identification of a transformation route, which allows the maximum use of the energy content of a raw material to be obtained. In addition, it makes it possible to identify the distribution of energy both in the products and in the waste generated by the process. Thus, in complex processes such as biorefineries, is a tool allows the identification of products that allow the best energy use of the raw material. In addition to the energy potential of waste.

5. Chapter 5: Economic assessments

5.1. Stand-alone processes

5.1.1. Compounds extraction

The extraction processes of polyphenolic compounds present different production costs. The differences depend on the raw material flow and reagents used in each case. As well as the costs associated with the extraction process. Where these depend primarily on the utility costs and costs associated with the equipment. While the SE process total costs was 52.04 mUSD/year, the costs for the SFE process was 22.36 mUSD/year. The distribution of the total costs for the SE and SFE process are presented in **Figure 5-1** and **Figure 5-2**, respectively.

As for the raw material, it is important to mention that the SE uses a greater amount of solvent for the ratio 1:20 that it has, in comparison with a ratio 1:3 that the SFE uses. Although the SFE additionally uses CO₂ in the extraction process, the material costs are lower. However, due to the specialized equipment requirements for the SFE process, depreciation costs are higher for this case.

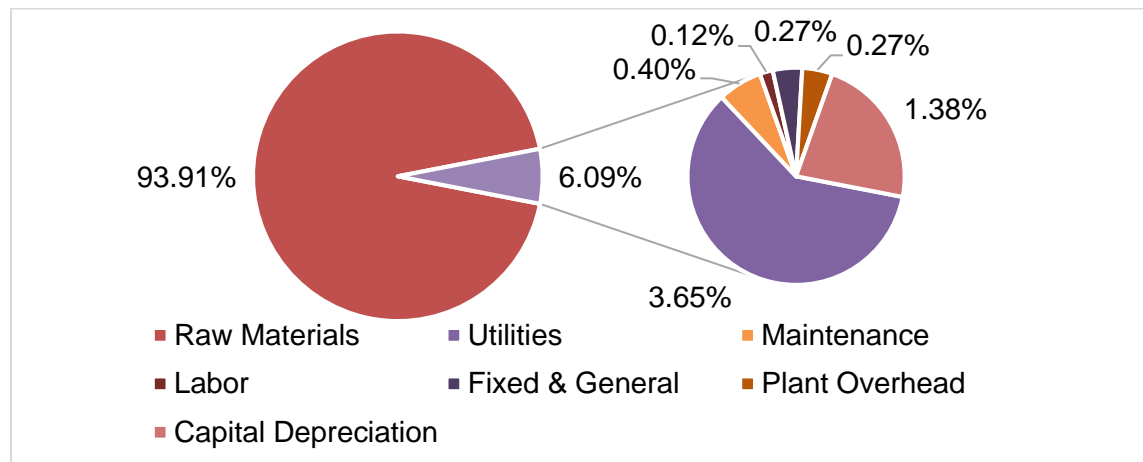


Figure 5-1. Cost distribution for the polyphenolic compounds extraction employed SE

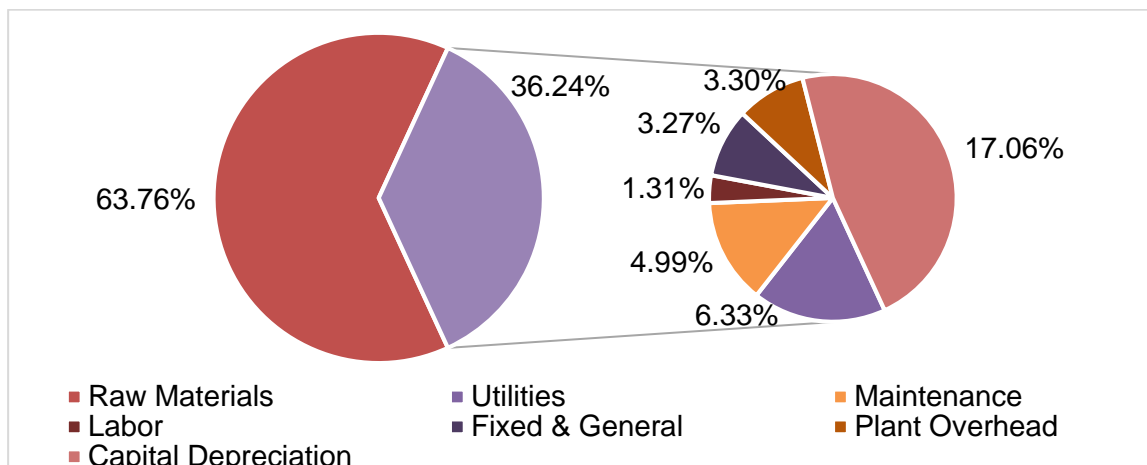


Figure 5-2. Cost distribution for the polyphenolic compounds extraction employed SFE

Considering the different costs of the process and the product flow obtained in each case, it is possible to determine the cost of production. Thus, in the case of SE, the cost of obtaining 1 kg of polyphenolic compounds was 18.32 USD. While the cost for the SFE case was 8.23 USD. The SFE thus shows a profit margin of 8.58% (considering an average cost of 9 USD/kg for polyphenolic compounds in the market). These values are reflected in the NPV of the process. This value with respect to time is presented in **Figure 5-3**. This figure shows the process value as a function of time. In the case of the SE, the investment incurred at the beginning of the process was not recovered within a project lifetime of 10 years. This is due to the fact that with this process the production cost was higher than the market cost. Therefore, a return on the capital invested was not possible. On the other hand, for SFE, which obtained a lower production cost than the market, the economic viability of the project is evidenced by its positive NPV. For the conditions analyzed, the return on capital period for SFE was 1.9 years. Considering that these values are a function of the raw material flow (tree tomato peel), a sensitivity analysis of this value was performed. This analysis identified that the minimum flow of raw material that must be processed to obtain the return on investment at the end of the useful life of the process is 0.13 ton/hour (see **Figure 5-4**).

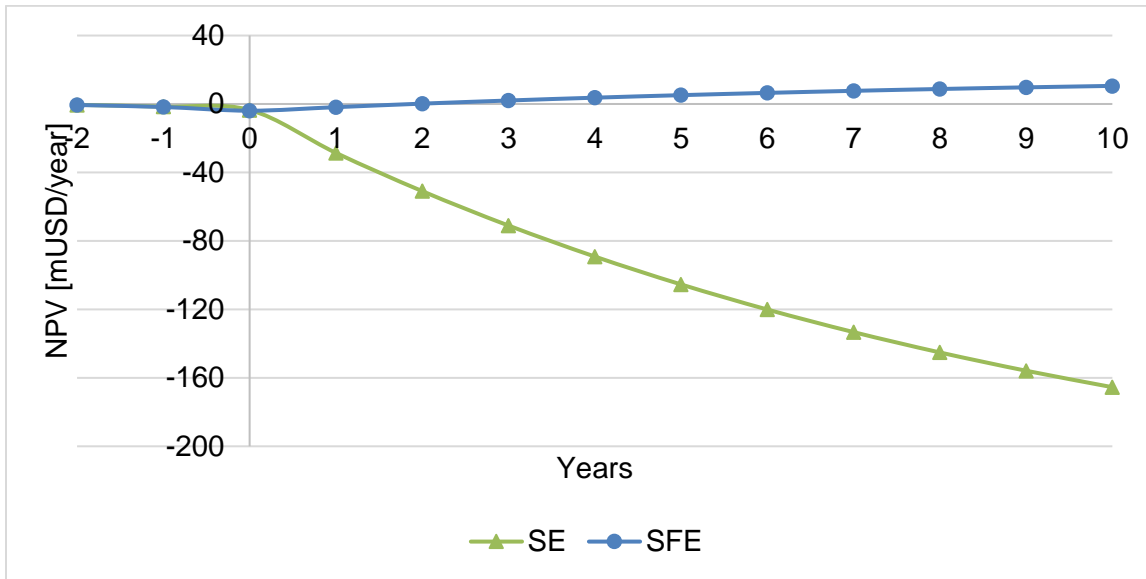


Figure 5-3. Net Present Value for polyphenolic extraction from SE and SFE

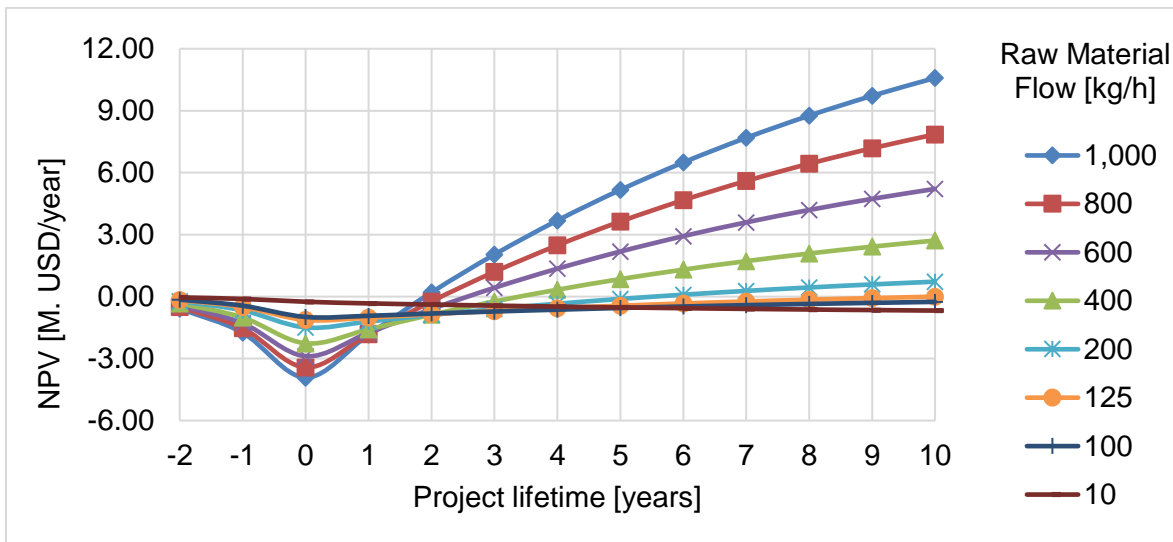


Figure 5-4. VPN over project lifetime for the SFE process

5.1.2. Ethanol production

In **Table 5-1** are presented the results of economic analysis. From these results the cost of fuel ethanol production and the profit margin are determined for each process assuming the sale price in Colombia of 1.24 USD/L (Moncada et al., 2015) and also can see the percentage share in the production cost of fuel ethanol for each of the operating and financing costs related with the projection and implementation of an industrial process. For each cases an economic feasibility of process exists with profit margin of 34.87% for Cassava and 52.34% for sugarcane bagasse. Production cost of fuel ethanol from Cassava is lower than the sugar cane in Brazil 0.47 USD/L and too high compared with other countries as Thailand that its 0.18 USD/L and other materials as 0.40 USD/L from corn in United States, 0.42 USD/L from wheat in Europe (Gupta & Verma, 2015; Mussatto et al., 2010; Renewable Fules Association, 2016). This difference is attributed to the market price of Cassava in countries as Thailand where the productivity of crop is higher than demand allowing to reduce the cost of raw material and at the same time the fuel ethanol production cost doing the process more profitable. Reason why improving logistic in the Cassava supply chains must be taken into account in the Colombian context for reduce the cassava cost in the fuel ethanol production. Situation that happens nowadays in Colombia by putting the distilleries around of supply chains of sugar cane.

