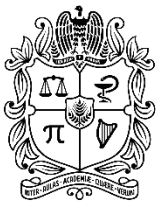

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Evaluation of the influence of ultrasound and supercritical fluids in processes of polyphenolic compounds extraction from agroindustrial wastes

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Evaluación de la influencia del ultrasonido y fluidos supercríticos en procesos de extracción de compuestos polifenólicos a partir de residuos agroindustriales

Ashley Sthefanía Caballero Galván

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Universidad Nacional de Colombia sede Manizales
Facultad de Ingeniería y Arquitectura, Departamento de Ingeniería Química
Manizales, Colombia
2017

"A Dios por su grandes bendiciones,
a mis padres por su amor incondicional,
a mis hermanos y seres queridos por la ayuda y comprensión"

"Comienzo de la sabiduría:
Adquiere la sabiduría;
cueste lo que te cueste,
Adquiere la inteligencia,
tenla en gran estima y ella te exaltará;
ella será tu honor, si la abrazas."
Proverbios 4: 7-8

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List of Publicacions

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1. Published and accepted

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2. Submitted and review

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production from banana peel in a biorefinery concept (*Musa paradisiaca*)". Environmental Science & Pollution Research. Status: Submitted.

Ashley Sthefanía Caballero G., Daissy Lorena Restrepo S., Carlos Ariel Cardona A."Analysis of biorefineries for value-added products from naranjilla peel (*Solanum quitoense*): Colombian case". Status: Revision.

Ashley Sthefanía Caballero G., Juan Miguel Romero G., Eulogio Castro G., Carlos Ariel Cardona A. "Effect of supercritical fluid extraction in obtaining polyphenolic compounds from olive waste". Status: Revision.

Ashley Sthefanía Caballero G., Carlos Ariel Cardona Á. "Analysis of polyphenolic compounds extraction from spent coffee grounds". Status: Revision.

Ashley Sthefanía Caballero G., Daissy Lorena Restrepo S., Jhonny Alejandro Poveda, Carlos Ariel Cardona A. "Evaluation of biorefineries schemes from spent coffee grounds". Status: Revision.

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Ashley Sthefanía Caballero G., Carlos Ariel Cardona Á. "Polyphenolic compounds from spent coffee grounds through ultrasound assisted extraction". Status: Revision.

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Ashley Sthefanía Caballero-Galván, Daissy Lorena Restrepo-Serna, Carlos Ariel Cardona-Álzate. "Prefeasibility analysis in obtaining antioxidants from tree tomato peel". Status: Revision.

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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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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.

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Pasantia

National Technical University of Athens. Duration: 1 month.

Abstract

This work demonstrates the potential for obtaining polyphenolic compounds through the use of unconventional technologies: ultrasound assisted extraction and supercritical fluids extraction. The raw material employed in to develop the present work were spent coffee grounds, coffee cut-stems and naranjilla peel. Where these residues are produced in larg amount in Colombia. In addition, other raw materials from fruit and olive residues were analyzed. For this experimental stage, the physical-chemical characterization of the raw materials was initially carried out. Subsequently, the extraction conditions of chlorogenic acid was theoretically evaluated, in order to determine the best operating conditions. Then, extractions of the compounds of interest were carried out with technologies such as solvent extraction, Soxhlet extraction, ultrasonic assisted extraction and supercritical fluids extraction. This last was realized using CO_2 as supercritical fluid. From this, it was determined the influence of each of these technologies in the polyphenolic compounds extraction. As a results were obtained compounds such as chlorogenic acid, ferulic acid, quercetin, vanillin, among others. In addition, these raw materials were used in integrated processes, through the development of different biorefineries. In these analysis were obtained of value-added products such as antioxidants, ethanol, xylitol, furfural and energy generation. Where, the economical, energetic and environmental aspects were evaluated.

KEYWORDS: ultrasound assisted extraction, supercritical fluid extraction, agroindustrial waste, polyphenolic compounds.

RESUMEN

Este trabajo demuestra el potencial para obtener compuestos polifenólicos mediante el uso de tecnologías no convencionales: extracción asistida por ultrasonido y extracción de fluidos supercríticos. Las materias primas empleadas para desarrollar el presente trabajo fueron borra de café, zoca de café y cáscara de lulo. Donde estos residuos se producen en gran cantidad en Colombia. Además, se analizaron otras materias primas de residuos de frutas y olivo. Para la etapa experimental, inicialmente se llevo a cabo la caracterización físico-química de las materias primas. Posteriormente, fueron evaluadas teóricamente las condiciones de extracción del ácido clorogénico, para determinar las mejores condiciones de operación. Luego, las extracciones de los compuestos de interés fueron llevaradas a cabo con tecnologías de extracción por solvente, extracción Soxhlet, extracción asistida por ultrasonidos y extracción de fluidos supercríticos. Esto último fue realizado utilizando CO_2 como fluido supercrítico. A partir de esto, fue determinada la influencia de cada una de estas tecnologías en la extracción de compuestos polifenólicos. Como resultado, se obtuvieron compuestos tales como ácido clorogénico, ácido ferúlico, quercetina, vainillina, entre otros. Además, estas materias primas se utilizaron en procesos integrados, a través del desarrollo de diferentes biorrefinerías. En estos análisis se obtuvieron productos de valor agregado como antioxidantes, etanol, xilitol, furfural y generación de energía. Donde se evaluaron los aspectos económicos, energéticos y ambientales.

Palabras claves: extraccion asistida por ultrasonido, extracción con fluidos supercríticos, residuos agroindustriales, biorrefinerias, compuestos polifenólicos.

Thesis Hypothesis

The application of technologies as ultrasonic extraction and supercritical fluid extraction can be as efficient as conventional technologies in the extraction of polyphenolic compounds from coffee and naranjilla residues.

Thesis Objectives

General Objective

- To evaluate technically, economically and environmentally the polyphenolic compounds obtained from agroindustrial residues, through the use of ultrasonic assisted extraction and supercritical fluids.

Specific Objectives

1. To perform the physico-chemical characterization of the raw materials (spent coffee grounds, coffee cut stems and naranjilla peel).

2. To theoretically evaluate the extraction conditions of polyphenolic compounds from the selected raw materials.

3. To evaluate experimentally the extraction of polyphenolic compounds with soxhlet technology.

4. To evaluate experimentally the extraction of the polyphenolic compounds with the ultrasound assistant extraction technology.

5. To evaluate experimentally the extraction of the polyphenolic compounds with the supercritical fluids extraction technology.