Table 5-1. Fuel ethanol production cost from cassava and sugarcane bagasse case.

Item	Cassava case		Sugarcane bagasse case	
	USD/L	Share of total cost (%)	USD/L	Share of total cost (%)
Raw Materials	0.272	62.91	0.309	47.7
Utilities	0.027	6.34	0.178	27.4
Operating Labor	0.008	1.80	0.008	1.2
Maintenance	0.005	1.13	0.007	1.0
Operating Charges	0.002	0.45	0.002	0.3
Plant Overhead	0.006	1.46	0.007	1.1
General and administrative	0.026	5.93	0.041	6.3
Depreciation of Capital	0.086	19.99	0.097	15.0

Production cost (total)	0.432	100.00	0.649	100.0
Profit margin (%)		34.87		52.34

In sugarcane bagasse case, the production cost of fuel ethanol compared with the first generation fuel ethanol turns out to be higher for needing more raw materials and equipment in pretreatment stage. However, it is close to the cost of France from sugar beet of 0.60 - 0.68 USD/L (Gupta & Verma, 2015). With respect to other lignocellulosic biomass the fuel ethanol production cost was to close where were used the hemicellulose and cellulose from empty fruit bunches 0.57 USD/L, rice husk 0.63 USD/L, coffee cut-stems 0.68 USD/L and lower for cellulose from plantain pseudostem 2.49 USD/L due to the differences in physicochemical composition and raw material cost used (Daza Serna et al., 2016; Julián A. Quintero et al., 2013a). Also, production cost was similar to reported in United States when it is used corn stover (Gupta & Verma, 2015). It represents an advantage for Colombia because as mentioned in Section 1.2.3 for both lignocellulosic biomass are inside of the main wastes of each country which could be better the market of fuel ethanol if pretreatment technologies that improve the formation of fermentable sugars will be used.

As it expected the percentage share of utilities cost for the fuel ethanol cost from sugarcane bagasse is highest than the Cassava case for the amount of energy required for heating and concentrate in the pretreatment steps to obtain fermentable sugars, which in turn are relate with depreciation cost for requiring a greater number of equipment resistant to corrosion by acid and maintain sterile the fermentation process. Due to the high energy requirements of both processes is necessary the implementation of alternatives which allow reduce it. An alternative of energy and steam production could be the use of wastes from cassava crop (i.e. stems and leaves) or the lignin produced in the sugarcane bagasse case as raw material for gasification, pyrolysis or combustion technologies. Thus it would be achieved a better uses for biomass and reducing waste generated in the production process. Where the biggest impact would reflect in the decrease of production costs due to decrease of utilities cost with the implementation of this alternative.

5.2. Analysis of biorefinery scenarios

Analyzing the production costs presented in each scenario, it is observed that the items that presented the greatest contribution were the costs of raw materials and utilities (see **Table 5-2**). Raw material costs ranged from 45.55% (scenario 1) to 66.06% (scenario 5). While profit costs ranged from 35.11% (scenario 3) to 50.67% (scenario 1). The scenario that presented the lowest production costs was scenario 3. This scenario presented the lowest raw material and profit costs. However, the CAPEX and OPEX of this scenario were the highest in comparison to the other scenarios analyzed. The CAPEX of the process is associated with the costs related to the equipment. In other words, among the scenarios analyzed, number three presented the highest costs in terms of equipment related to the production process. The OPEX correlates the costs associated with the production process. Among these are maintenance, labor, fixed & general and over-design costs.

Table 5-2. Distribution of production cost

Item	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
CAPEX	43.26	49.03	113.38	50.41	53.82
OPEX	27.25	30.84	70.91	31.70	33.83
Raw material	850.36	850.36	292.98	276.68	737.75
Utilities	945.88	877.74	258.24	283.30	291.34
Total (M. USD/year)	1,866.75	1,807.98	735.51	642.09	1,116.75

The

Table 5-3 shows the production costs of each of the products obtained in each of the scenarios analyzed. In each case, the production costs were lower than the cost they present in the market. Showing profit margins of 1.70%, 4.79%, 43.25%, 34.70% and 39.53%, for scenarios 1, 2, 3, 4 and 5, respectively. Where the production costs obtained for methanol, ethanol and xylitol in scenario 3 were the lowest among the scenarios analyzed. As a result, this scenario presents the highest profit margin. However, analyzing the return on investment period for each scenario, values of 4.04, 2.41, 1.14, 0.87 and 0.46 years were obtained for scenarios 1, 2, 3, 4 and 5, respectively (see **Figure 5-5**). This is

due to the fact that the market prices of the products obtained in scenario 5 are higher than those of the other products. Thus, by presenting a profit margin of close to 40% in scenario 5, it is possible to recover the investment made in a short period of time. Analyzing the economic viability of each scenario through an analysis of the NPV, it is observed that scenario 5 presents the highest values followed by scenario 3.

Table 5-3. Cost of production of each product in each scenario in USD/kg

Product	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Xylitol	2.26	2.19	1.31	-	-
MP Steam	0.008041	-	-	-	-
PHB	1.82	1.76	-	-	-
Methanol	1.89	1.83	1.09	1.25	1.16
Ethanol	-	-	0.7	0.81	0.75
Furfural	-	-	-	1.11	
Octane	-	-	-	-	7.56

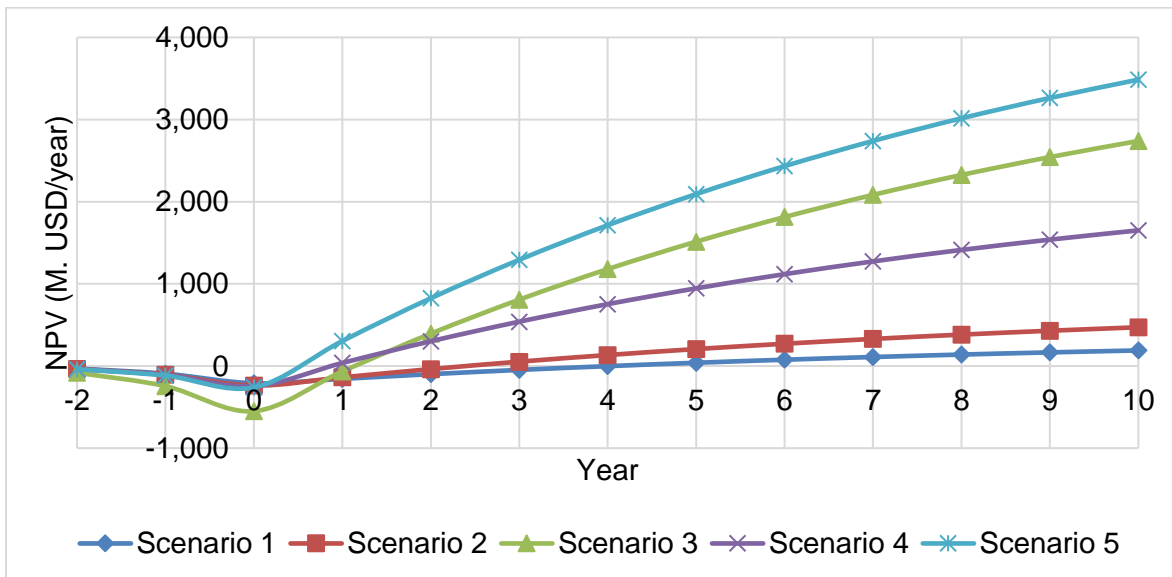
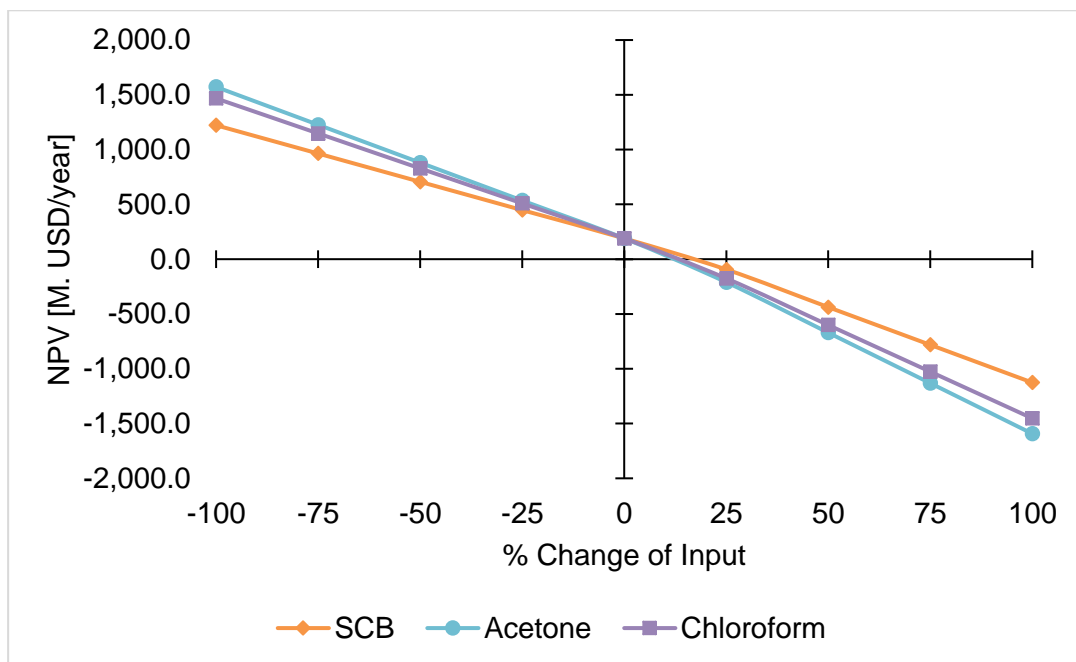