6. To evaluate the potential of low-scale biorefineries from the selected raw materials.

Nomenclature

AA	Antioxidant activity
AD	Dilute acid
AP	Acidification Potential
ATP	Aquatic Toxicity Potential
CCS	Coffee cut-stems
CGA	Chlorogenic acid
Ex	Exergy Total of the stream [KW]
Ex^{ch}	Physical exergy [KJ/h]
Ex^{ph}	Chemical exergy [KJ/h]
GA	Gallic acid
G_f	Standard gibbs energy
GWP	Global Warming Potential
H_f	Standard enthalpy of formation
H_{fus}	Standard enthalpy of fusion
h_j	Enthalpy of the stream *i* [KJ/kmol]
h_o	Reference enthalpy [KJ/kmol]
HTPE	Human Toxicity by Exposure
HTPI	Human Toxicity by Ingestion
H_v	Standard enthalpy of vaporization
MAE	Microwave assisted extraction
n_i	Flujo molar de la corriente *i* [kmol/h]
NPV	Net Present Value
ODP	Ozone Depletion Potential
P_c	Critical pressure
PCOP	Photochemical Oxidation Potential
PEI	Potential environmental impact
R	Universal constant of ideal gases
SCG	Spent coffee grounds
SE	Solvent extraction
SFE	Supercritical fluid extraction
S_j	Entropy of the stream *j* [KJ/kmol.K]
S_o	Reference entropy [KJ/kmol.K]
Sox-E	Soxhlet extraction

T_c	Critical pressure [K]
T_o	Reference temperature [K]
TPC	Total phenolic compounds
TTP	Terrestrial Toxicity Potential
UAE	Ultrasound assisted extraction
USD	American dollar
V_c	Critical volume
W	Acentric factor
WAR	Waste Reduction Algorithm
W_f	Final weight of the sample
W_i	Initial weight of the sample

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INTRODUCTION

Polyphenolic compounds are an important class of chemicals present in edible and inedible plants. These compounds have beneficial health effects, due to their antioxidant capacity, which inhibits the oxidative degradation of organic materials. Furthermore, the use of these compounds covers the medical, food and cosmetic industry. This last due to its multiple applications for its anticancer, anti-inflammatory, anti-diabetic properties, among others. To carry out the obtained of polyphenolic compounds are used extraction process. The traditional methods of extraction are characterized by the application of high temperatures, material size decrease, long operating time and low performance. However, the using of high temperatures can cause degradation of the compounds due to their sensitivity. For this reason, the use of techniques for the polyphenolic compounds extraction have been increasing. These techniques have the aim of reducing solvent consumption, lowering the process time and increasing extraction efficiency. Methods such as supercritical fluids extraction (SFE) and ultrasound assisted extraction (UAE) are of great interest for their application. This due a greater penetration of the solvent in the structural matrix of the raw material, providing a longer area of contact between the different phases.

The different types of polyphenolic compounds (flavonoids, phenolic acids, tannins) are usually obtained from fruits and vegetables. However, agroindustrial waste is a promising raw material for the extraction of these compounds. In Colombia, the residues from coffee and naranjilla have a large production, generating environmental and economic problems in the final disposition of the same. Therefore different studies showed the potential of these residues in the obtaining of antioxidants. Where these provide a value-added to each of these productive processes.

The main objective of this study was to evaluate of the extraction potential of polyphenolic compounds from agroindustrial residues. For this, the supercritical fluids extraction and ultrasound assisted extraction technologies were proposed. As a reference point, the Soxhlet extraction and solvent extraction will be used, allowing a comparative analysis of the influence of conventional and non-conventional methods on the performance in the analyzed process. In addition, the design of low-scale biorefineries were carried out from the aforementioned residues. This last to analyze the potential presented by each one, as a platform for obtaining value-added products.

1. POLYPHENOLIC COMPOUNDS

Polyphenolic compounds are molecules which contain in their structure a hydroxyl group on an aromatic ring, resulting in a phenolic structure. These compounds are part of the secondary plant metabolites as shown in **Figure 1.1.** Such compounds are commonly consumed in foods such as vegetables, fruits, legumes, cereals, among others. Where, diferents studies have identified around 8000 varieties of polyphenolic compounds (Adriana Farah and Marino Donangelo 2006). The importance of these compounds lies in the nutritional quality for their contribution to the maintenance of human and sensorial health of the same. Also, this compounds are in charge of the projection of the plants and their coloration (Bravo, Sources, and Significance 1998). It must be noted that the content and composition of the polyphenolic compounds in a plant may vary depending on the conditions and climate of the growing area (Martos 2013).

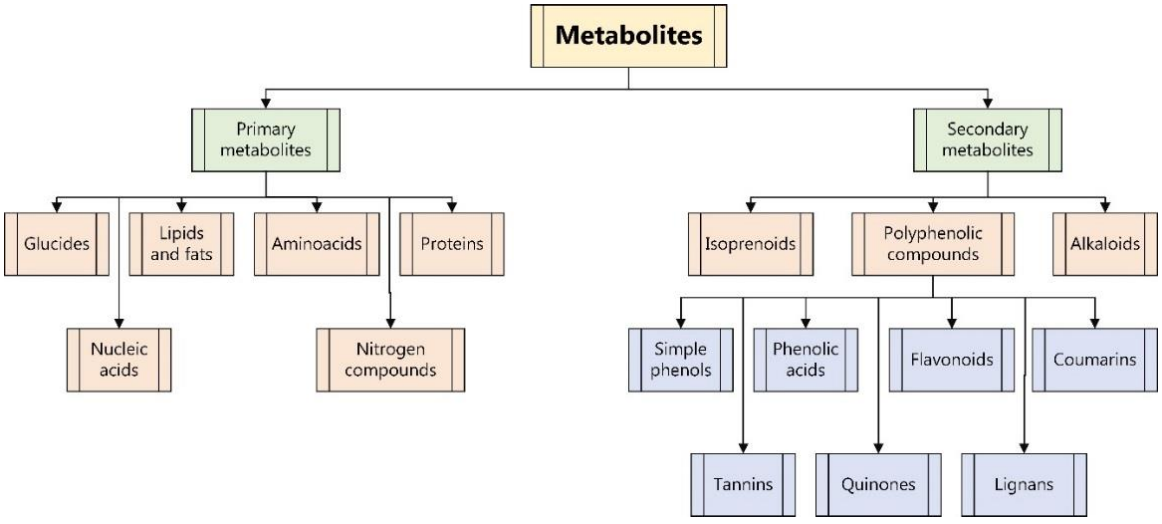


Figure 1.1. Classification of the main metabolites.

At the global level, these natural products have increased their consumption, due to consumers' awareness of using products that are beneficial to health. Futhermore, the great variety of applications that they present, as seen in **Figure 1.2** (Biochemicals 2008). These compounds mainly present applications of great interest in the pharmaceutical industry. This because of their properties in protection against chronic diseases such as cancer, diabetes and neurodegenerative diseases. Moreover, in the food industry, these compounds are used for their antioxidant potential, which prevent the formation of off-flavors resulting from the oxidation of lipids (Tuberoso and Orrù 2008).

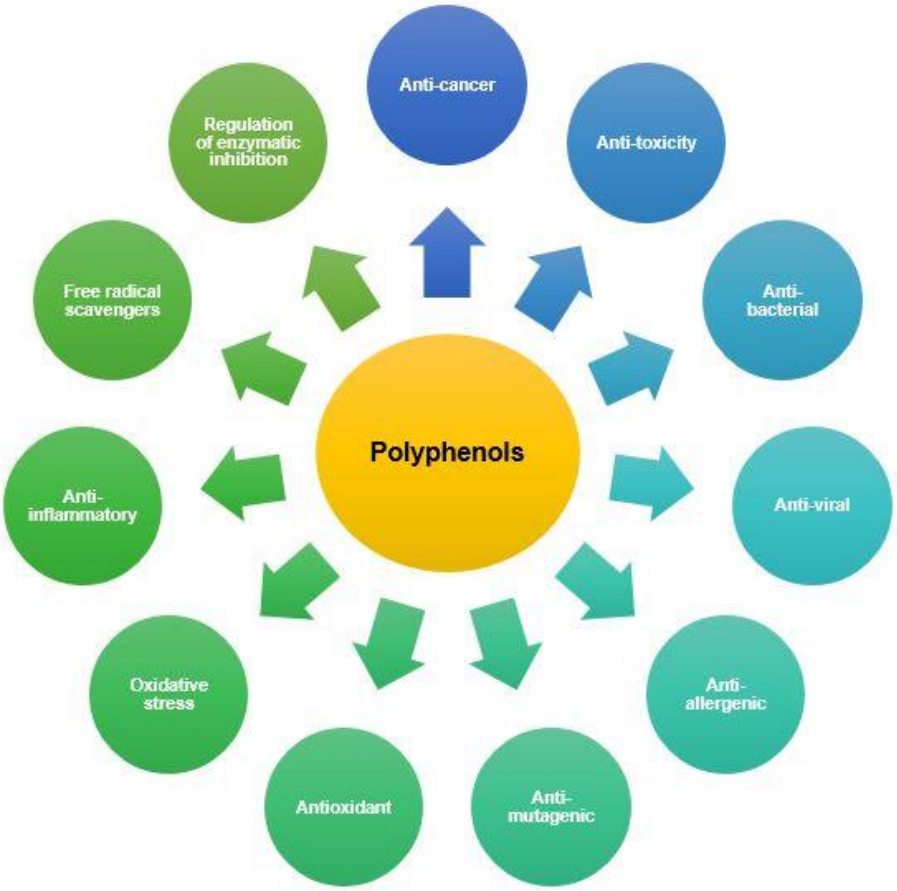


Figure 1.2. Applications of polyphenolic compounds.

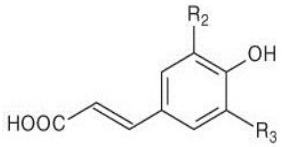
1.1. Classification of polyphenolic compounds

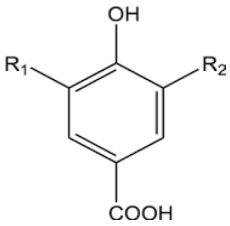
This type of compound has a division according to the structure in question number of phenolic rings, the elements connecting structures, among others. The most important polyphenolic compounds are described below: flavonoids, phenolic acids and tannins (Martins et al. 2011).

1.1.1. Phenolic acids

Phenolic acids are those compounds which possess a functionality of carboxylic acids. These compounds can only be hydrolyzed by means of alkaline, acidic hydrolysis or by the use of enzymes. The classification of phenolic acids can be divided into two main groups: hydroxycinnamic and hydroxybenzoic. Hydroxycinnamic acids are in the form of simple esters in conjunction with cyclic acid-alcohol. Where caffeic acid is the one with the highest presence in fruits and coffee (Reis-Giada 2013). Furthermore, hydroxybenzoic acids have more complex structure, highlighting in this group gallic acid used for the determination of phenolic compounds. The **Table 1.1** the hydroxycinnamic and hydroxybenzoic acids with their respective derivatives and industrial applications are presented.

Table 1.1. Main phenolic acids.

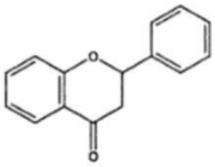
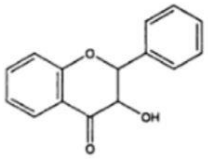
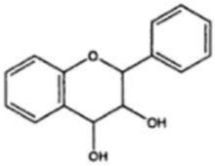
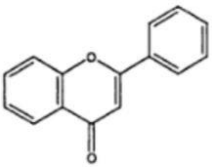
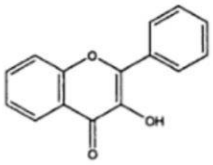
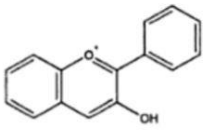
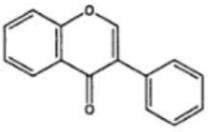
	Phenolic acids	Chemical formula	Applications
 **Hydroxycinnamic acid**	Ferulic acid	$C_{10}H_{10}O_4$	Cell renewal, antioxidant, anti-ultraviolet, anti-aging, anti-inflammatory, cholesterol reduction, muscle mass increase.
	Chlorogenic acid	$C_{16}H_{18}O_9$	Anti-diabetic, anti-inflammatory, antioxidant, anti-cancerigenic, slimming, protection of cardiovascular system, reduces the feeling of anxiety.
	Caffeic acid	$C_9H_8O_4$	Antioxidant, treatments for cancer, HIV and herpes, reduction of tumors, increases the level of body defenses.

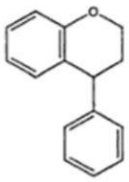
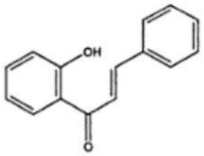
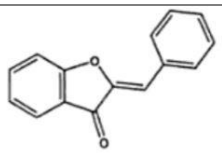
	p-coumaric	$C_9H_8O_3$	Antibacterial, activates microbial functions beneficial for intestinal function.
	Sinapic acid	$C_{11}H_{12}O_5$	Antioxidant.
	Cinnamic acid	$C_9H_8O_3$	Flavoring, antifungal, helps decrease fatigue and cough.
 **Hydroxybenzoic acid**	Vainillic acid	$C_8H_8O_4$	Flavoring agent, antioxidant.
	Syringic acid	$C_9H_{10}O_5$	Antioxidant.
	Gallic acid	$C_7H_6O_5$	Antimicrobial, anticancerigenic, antiviral, antioxidant, antifungal, astringent, treatment for hemorrhoids and psoriasis.
	Salicylic acid	$C_7H_6O_3$	Elimination of acne, warts, calluses, antidandruff, mouthwash. Treatment for keratosis and psoriasis.
	Protocatechuic acid	$C_7H_6O_4$	Antifungal, antioxidant, anti-inflammatory, antigenotoxic.
	Benzoic acid	$C_7H_6O_2$	Preservative and preservative of food, protection against mold, flavoring, germicide.

1.1.2. Flavonoids

Flavonoids are compounds with low molecular weight. Their base structure consists of two aromatic rings joined by means of a bridge of 3 carbons (Kushwaha and Karanjekar 2011). There are about 3000 varieties identified, which have wide uses in the pharmaceutical industry due to their anti-hepatotoxic, anti-inflammatory, anti-allergenic and anti-ulcer properties (Narayana et al. 2001). Also, the food industry uses this type of compounds to be potent antioxidants present. The Flavonoids have a classification according to the structure as presented in **Table 1.2**. Where according to the position of the benzene can be flavanone or isoflavonoids. Meanwhile, according to the position of the hydroxyl group and the double bonds in flavonols or flavone (Narayana et al. 2001; Carrión and García 2010).

Table 1.2. Classification of main flavonoids.