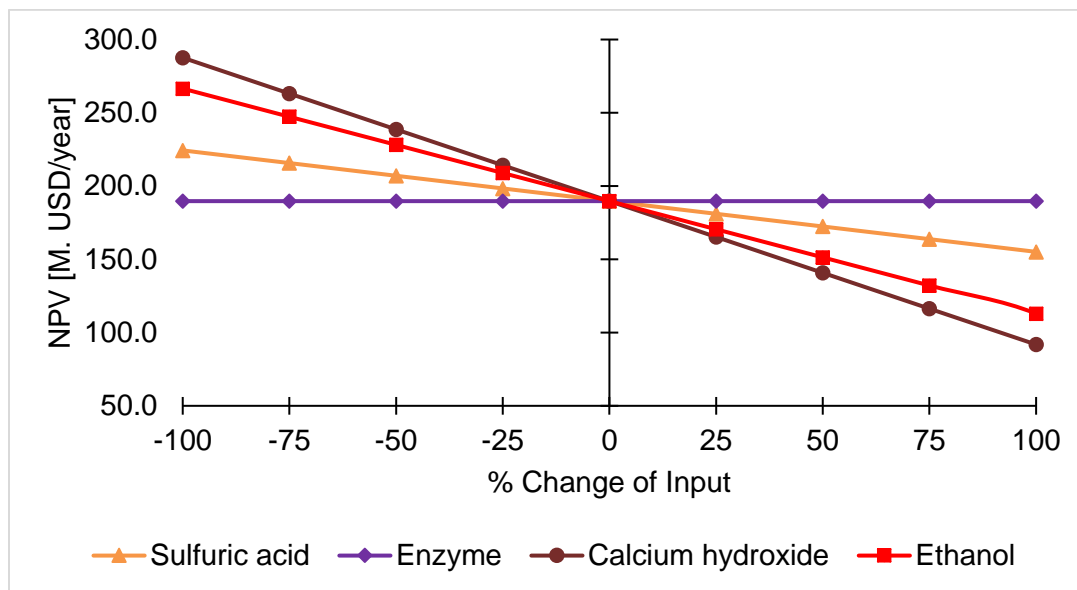
Figure 5-5. NPV for each scenario analyzed

5.2.1. Analysis of influence of raw material and products cost

In the case of scenario 1, as shown in the **Figure 5-6**, the raw material costs that have the greatest impact on the NPV of the process are the costs of SCB, Acetone and chloroform. These increases in acquisition costs, which are close to 10%, lead to the economic unfeasibility of the process. This is due to the sign change presented in VPN of the process. When considering the decrease in these costs, the NPV of the project can increase to about 1,500 M. USD/year. On the other hand, the costs corresponding to sulfuric acid, enzyme, calcium hydroxide and ethanol have a lower impact on the NPV of the process. With changes in these costs the NPV can range from 100 to 300 M USD/year (considering 189 M USD/year as the base case).



(a)



(b)

Figure 5-6. Influence of raw material costs for scenario 1 a. High importance. b. Low importance

Analyzing the influence of product costs for scenario 1 (see **Figure 5-7**), it can be seen that variations in the cost of steam do not lead to significant variations in the NPV of the process. While when considering decreases in the costs of xylitol, PHB and methanol, the NPV of the process becomes negative. Evidencing an economic unfeasibility which is reflected in the non-return of the investment made at the beginning of the process. The product that has the greatest impact on the VPN of the process is the PHB. This is because of the fact that of the three main products, it is the one with the highest flow.

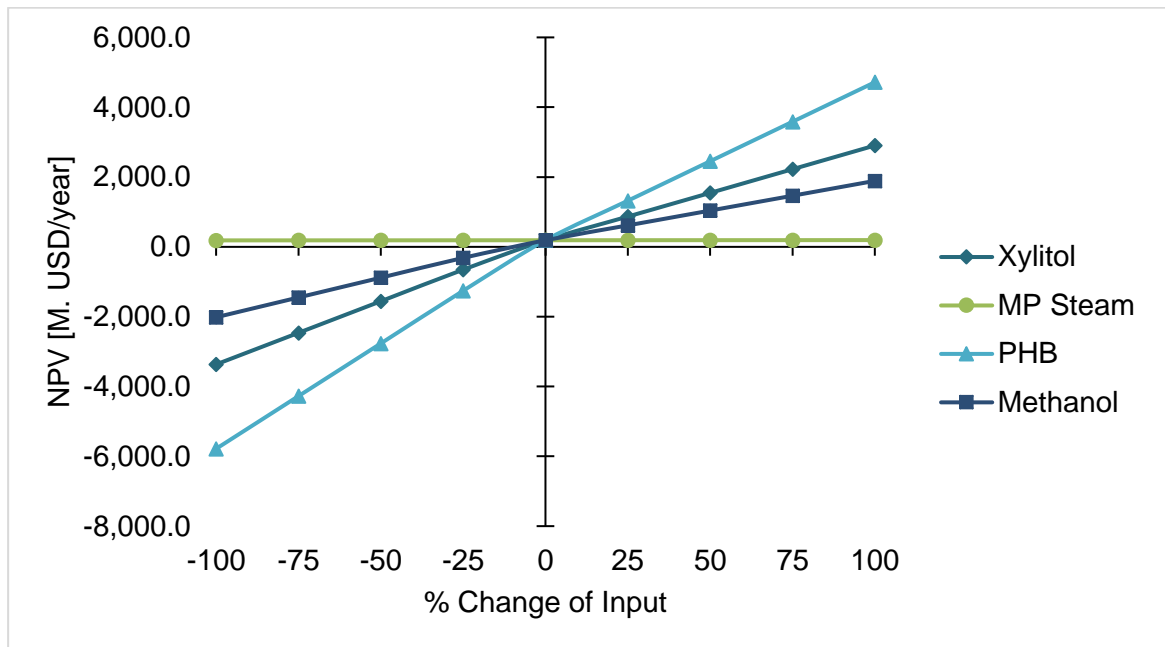


Figure 5-7. Influence of product costs for scenario 1

When analyzing the influence of the costs of both raw materials and products for scenario 2 (see **Figure 5-8** y **Figure 5-9**), which, unlike scenario 1, does not consider the cogeneration process, similar behaviors are observed. The difference between the two scenarios lies in the VPN value that is achieved with the modifications in raw material and product costs. Where variations in raw material costs can cause the NPV of the process to

oscillate between -1,217 and 1,748 M.USD/year. In the case of products, the NPV can vary between -5,408 and 4,508 M.USD/year.