Classification	Description	Chemical structure	Compounds
Flavanone	It has a carbonyl group in the fourth position.		Butin, sterubin, hesperetin, naringin, poncirin, sakuranin, sakuranetin, pinostrobin, eriodictyol, hesperedin, homoeriodictyol, isosakuranetin, naringenin, pinocembrin
Dihidroflavonol	It possesses a carbonyl group and the third position is hydrolyzed.		Dihydromyricetin, dihydroquercetin, dihydrokaempferol
Flavan-3,4 diol	The carbonyl group is reduced to the fourth position.		Leucocyanidin, catechin, gallocatechin, Catechin 3-gallate, Gallocatechin 3-gallate, Epicatechins, Epigallocatechin, Epicatechin 3-gallate, Epigallocatechin 3-gallate
Flavone	Introduction of a double bond in the second and third positions of flavonone.		Apigenin, luteolin, tangeritin, chrysin, wogoin, scutellarein, baicalein, 6-hydroxyflavone, 7,8-dihydroxyflavone
Flavonol	Introduction of a double bond in dihydroflavonol in the second and third positions.		Morin, quercetin, quercetin, robinin, fisetin, rutin, myricetin, kaempferol, myricitrin, galangin, kaempferide, rhamnetin
Anthocyanins	They present a conjugated system of double ligatures.		Cyanidin, aurantinidin, delphinidin, europinidin, malvidin, peonidin, petunidin, rosinidin, pelargonidin
Isoflavone isomer	A carbon ring is added in the third or fourth position of the overall structure.		Genistein, daidzin, glycitein, 17β-Oestradiol

Neoflavonoid isomer	A carbon ring is attached at the third position of the general structure.		Coutareagenin, dalbergin, nivetin, dalbergichromene
Chalcone	There is no formation of a heteroside with 15 carbon atoms.		Chalcona
Aurone	The heteroside C is forming by five members.		Aureusidin, leptosidin, 4,5,6-Trihydroxyaurone, hispidol, sulfuretin

1.1.3. Tannins

Tannins are water soluble compounds with the ability to precipitate proteins and alkaloids (Vihakas 2014). These compounds are mainly divided into three groups: florotanins, hydrolyzable tannins and condensed tannins or also known as proanthocyanidins. Hydrolyzable tannins are esters derived from gallic acid, easily hydrolyzed with bases, acids and enzymes. Moreover, the condensed tannins are oligo- or polymeric structures found in nature, with different structural and isomeric forms.

1.2. Polyphenolic compounds of high potential

Polyphenolic compounds are an essential part of the human diet and are of great interest because of their antioxidant properties and potential beneficial effects on health. These compounds can be from a phenolic molecule to complex polymers of high molecular weight (Fereidoon Shahidi and Priyatharini Ambigaipalan 2015). Intake of polyphenol compounds is affected by eating habits, the average daily ingestation in a diet considered normal is approximately 1 g per person. The main sources of these compounds are beverages, fruits and to a lesser extent vegetables and legumes (Fereidoon Shahidi and Priyatharini Ambigaipalan 2015). These compounds have effects against important diseases such as

cancer, cardiovascular diseases, oxidative stress and neurodegenerative diseases (Fereidoon Shahidi and Priyatharini Ambigaipalan 2015). Different polyphenolic compounds can provide these benefits which include chlorogenic acid, ferulic acid, vanillin, vanillic acid, quercetin, caffeic acid, hydroxytyrosol, among others.

1.2.1. Chlorogenic acid

Chlorogenic acid (CGA) is a compound formed from the esterification of cinnamic acid (caffeic acid, p-coumaric or ferulic acid) with quinic acid (see **Figure 1.3**). Where the main CGA found in nature are caffeoylquinic acid (CQA) and dicaffeoylquinic acid (diCQA) (A. Farah et al. 2008; Martos 2013).

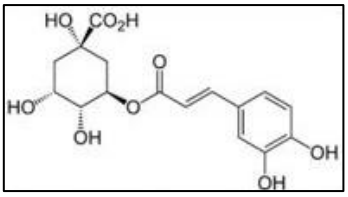


Figure 1.3. Chemical structure of the chlorogenic acid.

The CGA is a thermosensitive polyphenol with a high added value because it is a highly potent antioxidant. In addition, its uses as hypoglycaemic, anti-diabetic, anti-inflammatory, anti-aging and other biological effects (Miura et al. 2015; Moreira et al. 2015; Tan et al. 2014). This compound has been detected in different varieties of fruits, vegetables as shown in **Table 1.3**. However, it is mainly known for its presence in green coffee beans, containing about 5 - 12 g per 100 g of coffee (Adriana Farah and Marino Donangelo 2006; Naegele 2013).

Table 1.3. Raw materials identified with presence of chlorogenic acid.

Raw material	Scientific name	Chlorogenic acid (mg/g)	References
Coffee grains	*Coffea arabica*	6.79	(Marín and Puerta 2008)
	Coffea canephora	9.25	
Eggplant	*Solanum melongena L.*	3.75	(Martos 2013)
Potato	*Solanum tuberosum*	3.52	(G. Li et al. 2011)
Apple	*Malus domestica*	0.38	(Awad, De Jager, and Van Westing 2000)
Plum	*Prunus domestica*	0.02	(Bouayed et al. 2007)

Artichoke Leaves	*Cynara scolymus L.*	8.40	(Saleh et al. 2016)
Tobacco leaves	*Nicotiana tabacum*	1.95	(Mazvimba et al. 2012)
Pasture	*Panicum virgatum*	0.20	(Escamilla-Treviño et al. 2014)
Tomato	*Solanum lycopersicum*	0.03	(Periago et al. 2002)
Cauliflower	*Brassica oleracea var. botrytis*	0.01	(Mattila and Hellström 2007)
Avocado	*Persea americana*	0.01	
Carrot	*Daucus carota*	0.01	
Aubergine	*Solanum melongena*	0.21	
Soya bean	*Glycine max*	0.02	

1.2.2. Ferulic acid

Ferulic acid or 3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid is a component of lignocelluloses, which confers rigidity to the cell wall (see **Figure 1.4**). This compound is used mainly in the cosmetic industry, because it provides protection to the skin from the rays of the sun. **Table 1.4** shows different studies, which have reported high concentrations of ferulic acid in fruits such as lemon, orange and grapefruit with 0.39, 0.45 and 0.39 mg/g, respectively (Gorinstein et al. 2001). In addition, the beet (0.25 mg/g) and soybean (0.12 mg/g) were found to be potential raw materials for obtaining this compound (Mattila and Hellström 2007).

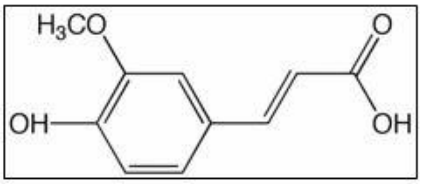


Figure 1.4. Chemical structure of ferulic acid.

Table 1.4. Raw materials identified with presence of ferulic acid.

Raw material	Scientific name	Ferulic acid (mg/g)	References
Raspberry	*Rubus idaeus*	0.02	(Häkkinen et al. 1999)
Blueberry	*Cyanococcus*	0.01	
Tomato	*Solanum lycopersicum*	0.01	(Periago et al. 2002)
Orange	*Citrus X sinensis*	0.39	(Gorinstein et al. 2001)

Lemon	*Citrus × limon*	0.45	(Mattila and Hellström 2007)
Grapefruits	*Citrus × paradisi*	0.32	
Potato	*Solanum tuberosum*	0.01	
Avocado	*Persea americana*	0.01	
Turnip	*Brassica rapa*	0.01	
Broccoli	*Brassica oleracea var. italica*	0.04	
Spinach	*Spinacia oleracea*	0.07	
Carrot	*Daucus carota*	0.01	
Radish	*Raphanus raphanistrum subsp. sativus*	0.05	
Red beet	*Beta vulgaris*	0.25	
Soya bean	*Glysine max*	0.12	
Peanut	*Arachis hypogaea*	0.09	

1.2.3. Vanillin

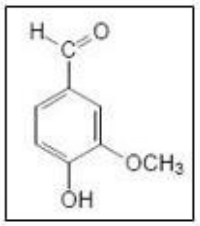


Figure 1.5. Chemical structure of vanillin.

Vanillin, also known as 4-hydroxy-3-methoxybenzaldehyde (see **Figure 1.5**). This one is derived from ferulic acid, which is used in the food industry as a flavoring and in cosmetics for its aroma (Westcott, Cheetham, and Barraclough 1993). On the other hand, it is mainly synthesized and only 1% is obtained naturally from the pods of the vanilla orchid presenting a higher cost than the synthetic (Walton, Mayer, and Narbad 2003).

1.2.4. Vanillic acid

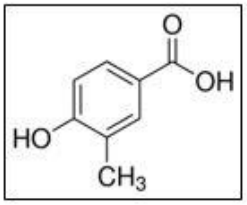


Figure 1.6. Chemical structure of vanillic acid.

Vanillic acid or 4-hydroxy-3-methoxybenzoic acid (see **Figure 1.6**) is a compound used as a flavoring agent. Furthermore, this compound have antioxidant properties and high antimicrobial activity against a wide range of

bacteria (YEMIŞ et al. 2011; Tai, Sawano, and Ito 2012).

1.2.5. Caffeic acid

Caffeic acid (3,4-dihydroxycinnamic acid), derived from hydroxycinnamic acid of natural origin (see **Figure 1.7**). It is found in a wide variety of plants. Investigations provided by Leung, Fenton and Clandinin (1981) demonstrated the presence of this compound in sunflower seeds (Leung, Fenton, and Clandinin 1981), being at the same time the most predominant phenolic compound in this raw material. Additionally, Rodriguez, Hadley and Holm (1994) reported the presence of caffeic acid in potato peel (2.49 ± 1.59 mg/100g) with low content (Rodríguez de Sotillo, Hadley, and Holm 1994). The caffeic acid presents multiple health benefits, having the property of reducing skin tumors (anticancer), antiviral activity, as well as being powerful antioxidants and anti-inflammatory (Y. Li et al. 2015).

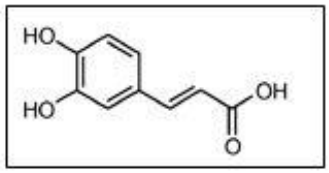


Figure 1.7. Chemical structure of caffeic acid.

1.2.6. Quercetin

Quercetin is the most representative compound of the flavonol group. It has many therapeutic uses such as: anti-inflamatoria, antioxidant, anti-histamines, treatments for cancer, allergies, asthma, urticaria, antidiabetic, treatments for rheumatoid arthritis. Besides it contributes the color in fruits, flowers and vegetables (Carrión and García 2010). In **Figure 1.8** the chemical structure of this compound is presented. Additionally, the quercetin has shown a high presence in raw materials such as onion (4.83 mg/g), cranberry (1.49 mg/g) and potatoes (0.77 mg/g), as shown in **Table 1.5.**

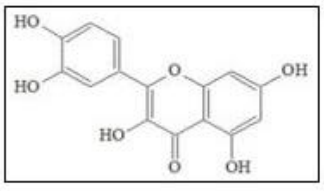


Figure 1.8. Chemical structure of quercetin.

Table 1.5. Raw materials identified with presence of quercetin.

Raw material	Scientific name	Quercetin (mg/g)	References
Strawberry	*Fragaria × ananassa*	0.50	(Hakkinen and Torronen 2000)
Raspberry	*Rubus idaeus*	0.03	(Häkkinen et al. 1999)
Blueberry	*Cyanococcus*	0.16	
Tomato	*Solanum lycopersicum*	0.04	(Periago et al. 2002)
Onion	*Allium cepa*	4.83	(Paganga, Miller, and Rice-Evans 1999)
Cranberry	*Oxycoccus*	1.49	
Lettuce	*Lactuca sativa*	0.32	(Hertog, Hollman, and Venema 1992)
Leek	*Allium ampeloprasum*	0.02	
Peas	*Pisum sativum*	0.04	
Apple	*Malus*	0.12	(Sultana and Anwar 2008)
Apricot	*Prunus armeniaca*	0.32	
Aloe vera leaves	*Aloe vera L.*	0.09	
Plum	*Prunus domestica*	0.02	
Peach	*Prunus persica*	0.01	
Blackberry	*Rubus*	0.03	(HERRMANN 1976)
Potato	*Solanum tuberosum*	0.77	
Broccoli	*Brassica oleracea*	0.01	
Carrot	*Daucus carota*	1.50	

1.2.7. Hydroxytyrosol

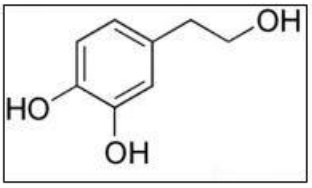


Figure 1.9. Chemical structure of hydroxytyrosol.

Hydroxytyrosol or 2- (3,4-dihydroxyphenyl) – ethanol (see **Figure 1.9**) is a white powder mainly obtained from the fruit and leaves of the olive tree either by mechanical extraction or chemical processes (Vilaplana-Pérez et al. 2014). This polyphenol is one of the compounds with greater antioxidant activity, being highlighted by the protection that confers to the low density lipoproteins (decrease in the risk of cardiovascular diseases) (Ferrán 2015; Vilaplana-Pérez et al. 2014).

1.3. Influence of Polyphenolic Compounds on Human Health

The consumption of polyphenolic compounds is an important factor to prevent the development of chronic diseases. These complications are associated to a damage caused by free radicals generated in an inefficiently oxidative phosphorylation (Hintze et al. 2011). Free radicals and reactive oxygen species (ROS) can be also generated due to external conditions such as, cigarette smoking, air pollution, X-ray and UV-ray exposure and chemicals produced in industry (Bagchi and Puri 1998).

This oxidative phenomenon generate a progressive deterioration in constituent molecules such as DNA, lipids and proteins (Hintze et al. 2011). ROS attack all type of macromolecules in the body causing cell damage and homeostatic disruption (Lobo et al. 2010). An equilibrium between antioxidants and oxidants molecules can be disrupted due to an excess of free radicals, increasing the rate of degradation in cells structures (Fusco et al. 2007). In some cases, a person with a pathologic condition as diabetes oxidative stress causes a fall in the antioxidant concentration in the body (Sardesai 1995). The free radical theory of aging is not fully established but some evidences support it, such as a linear correlation between antioxidant activity and the maximal life span potential or a correlation between high antioxidant enzyme expression and increased longevity (Sardesai 1995; Borrás et al. 2003; Lee and Wei 2012). According with this theory the human antioxidant systems are divided into two groups: enzymatic and non-enzymatic antioxidants.

The first one can be sub-divide in two groups, primary and secondary enzymes that allow the prevention or neutralization of free radicals (Carocho and Ferreira 2013). Non-enzymatic antioxidants are a group of molecules such as polyphenolics, uric acid and minerals. These are present in endogenic form to prevent the formation and the presence of free radicals. However, the endogenous antioxidant system is not sufficient. For this reason, humans are dependable of antioxidants that are present in the diet to maintain the equilibrium of free radicals in the body (Pietta 2000). The polyphenolic compounds are of great interest due to

they are potential candidates for use in disease treatments like SIDA, heart ailments, ulcer formation, bacterial infections and neural disorders (Tückmantel, Kozikowski, and Romanczyk 1999). These compounds can react with an oxidant electron, preventing the formation of free radicals in biologicals systems (Handique and Baruah 2002). These polyphenolic compounds are synthetized in the normal biological function in plants as well as stress situation like UV radiation and infections. In this sense, the polyphenolic compounds are considered the most important a common compounds in the plant kingdom (Haminiuk et al. 2012).