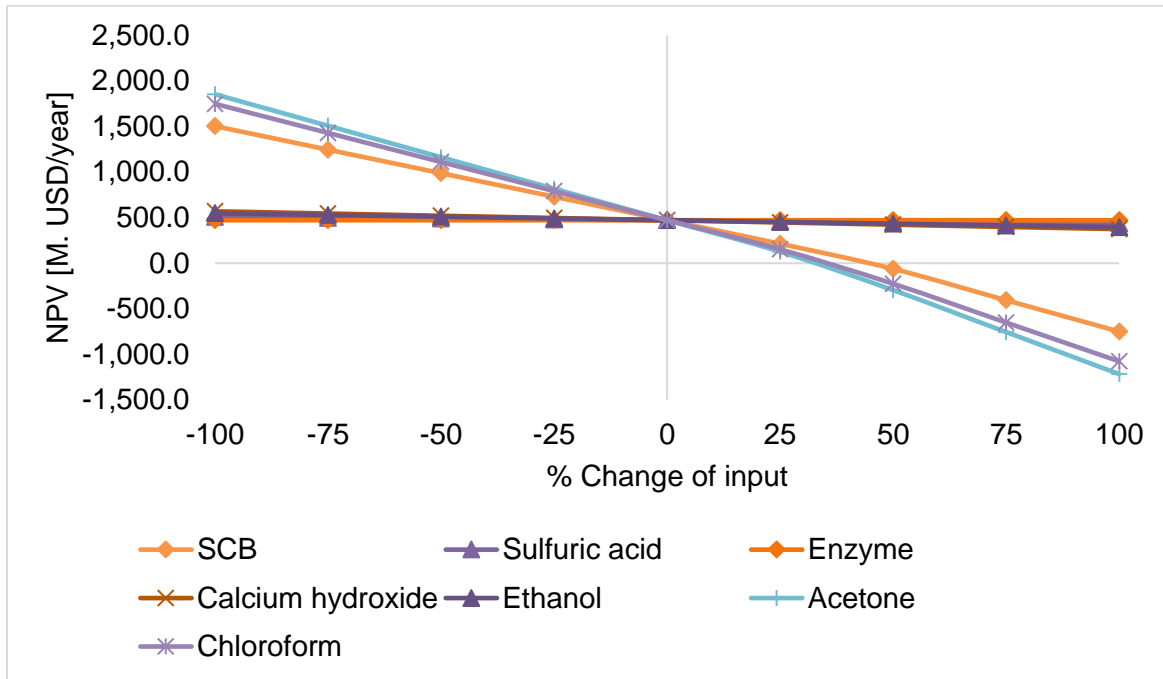


Figure 5-8. Influence of raw material costs for scenario 2

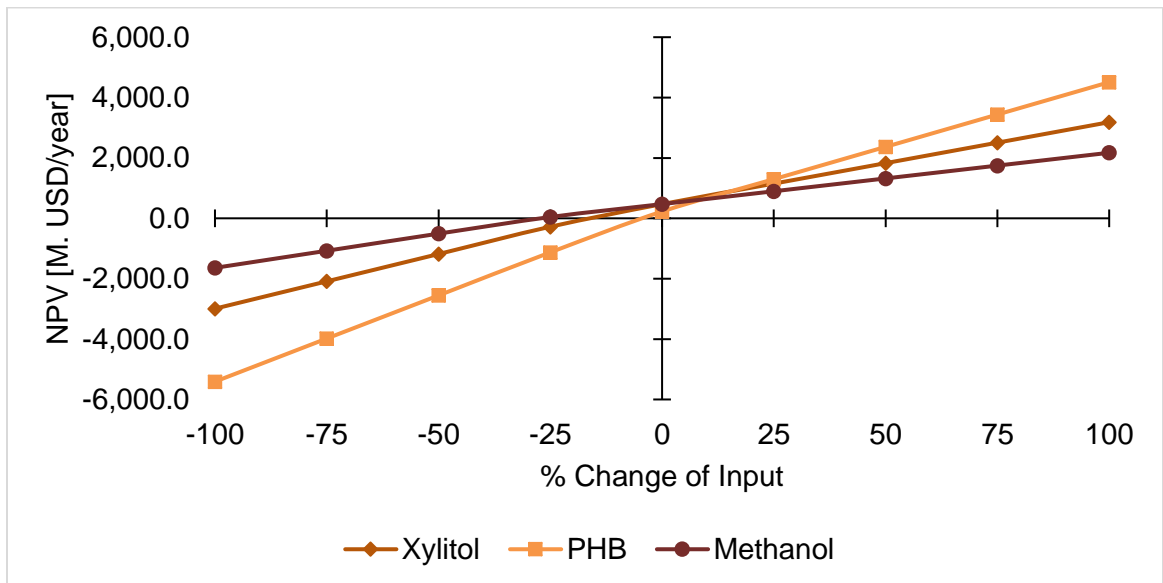


Figure 5-9. Influence of product costs for scenario 2

In the case of scenario 3, the raw material that has the greatest influence on the NPV of the process is the SCB (see **Figure 5-10**). While variations in the costs of the other raw materials do not lead to significant variations in the NPV of the process. Even with 100% increases in raw material costs for this scenario, NPV does not show a change in direction. In other words, increases in the costs of raw materials do not lead to the economic unfeasibility of this scenario. While changes in the cost of sale xylitol can lead to the VPN of the process becoming zero (see **Figure 5-11**). As long as the other two products (ethanol and methanol) continue at their base case price. Changes in the selling prices of both ethanol and methanol do not lead to the economic viability of the process. Whereas xylitol has a constant price to cover the different production costs.

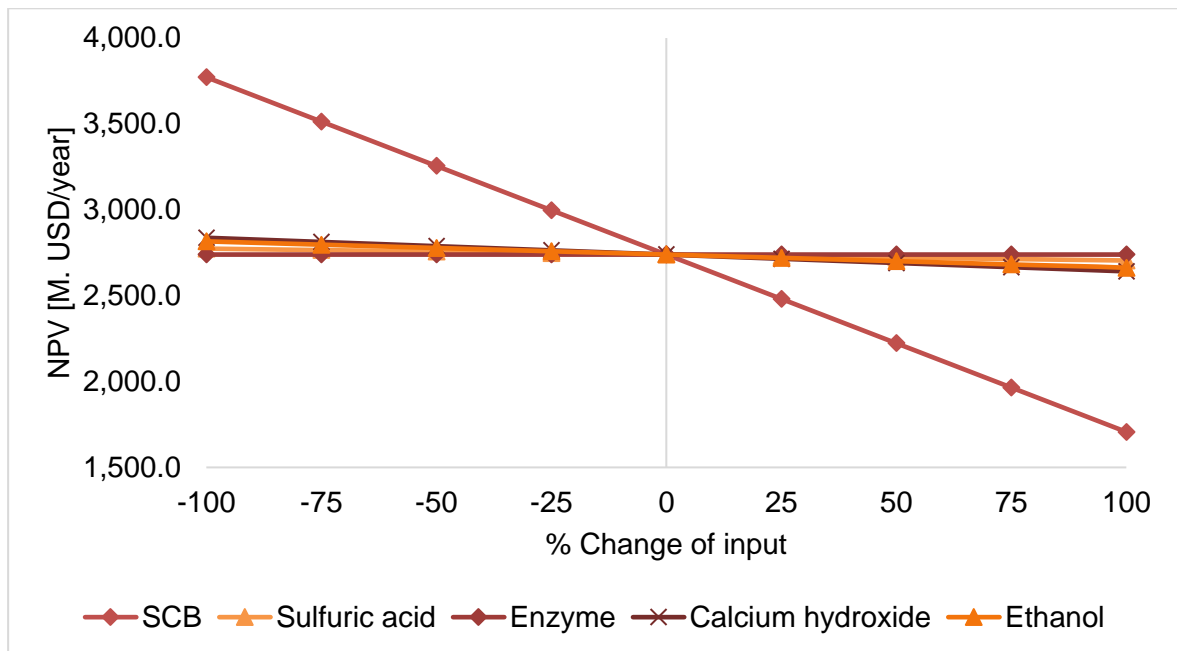


Figure 5-10. Influence of raw material costs for scenario 3

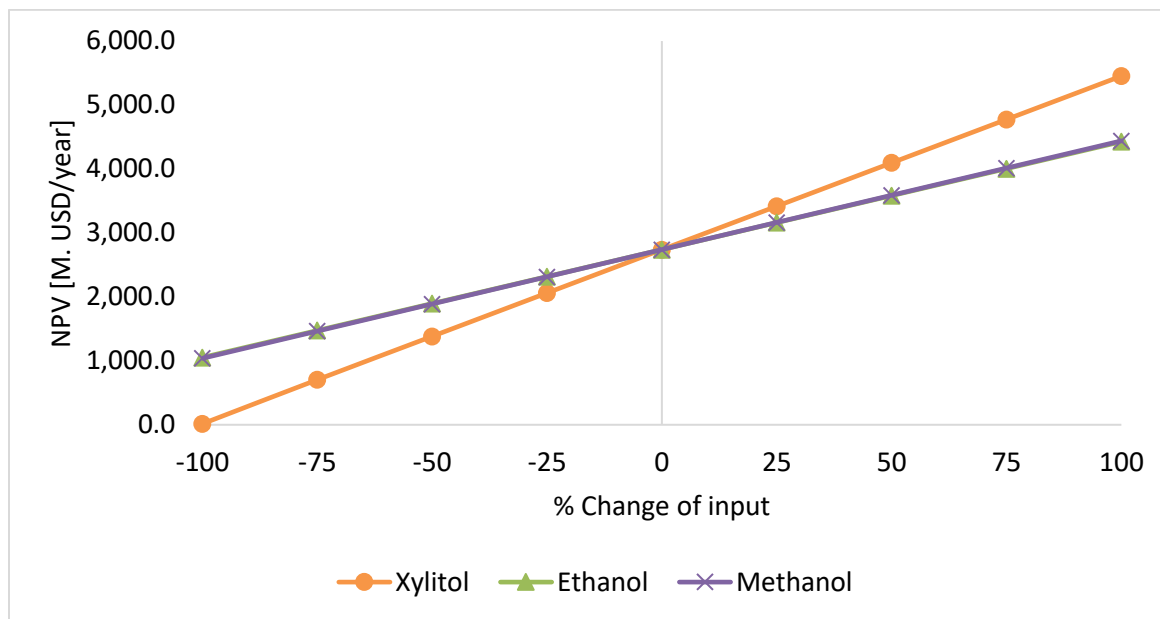


Figure 5-11. Influence of product costs for scenario 3

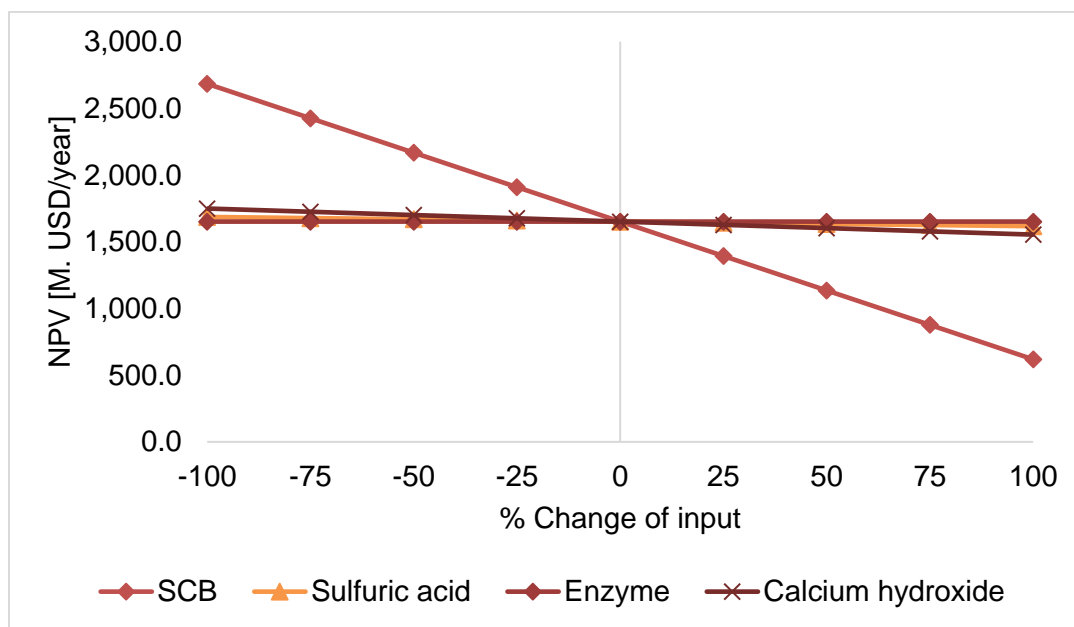


Figure 5-12. Influence of raw material costs for scenario 4

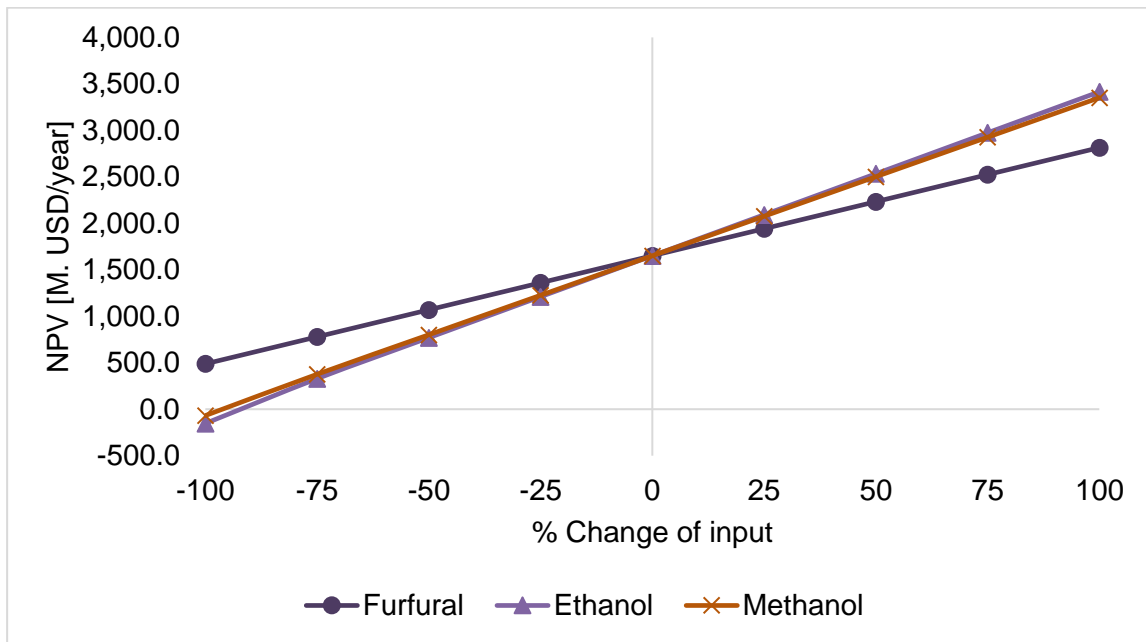


Figure 5-13. Influence of product costs for scenario 4

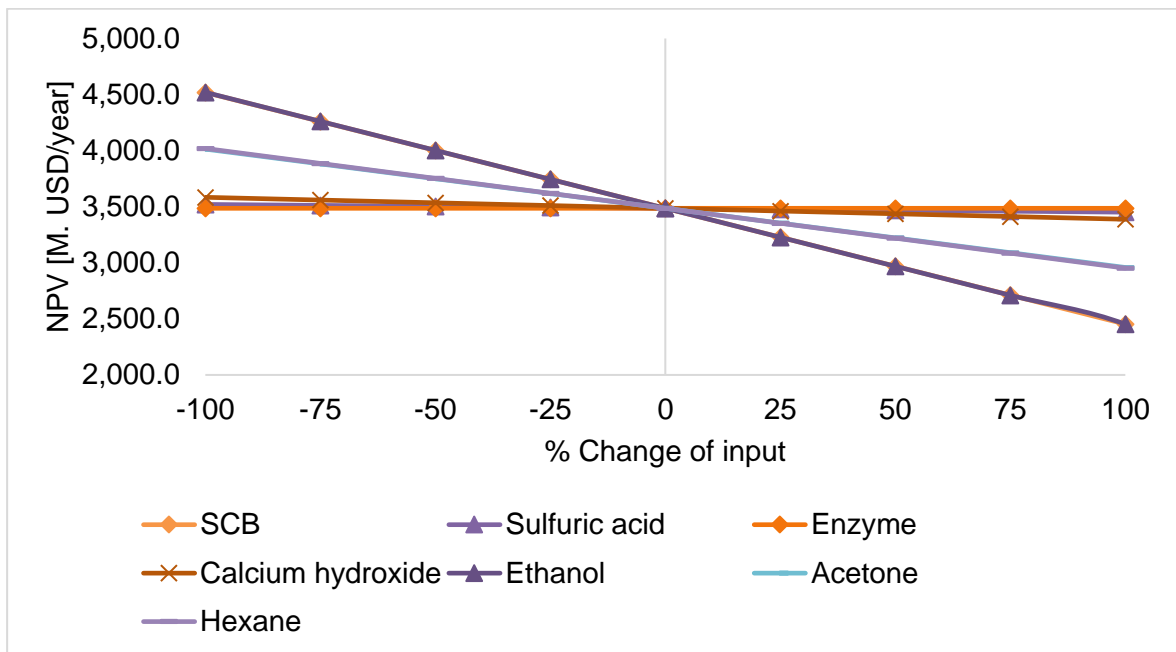


Figure 5-14. Influence of raw material costs for scenario 5

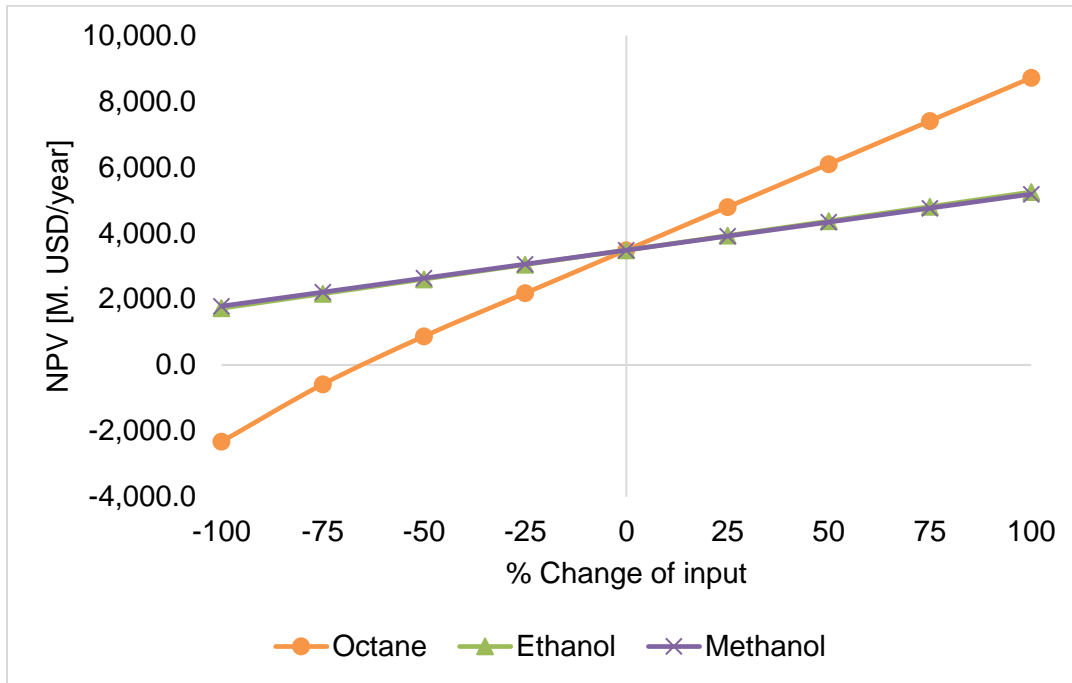


Figure 5-15. Influence of product costs for scenario 5

5.2.2. Processing scale analysis

The **Figure 5-16** shows a sensitivity analysis of the raw material flow for scenario 1. This figure shows that considering a raw material flow of 3,132 tonne/year, there is a return period of 4.04 years. Analyzing the minimum processing scale for which in a period of 10 years the return on investment is achieved, this corresponds to 2,847 tonne/year. For lower processing scales the VPN of the process does not become positive in the period of time analyzed showing the economic unfeasibility of the process. Not considering the cogeneration stage, the minimum raw material flow rate for scenario 2 is 2,192 tonne/year (see **Figure 5-17**). Compared to scenario 1 in which the same three main products are obtained, this shows a decrease in the minimum raw material flow. When considering a change in the process, such as changing the production of PHB for the production of ethanol, not only is there an increase in process profits, but also a decrease in the flow of raw material to be obtained. For scenario 3, the minimum flow of raw material that must be processed to obtain a return on investment is 0.365 M. tonne/year, which corresponds to 11.66% of the feed flow of the base case (see **Figure 5-18**). For scenario 4, the minimum material flow is 0.313 M. tonne/year, which represents 18.29% of the base case material

flow (see **Figure 5-19**). For scenario 4 the return on investment period is less than 3 years up to 30% of the raw material flow of the base case. When this decreases to 20%, there is a considerable increase in the period of return on capital. For this flow the return period corresponds to 6.8 years. Showing that the payback time of the investment doubled. Finally, for scenario 5, the minimum material flow is 0.202 M. tonne/year (see **Figure 5-20**). In this case, it was observed that even for raw material flows corresponding to 10% the return on investment period was less than 4 years. This is because the products obtained in this case present a high cost in the market.