In a dairy diet antioxidants could be present in many foods and beverage. Even so, it was found that plant-based foods have the highest median of antioxidant concentration (0.88 mmol/100 g) in comparison with animal based foods (Pellegrini et al. 2006). In natural beverages the highest antioxidant levels were found in unprocessed tea leaves and coffee. For the last, it was found a range of concentration between 0.89 to 16.33 mmol/100. Where, it depended of the coffee specie and the preparation of the beverage. On the other hand, the antioxidants can be found in other beverage such ad red wine, grape juice and pomegranate juice (Pellegrini et al. 2006). But nowadays, the busy-lifestyle does not allow to consume this compounds in this kind of preparations. For this reason, functional formulated foods and beverage has been created.

The demand of health-promoting foods and beverages has been increased, due to a growth in the interesting of healthcare. The diffusion of this functional foods is led for many factors such as busy lifestyle, health deterioration, lack of exercise and un-healthy environments (Corbo et al. 2014). Studies have demonstrated that exposure to chronic psychological stress is related to increase free radical levels that in a long term may cause neurodegenerative diseases such Alzheimer's and Parkinson's diseases (McEwen 2004; Kumar et al. 2006). In 2008 the functional foods market was estimated in USD $80 billion approximately, led by United States nutraceutical market (35%), Japan (25%) and the European market. In 2007

antioxidant ingredients and supplements represented a market of USD 3.7 billion with a growth of 3% per year in the USD market (Vergari, Tibuzzi, and Basile 2010).

Some antioxidants have been studied for their direct application in functional foods and beverage. This has the aim to reduce the damage caused by free radicals. Therefore, It has been suggested that natural ingredients with strong antioxidant activity may be used to design novel functional beverages (Sun-Waterhouse 2011). To applicate the use of antioxidants in beverages some conditions are necessary. For this reason, the antioxidants have to be inexpensive, high stable, non.-toxic and effective in low concentrations. Also, these must have a good solubility in the final beverage (Kiokias, Varzakas, and Oreopoulou 2008). To accomplish these characteristics natural sources of antioxidants must be proposed for their application and healthy beverages (Park et al. 2017).

Different authors have studied how the consumption of these compounds by means of beverages favor the nutritional value and increases the added value of the food. Rosenblat et al (2010) analyzed the effects of antioxidants in vitro of various beverages and how the type of food affects their quality. Also, these studies determined the short-term effect of drinks rich in polyphenols by healthy people, finding that they increase their properties (Rosenblat et al. 2010). On the other hand, Gollucke (2010) has studied the application of polyphenols present in grapes in different types of foods, beverages and supplements (P.B. Gollucke 2010). In their research, they present a review of the polyphenols that abound most red grapes and how these depend on agro-geographical factors and processing conditions. Among some of its conclusions, it present revisions of how the extraction method over the years has been changed. Therefore, it looks for alternatives to the use of organic solvents and products tending to use grape juice and wine as raw materials, to maximize their polyphenolic contents (P.B. Gollucke 2010). Cilla et al (2010) have studied how the content of other nutritional compounds such as zinc adversely affects the presence of the polyphenolic compounds in drinks based on futsal juice (A. Cilla et al. 2010). This decrease after ingestion is given up to 32% with respect to the original fruit drinks. The above

demonstrate the importance of the previous analysis of the content of the beverage and food to which it wishes to enrich in polyphenolic compounds. On the other hand Wootton and Ryan (2011) have concluded that the foods of daily consumption rich in antioxidant activity (polyphenolic compounds) are mostly vegetal sources (Peter C. Wootton-Beard and Lisa Ryan 2011). Meanwhile, different publications show as the content and type of polyphenolic compounds of thousands of foods and beverages. In this include beverages, tea, coffee, cocoa, wine, fruit and vegetable juices and beers (Carlsen et al. 2010). In the **Table 1.6** are show the results by Lugasi and Hóvári (2003) (Lugasi and Hóvári 2003). Where the contents of polyphenolic compounds of different beverages are presented:

Table 1.6. Polyphenolic compounds content (TPC) of beverages.

Beverage	TPC (mg/L)
Red wines	1,720 ± 546
Elderberry juice	5,680
Prunes juices	1,807
Fruit juices	159 – 5,680
Vegetable juices	255 – 696
Dark and lager beers	473,376
White wines	392

As can be observed, polyphenolic compounds have been studied not only in the medical area because of the benefits that their consumption brings, if not also in their possible sources and extraction technologies. The source of extraction of these high value-added compounds has become a concern not only for scientific reasoning but for ministries of health due to the safety. Moreover, it limitations that have been applied to the use of synthetic antioxidants because of the effects these lead to health, nutrient degradation and toxicity. (Fereidoon Shahidi and Priyatharini Ambigaipalan 2015).

The replace of synthetics antioxidants is great interesting due to benefits in health because the implication and functionality of them (J Moncada, Cardona, and Pisarenko 2013) and possibility toxicity of synthetic antioxidants (Fereidoon Shahidi and Priyatharini

Ambigaipalan 2015). From this, it is necessary to obtain antioxidant compounds as polyphenolic compounds from natural sources with appropriated methods that allow a non-toxic, unaltered final antioxidants structure. Selection of suitable techniques is necessary to allow the obtaining of desirable soluble constituents and good yield to be added in functional beverages (Dhanani et al. 2017). The most studied technologies for the extraction of bio-compounds are the solid-liquid (solvent extraction) and Soxhlet extraction. Nevertheless, faster extraction methods that increase the selectivity with low operation costs are required. In this sense, non-conventional methods have begun to be study as alternative extraction methods (I. X. Cerón, Higuita, and Cardona 2012).

2. EXTRACTION TECHNOLOGIES

The extraction process has different definitions depending on the final application of the products obtained. It is generally defined as the separation of an active agent by the use of solvents, resulting in liquid, semi-solid or solid products (Kostova et al. 2010; Gamse 1998). Research on these extraction processes has increased over the years. Where, between 2001-2018, about 6899 articles related to the extraction of polyphenolic compounds have been published. This number of articles has been reached due to the high interest in the behavior of the technologies, raw materials, solvents and operating conditions used and the multiple applications in different industries.

Extraction technologies used actually are commonly divided into two categories: conventional and non-conventional. Conventional methods include solvent extraction, Soxhlet extraction, mechanical extraction, among others (Saleh et al. 2016), which in spite of their extensive studies do not present a good environmental impact. In addition, these extraction technologies has low yields and high solvent requirements. Meanwhile, non-conventional methods such as supercritical fluids extraction, ultrasound assisted extraction or microwave assisted extraction present high potential. This last due to the high selectivities, yields and short-term performance of each of these technologies (A et al. 2003; Mazvimba et al. 2012; B. Zhang, Yang, and Liu 2008). **Figure 2.1** presents a brief description of some conventional and non-conventional technologies with their respective characteristics. These technologies require presence of solvents, high temperature, high pressure, radiation and sonification for its development.