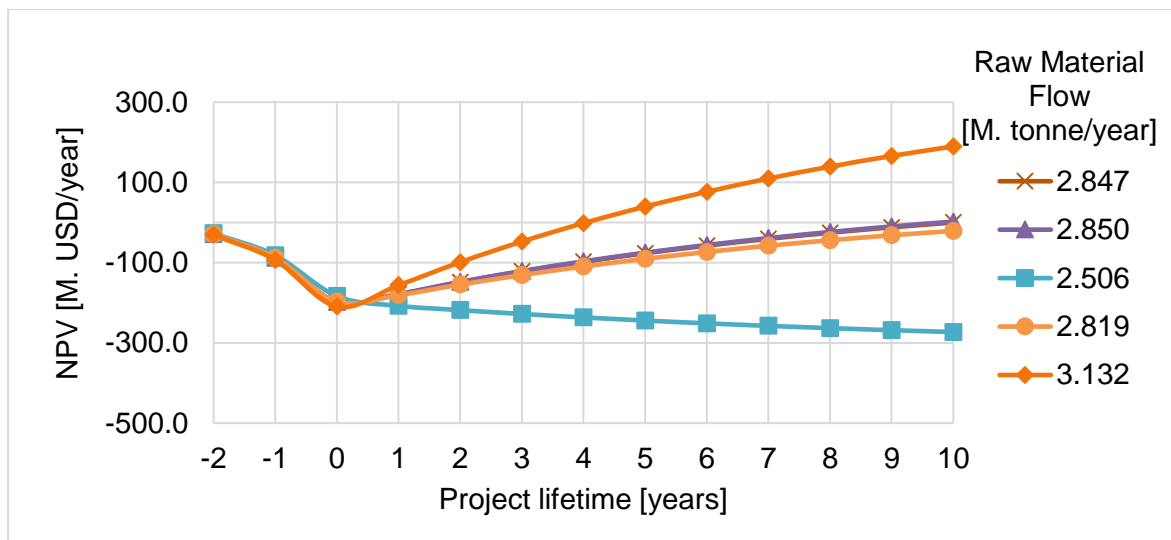


Figure 5-16. VPN over project lifetime for the scenario 1

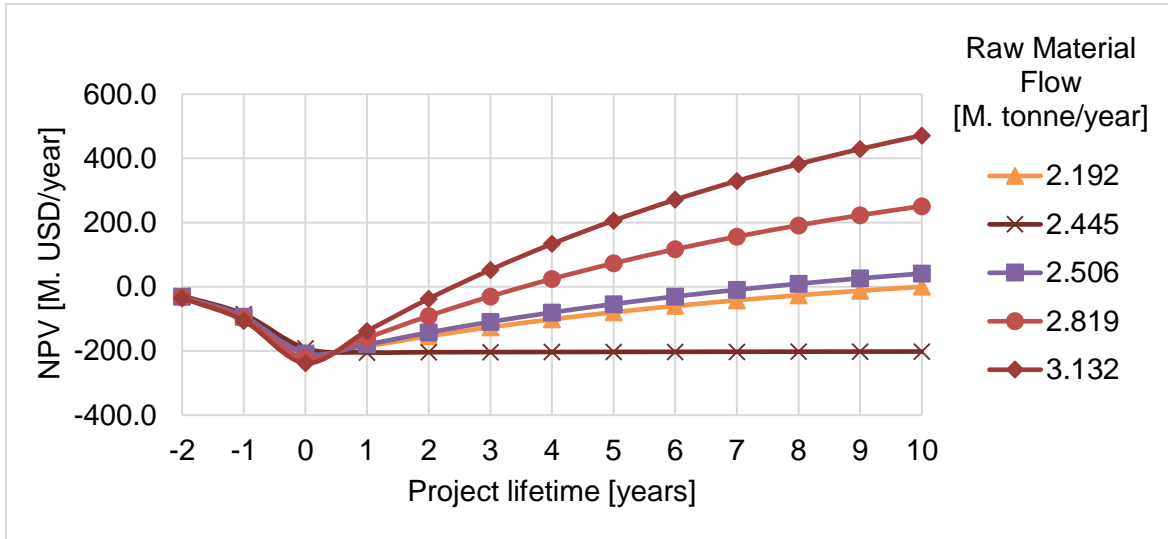


Figure 5-17. VPN over project lifetime for the scenario 2

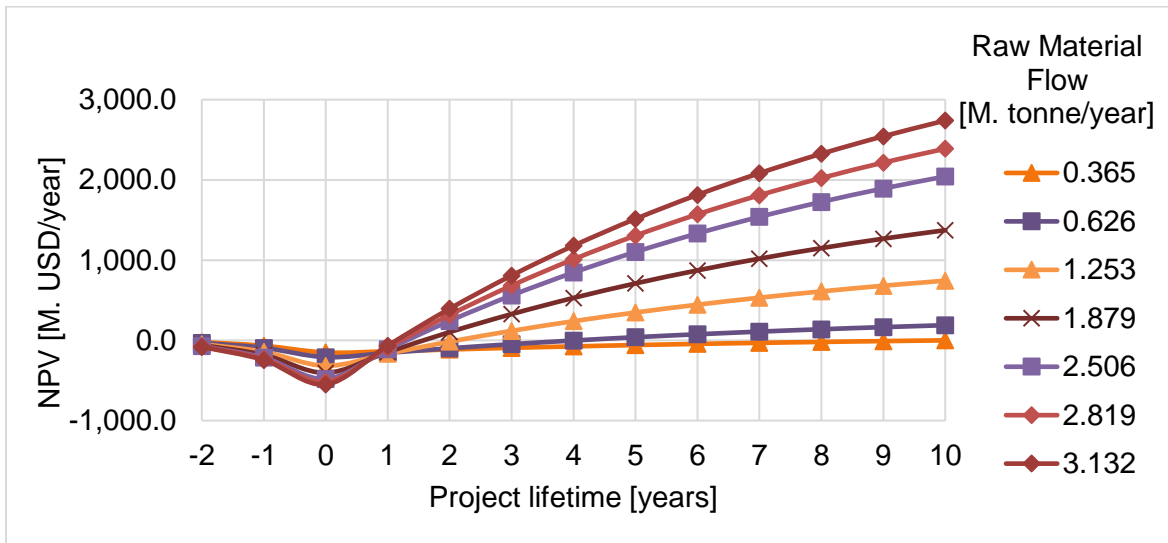


Figure 5-18. VPN over project lifetime for the scenario 3

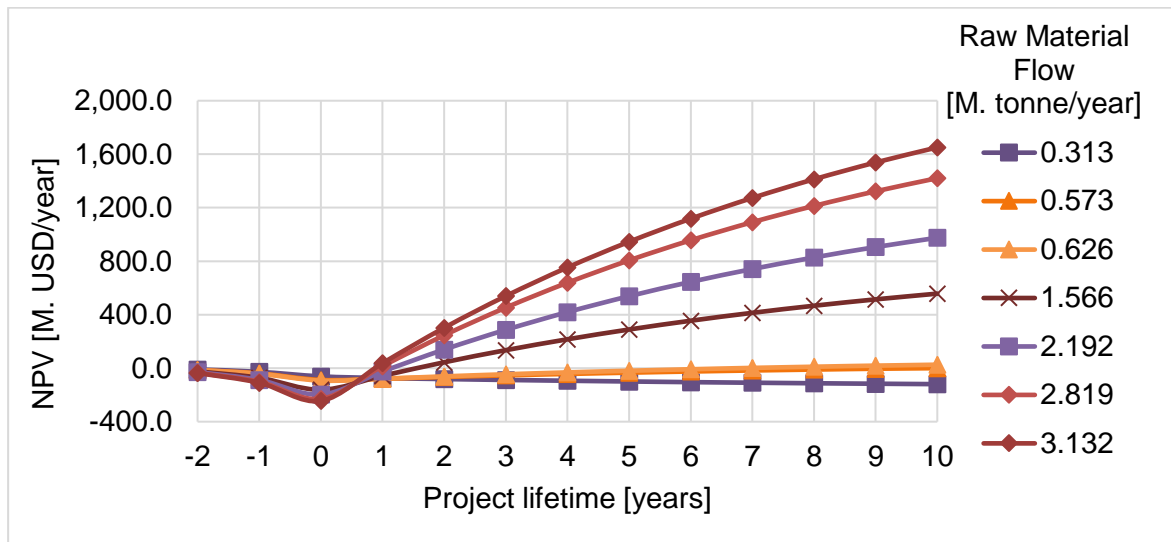


Figure 5-19. VPN over project lifetime for the scenario 4

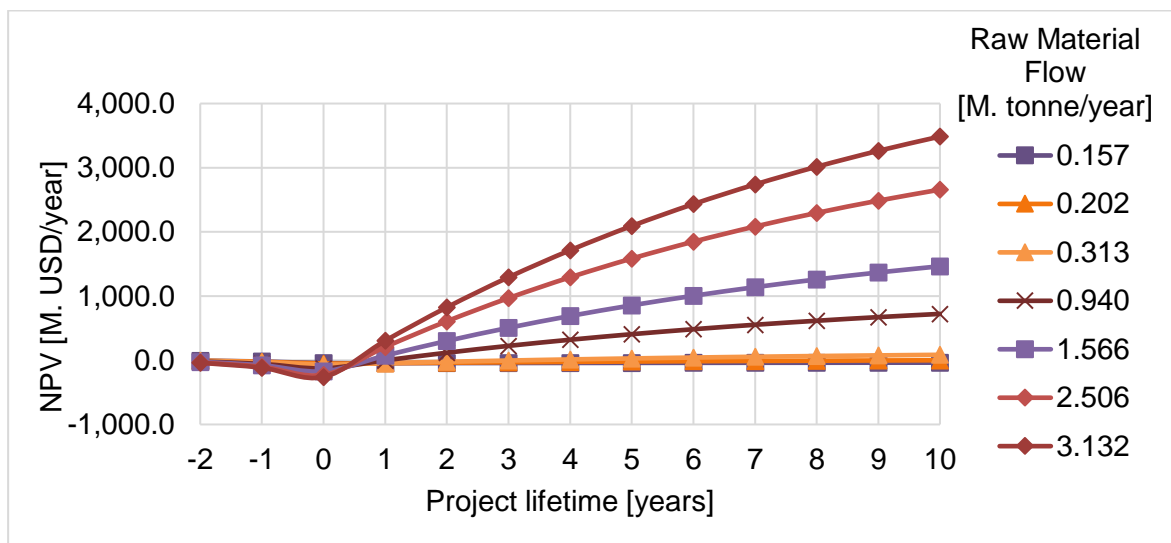


Figure 5-20. VPN over project lifetime for the scenario 5

5.3. Final remarks

Changes in the technology of obtaining a product can lead to lower investment costs in a process. As long as the yields presented in both technologies differ in terms of production (quantity of product) and the costs of the equipment involved.

The scale analysis of a process allows the identification of the minimum amount of raw material to be processed so that the investment can be recovered in a specific period of

time. Where this value is dependent on both the market value of the different products obtained in the process and the cost of raw materials and reagents. For this reason, a price sensitivity analysis of both reagents and products on the market is of great importance. This allows to identify the maximum cost that the different reagents of the process can present. Likewise, it allows the identification of the minimum price in the market that the products can reach in order to make the process unviable.

6. Chapter 6: Environmental assessments

6.1. Stand-alone processes

6.1.1. Compounds extraction

Two different technologies for the obtaining of a value-added product are presented as in the case of the Polyphenolic compounds extraction, a way to compare both technologies is an environmental analysis. The **Figure 6-1** shows the result of the environmental analysis for both SE and SFE. Negative values in each case indicate the decrease of the impact that can be obtained when the raw material was used for the obtaining of polyphenolic compounds. Both SE as SFE does not show significant differences in the indicators analyzed except for the AP. This last indicator has been presented a higher value compared with the value obtained for SFE, do that in the process of energy obtain gases of combustion was generated (NO_x , SO_2 , CO_2 , amount others) which contribute to the generation of the rain acidic. The main reason for which SE presented an energy consumption higher in comparison with SFE was longer operation time employed for the SE. Another factor that contributed to the high value of the AP for SE was the high amount of solvent that is required in this process, which was superior to amount used in SFE. From these results was possible to see that from the point of view environmental SFE is presented as a promising alternative for the obtaining of polyphenolic compounds using the tomato tree peel as raw material.

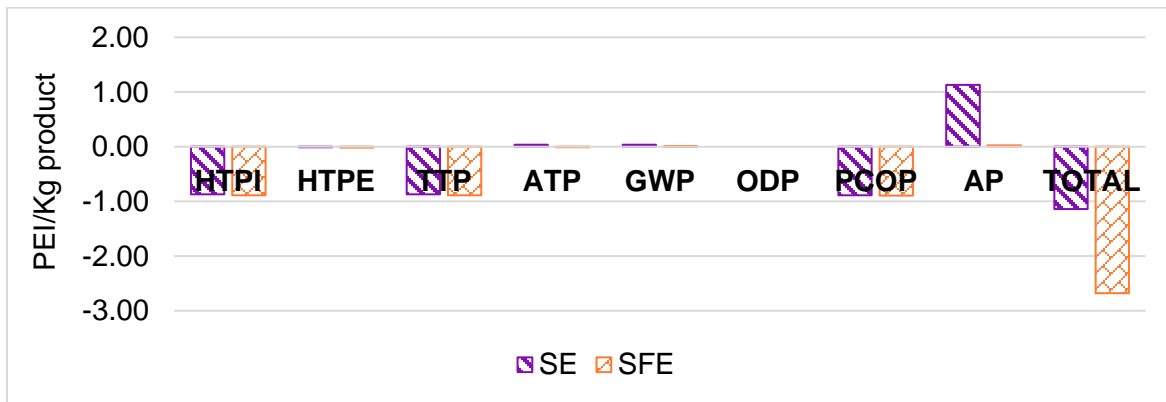
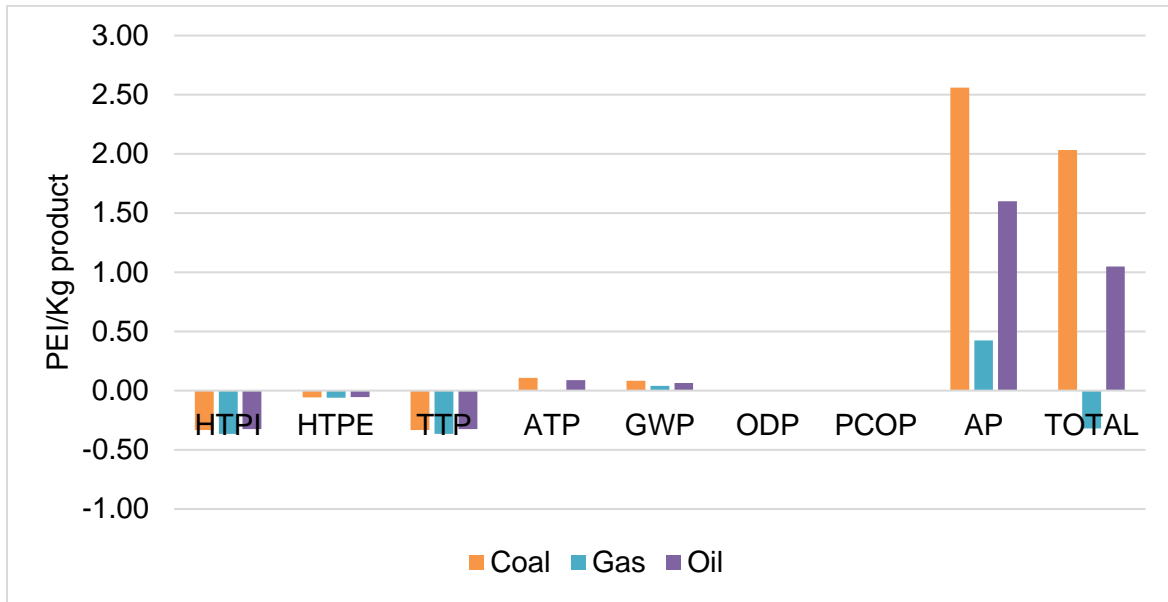


Figure 6-1. Environmental impact for the polyphenolic extraction from tomato tree employing SE and SFE

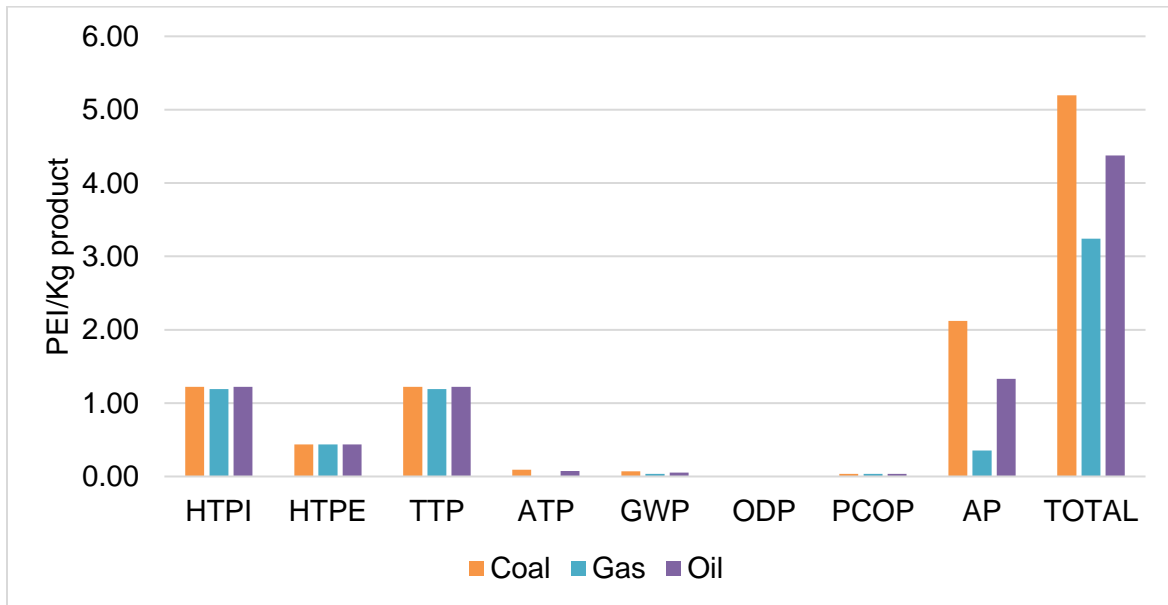
6.1.2. Ethanol production

In **Figure 6-2** are presented the results of potential environmental impact (PEI), calculated using the software WAR. This figure shows the comparison of three sources of energy (coal, gas and oil) for both feedstocks. In this is observed that in both cases the fuel that generated the least environmental impact per kilogram of product was the gas. In the case of ethanol production from cassava and using gas as fuel, is obtained a negative PEI which means a reduction of pollution in the environment. In other words, the waste generated in the process are less polluting than raw materials used for this purpose. Also a high impact is presented in acidification potential since the amount of CO₂ emissions that was having throughout the fermentation process. When analyzing the different fuels, different values are obtained for this category, because each fuel generates a different amount of CO₂ in the combustion process. This highlights the need for an analysis for the selection of fuel to be used in the process.

Among the differences in both processes are found microorganism using and the pretreatment given to the feedstock. These differences are reflected in the amount of waste obtained. Although the amount of ethanol produced by the two processes does not present a very great difference, purification of this generate a large quantity of wastes. Mainly by the microorganism metabolism. Due to this different substances product of the fermentation process are obtained. Therefore in the purification process of ethanol concentration stillage it is different, as the generated amount of this.



a. Cassava



b. Sugarcane bagasse

Figure 6-2. Potential environmental impact per kg of product leaving the system for fuel ethanol production from cassava and sugarcane bagasse case.

In the **Table 6-1** are presented the flows of residue streams analyzed both processes. In this can be observed that ethanol production from bagasse sugarcane generates more than

three times the amount of stillage generated when cassava is used as feedstock. The same is presented in the liberation of CO₂ in the process, which is 1.2 times higher than that generated with cassava. When sugarcane bagasse is used, other waste besides to those already mentioned is obtained. These are the result of processes of acid pretreatment and detoxification process. So when sugarcane bagasse is used a greater amount of additional waste is generated compared with the using cassava.

Table 6-1. Waste obtained in the ethanol production

Waste Process [L/h]	Cassava	Sugarcane bagasse
Impurity and wastes	28.72	60,428.35
CO ₂ emission	1,334.25	1,701.76
Stillage	13,671.52	46,346.79

In the **Table 6-2** are presented waste generated during pretreatment with dilute acid by sugarcane bagasse. In this can be appreciated the comparison with the cassava case in which the pretreatment only takes into account the milling and coking the material. In contrast to pretreatment of sugarcane bagasse that not only uses chemical agents for pretreat the material but also it is necessary to carry out detoxification processes in order to removing toxic compounds for both enzymatic hydrolysis as for fermentation.

Table 6-2. Products generated during hydrolysis process with dilute acid of sugarcane bagasse

Component	Flow [L/h]	Component	Flow [L/h]
Sulfuric Acid	0.76	Furfural	0.29
Calcium Oxide	0.12	Cellulose	1,399.04
Calcium Hydroxide	80.97	Xylan	37.67
Protein	28.99	Lignin	1,110.96
Glucose	127.80	Calcium Sulfate	1,538.43
Xylose	92.43	Ash	32.56

Total	4,450.02
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In the **Table 6-3** there are presented the percentage composition of stillage obtained for both processes. This shows that in both cases have a composition close to water. For cassava it is shown that other components are present in considerable quantities (ash, cellulose, dextrin, glucose, hemicellulose, protein and biomass). Compared with cassava, sugarcane bagasse stillage present different components in smaller proportions.

Table 6-3. Stillage percentage composition of the ethanol production

Component	Cassava	Sugarcane bagasse
Ash	0.50	0.00
Cellulose	0.11	0.00
Dextrin	0.19	0.00
Ethanol	0.00	0.23
Glucose	0.56	0.00
Hemicellulose	0.14	0.00
Protein	0.58	0.46
Water	97.57	98.06
Yeast	0.31	1.23

6.2. Biorefineries based on SCB as raw material

Complex processes such as biorefineries in general can have a large number of waste streams. These streams are associated with compounds that must be removed from the product stream in order to achieve high purity. Analyzing the different scenarios, it is observed that changes in the transformation route of a raw material such as SCB will have different potential environmental impact (PEI) (see **Figure 6-3**). Comparing scenarios 1 and 2, which differ in the implementation of a cogeneration process as a main difference, present differences in the value of the PEI obtained. This difference is due to the difference in energy of the process. Because with the implementation of the cogeneration process it

is not possible to supply all the energy demand of the first scenario. On the other hand, the reduction in the energy potential of syngas in the cogeneration process means that for methanol production a higher energy flow must be provided in order for it to reach the appropriate conditions for the reaction process. This energy difference is reflected in the AP (acidification potential) of the process. Where this value is lower for scenario 2 in comparison to scenario 1. This value is affected by the emissions generated by scenario 1 in order to be able to meet all its energy demand by burning fuels. The other categories analyzed present the same values, due to the fact that in both processes the same main products are obtained.