Many techniques have been studied to extract antioxidants from different materials such as plants, fruits, vegetables and agro-industrial waste. Among these technologies, the Soxhlet

extraction, maceration, supercritical fluids extraction, subcritical water extraction and ultrasound assisted extraction can be mentioned (Do et al. 2014). Different authors have studied their applications, advantages and disadvantages. Do et al (2014) studied the polyphenol compounds extraction from *Limnophilia aromatic*, a medicinal plant from Southeast Asia. From this used four solvents for their extraction (water, methanol, ethanol and acetone) with a greater quantity using ethanol (40.5 mg GA/g) (Do et al. 2014). On the other hand, Ramíc et al (2015) studied an optimization model for the bioactive compounds extraction from the byproducts of *Aronia melanocarpa* (tea manufacture) through UAE (Milica Ramić et al. 2015).

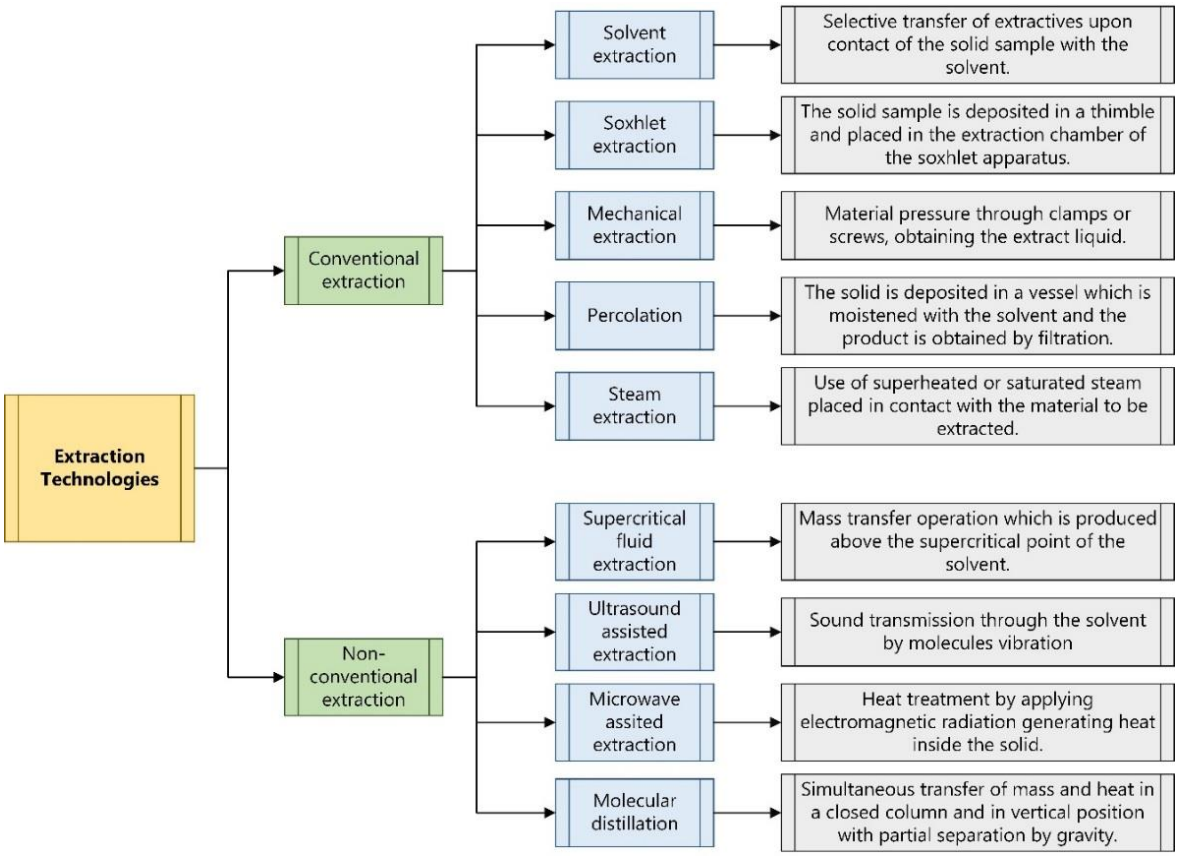


Figure 2.1. Classification of extraction technologies.

Meanwhile, Paes et al (2014) studied the potential of using subcritical fluids (water, ethanol and acetone) and supercritical carbon dioxide in the phenolic compounds extraction from

cranberry. From this was obtained 808 mg/100 g of anthocyanins using 10% of water, 85% of ethanol and 5% of CO_2 as solvents (Juliana Paes et al. 2014).

2.1. Conventional Extraction

2.1.1. Solvent extraction

Solvent extraction (SE) or solid-liquid extraction consists on the contact of a solid material with an organic solvent. In this process ocurres the mass transfer. The soluble components are displaced to the solvent until reaching equilibrium (the active principle of the solid material and the solvent are the same) (Kostova et al. 2010). This technology is used in laboratory and industry scale. Even so, the SE is an expensive process because of the amount of solvent required for the extraction (Peredo Luna, Palou García, and López Malo 2009). A key factor to carry out this type of extraction is the adequate selection of the solvent taking into account its solubility and the type of polyphenolic compound to be extracted. **Table 2.1** shows the results from different studies using this technology for the polyphenolic compounds extraction. Where raw materials such as grapes and Myrtle leaves contain high antioxidant activity.

Table 2.1. Raw materials studied with solvent extraction.

Raw material	Total Phenolic Compound	Antioxidant activity	References
Myrtle leaves	128.00 ± 18.07 mg GA/g	21.56 ± 0.10 µmol/mL	(Dahmoune et al. 2015)
Potato	9.6 ± 0.6 mg GA/g	93.08 ± 0.8 µmol/g	(Wu et al. 2012)
Mengkudu leaf	92.39 ± 4.13 mg GA/g	0.86 mg/mL	(Pak-dek et al. 2011)
Soybean	3.45 mg GA/g	427.20 ± 21.92 µmol TE/g	(Chung et al. 2010)
Grape	148.3 ± 0.3 mg GA/g	190.9 ± 3.2 mg/g	(Cheng et al. 2012)
Yellow passion fruit	1.58 mgGA/g	30.94 ± 2.96 µg/g	(Wong et al. 2014)

Spent coffee grounds	2.6-16.2mgGA/g	0.109mM Fe(II)/g	(Mussatto, Ballesteros, et al. 2011)
Sweet granadilla	137.90 ± 1.52 mgGA/g	19.13 µg/mL	(Saravanan and Parimelazhagan 2014)

2.1.2. Soxhlet extraction

Soxhlet extraction or also known as hot continuous extraction is a technology mainly used at laboratory level. This technology obtains higher yields in compared to other conventional methods (Kostova et al. 2010). This technique consists in depositing in the camera of the soxhlet equipment the thimble (porous bag) and the solvent in the balloon, which is heated until reach its boiling point. The vapors generated are condensed in order to fill the chamber of the equipment having contact with the thimble and resulting in the extract. **Figure 2.2** illustrates the Soxhlet extraction equipment.

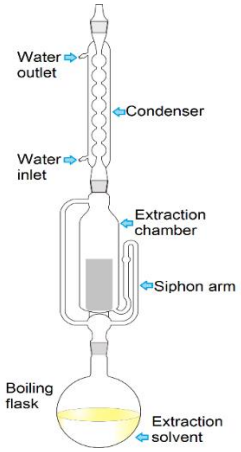


Figure 2.2. Soxhlet extraction equipment.

Different raw materials have been used to obtain polyphenolic compounds through Soxhlet extraction as shown in **Table 2.2**. In the analysis of phenolic compounds studies have shown high values in the cactus and coffee grounds, which have high potential because they do not jeopardize food security.