By varying from PHB production (scenario 2) to ethanol production (scenario 3), the process PEI becomes negative. This shows that this modification shows that the waste generated in this scenario is less polluting than that generated in scenario 2. Scenario 3 presents a smaller number of compounds in its output streams compared to scenario 2. Where those who did not react or should be removed from the process as purges present a high PEI. This change in the transformation route causes categories such as HTPI, HTPE, TTP, PCOP and AP to show a decrease in their values. Where the greatest change is observed in HTPI, which presents a decrease of 1.15 PEI/kg product.

Considering the production of furfural (scenario 4) in replaces the production of xylitol in scenario 3, the PEI decreases with this change in the transformation route. This change causes categories such as HTPI and TTP to show a change in their sign. Showing that the PEI of the waste associated with these categories is lower than that presented by the reagents and raw materials used in the process. Thus, the PEI per product of scenario 4 decreases by 1.82 compared to scenario 3. When using the furfural obtained in scenario 4 for octane production (scenario 5), the PEI per kg of product presents a small decrease (0.13 PEI/kg product). This shows that although the flow and quantity of components present in the waste increases, the PEI of the waste is lower than that of the reagents and raw materials used in the process.

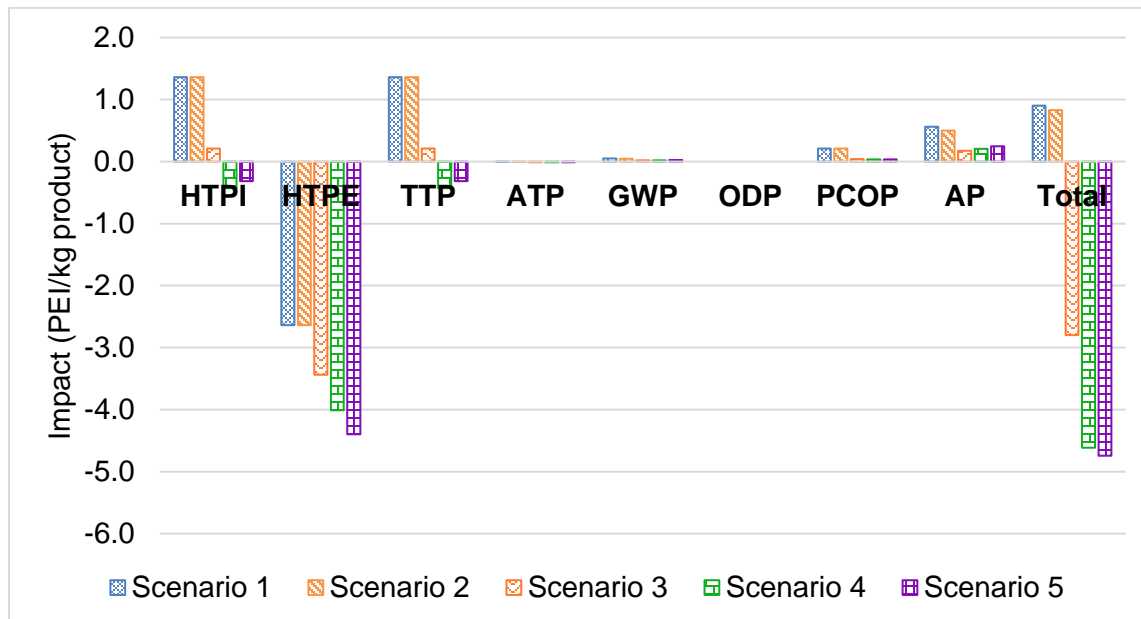


Figure 6-3. Distribution of PEI by category in each scenario

Analyzing the PEI generated in each scenario to supply the energy demand presented in **Figure 6-4**, it is higher for scenarios 1 and 2. While for the other scenarios it presents values that range between 0.195 and 0.272 PEI/kg product. Showing that the scenario that presents the least pollution in the process of supplying its energy demand is scenario 3 with 0.195 PEI/kg product. This is due to the fact that of the scenarios analyzed, it is the one with the lowest energy consumption and therefore the emissions generated in the energy generation processes are lower.

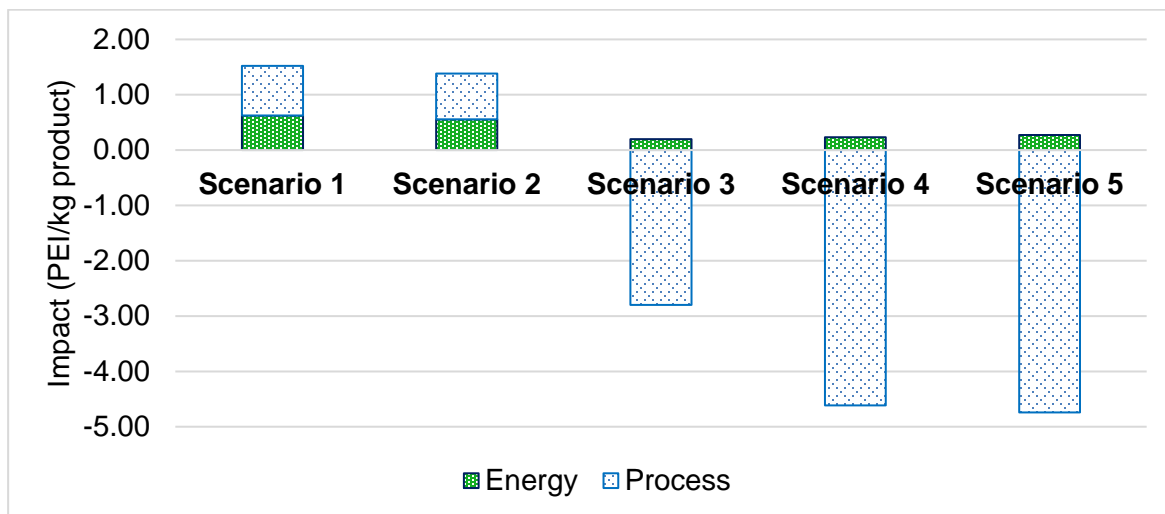


Figure 6-4. Impact for each scenario considering both energy and process

6.3. Final remarks

In extraction processes, an increase in process efficiency as well as a decrease in the amount of reagents used can lead to a decrease in the process PEI. Thus showing the environmental importance of the selection of the technology used in a process.

The selection of the fuel used to meet the energy demand of the process can reduce pollution in the processes. This is evident in the production of ethanol, a process for which two different raw materials were analyzed, which use different transformation processes. Three different energy sources were also analyzed: coal, gas and oil. Where for each of the cases analyzed the use of gas as a fuel the process PEI was the lowest.

The amount of waste generated during the process not only depends on the amount of reagents that did not react or on the by-products of the process, but also on the waste generated in the pre-treatment of the raw material. Thus, when ethanol is produced from SCB, more waste is generated. This is because SCB presents higher compositions of components that cannot be used in ethanol production. While when cassava is used as raw material, it is possible to process a larger amount of raw material in the production of ethanol.

When only the ethanol production from SCB was considered, an amount considerable of wastes was generated. These wastes has a great potential for obtaining added value products if the biorefinery concept is employ. In the cassava case was not generated

wastes that can be employed in other process. All the main compounds (starch) was used in the ethanol production.

The selection of the processing route of a raw material such as SCB will have a high influence on the PEI of the process. Thus with modifications it is possible to obtain a considerable change in the PEI of the process.

Conclusions

The exergy analysis allows to identify the steps of the process that have the main irreversibilities. At the same time, it identifies the causes and provide a preliminary idea of optimization. This allows reducing the cost of production, the environmental impact and to obtain better yields.

This type of analysis is presented as a powerful tool for the comparison of processes and the identification of the inefficiencies of the process from the energetic point of view. Likewise, the relationship between the economic, energetic and environmental analyzes is evidenced. In the design of biorefineries, exergetic analyzes allow the identification of the products where the best use of the raw material's energy content is obtained.

As it was demonstrated in the case that the exergy analysis allows understanding the processes possibilities. This allows the prediction of the energy yield as well as the efficiency of the process. These analyzes allow the identification of inefficient energy zones of the process, and which of these can be optimized through technological improvements enabling the maximization of operational efficiency. In this sense, the exergy analysis is presented as a tool for the formulation of solutions for the techno - economic problems presented in industrial processes.

In processes of extraction of polyphenolic compounds where different technologies can be used, different values for both energy and exergy can occur. Processes such as SFE allow for better yields with lower energy consumption, enabling a better potential use of the raw material.

As it is demonstrated that the use of cassava as a raw material allows higher yields in comparison to the SCB. In addition, it uses less energy. This is reflected in both an energy and an exergetic analysis. These analyzes allow to identify where the main physical changes in the transformation of the raw material occur. Likewise, it allows the identification of the stage of the process in which the highest energy consumption is presented. In this sense, the process where the main physical changes are made are the hydrolysis and fermentation processes for both the cassava and SCB. While the concentration of the stillage is the stage that presents the highest energy consumption for the case of cassava, whereas in the case of SCB, this stage corresponds to the pre-treatment processes of the material.

Energy, exergy and environmental use of cassava as raw material for obtaining ethanol is projected as a better alternative to SCB. Considering that similar results were obtained from the technical point of view, in this case it would not be an aspect that would allow an adequate decision to be adopted.

The comparison from the different points of view analyzed shows that scenario 3 is projected as the best combination of biorefinery between the configurations analyzed from the economic, energy and exergetic aspects. This scenario together with scenarios 4 and 5 are projected as the most viable alternatives from the environmental point of view. From this aspect, any of these three scenarios is viable.

From the results obtained in each of the cases analyzed, it can be observed that the exergy analysis is a tool with a high potential to compare processes. Where the alternatives selected in each case were those that presented adequate behaviors in energetic and economic aspects. This last one being an aspect of great influence now of selecting a process and a technology of transformation.

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