Table 2.2. Raw materials studied with Soxhlet extraction.

Raw material	Total Phenolic Compound	Antioxidant activity	References
Guava seed	1.76 mg GA/g	2.24 mmol/g	(Castro-Vargas et al. 2010)
Spent coffee grounds	119.5 ± 2.1 mg GA/g 177.5 ± 25.2 mgGA/g	537.37 µg/mL 1421.53 µg/mL	(Andrade et al. 2012a)
Coffee husk	151 ± 12 mg GA/g 65 ± 6 mg GA/g	235.4 µg/mL 1029.5 µg/mL	(Andrade et al. 2012a)
Peach	128 ± 5 mg GA/g		(Mezzomo et al. 2010)
Limnophila aromatica	40.5 mg GA/g	180 µg/mL	(Do et al. 2014)
Quercus infectoria	143.75 ± 1.06 mg GA/g	50% inhibition	(Hasmida et al. 2014)
Mango peels	50.25 mg GA/g		(Tunchaiyaphum, Eshtiaghi, and Yoswathana 2013)
Cactus	270.9 ± 7.2 mg GA/g	200 ± 19.2 µg/mL	(Ammar, Ennouri, and Attia 2015)
Guava leaf	250 mg GA/g	25 mM/mg	(Nantitanon, Yotsawimonwat, and Okonogi 2010)
Soybean seed	4.16 ± 0.01 mg GA/g	221.33 ± 11.97	(Chung et al. 2010)

2.1.3. Mechanical extraction

This technique consists on the use of a press or screws, which exert pressure on the raw material obtaining the extracts. (Ulises Morales, Alamilla, and Mora 2013). Such technology can be carry out continuous or batch wise, presenting a disadvantage to require high power for their operation. The obtained extract by this technology must be subjected to purification by sedimentation, refining and bleaching to be subsequently analyzed and used.

2.1.4. Percolation

Percolation is commonly used in daily life in the preparation of coffee. This technology can have a yield of up to 95% depending on the contact time of the solvent with the sample during percolation (Carrión and García 2010). The methodology consists of wetting the solids

in the percolator, which is previously closed in the bottom (see **Figure 2.3**) and capped for 24 hours. Then the percolator is opened by dripping the liquid slowly while being filtered (Kostova et al. 2010).

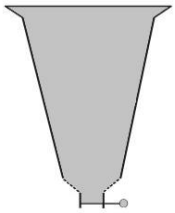


Figure 2.3. Percolation equipment.

2.2. Non-Conventional Extraction

The most studied technologies are the solvent extraction and Soxhlet extraction. However, faster extraction methods are required to increase the selectivity with low operating costs. In this sense, non-conventional methods have begun to be presented as an alternative in the polyphenolic compounds extraction (I. X. Cerón, Higuita, and Cardona 2012). In addition, the increased interest in extract at temperatures close to the environment, increased yields of the compounds have led to the study of non-conventional extraction technologies. This type of technologies can be supercritical fluids extraction, ultrasound assisted extraction and microwave assisted extraction, among others.

2.2.1. Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) is a mass transfer technology above the critical point of the solvent (critical temperature and critical pressure) as shown in **Figure 2.4**. Additionally, in this region the fluid has gas properties (due to the high diffusivity), causing a greater penetration in the solid materials. Furthermore, the liquid phase provides a high density helping to dissolve solutes. The SFE utilizes the solvent properties of a solvent at temperature and pressure properties above the critical values to perform a more optimal separation producing changes in the density and dissolving power of the solvent (Hongru Li, Li, and

Shen 2013). This technology works with low temperatures and absence of air. Thus avoiding the oxidation and thermal degradation of the thermolabile components to be extracted (Zou et al. 2011).

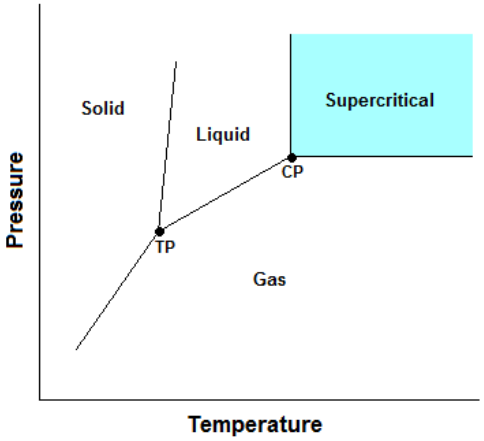


Figure 2.4. Supercritical fluid region. *PT Triple point, CP critical point.

The SFE has a wide range of applications in pharmaceuticals, food, oil industry and waste disposal (Knez et al. 2013). This extraction technology presents great advantages compared to conventional techniques, such as higher selectivity, higher efficiency and a cleaner technology. However, its disadvantage is the high operational expenditures due to compression and investment in equipment. It have been used many types of solvents such as water, ethanol, methanol, carbon dioxide, acetone, among others, for supercritical fluids extraction technology as presented in **Table 2.3**. The most commonly used solvent for this type of extraction is carbon dioxide due to its low critical temperature and critical pressure (31°C and 73.8 bars). Additionally it is non-toxic, easily recyclable, non-flammable, chemically inert and low cost (Carlos Ariel Cardona, Carlos, and Solano 2007). The CO_2 presents characteristics for a safe extraction of the components of interest present in the vegetal material. In the depleted solid there is no presence of the solvent due to its evaporation at temperature and ambient pressure.

Table 2.3. Solvents most often used for supercritical fluid extraction.

Solvent	P_c [MPa]	T_c [K]	Solvent	P_c [MPa]	T_c [K]
Carbon dioxide	7.38	304.15	Methane	4.60	190.4
Ethanol	6.14	513.9	Ammonia	11.35	405.55
Methanol	8.09	512.6	n-Hexane	3.01	507.5
Propylene	4.60	364.95	Toluene	4.10	591.8
Propane	4.25	369.8	Sulfur dioxide	7.88	430.8
Acetone	4.70	508.1	Acetronitrile	4.83	545.5
Ethyl acetate	3.83	523.25	Oxygen	5.04	154.6
Water	22.12	647.3	Carbon monoxide	3.50	132.9
Bencene	4.89	562.2	n-Heptane	2.74	540.3
Isobutane	3.65	408.2	Cyclohexane	4.07	553.5
Diethyl amine	3.71	496.5	Propadiene	5.47	393.15

This technology has been studied using different raw materials as seen in the **Table 2.4**, with variation of pressure, time, fluid and temperature. This technology requires a lower amount of solvent and extraction time than the other technologies, which present better performance and lower operating costs.

Table 2.4. Raw materials studied with SFE.

Raw material	Total phenolic compounds	Antioxidant activity	References
Eucalyptus	159.57 ± 6.75 mg GA/g	2.09 µg/mL	(Santos et al. 2012)
Guava seed	1.32 mg GA/g	1.30 ± 3 mmol Trolox/g	(Castro-Vargas et al. 2010)
Coffee husk	36 ± 1 mg GA/g	630 µg/mL	(Andrade et al. 2012a)
Spent coffee grounds	42 ± 2 mg GA/g	746.7 µg/mL	
Peach	34 ± 4 mg GA/g		(Mezzomo et al. 2010)
Apple	66.11 ± 0.36 mg GA/g	69.23% inhibition	(Peschel et al. 2006)
Artichoke	514.18 ± 14.92 mg GA/g	86.04% inhibition	
Pear	60.67 ± 0.86 mg GA/g	77.09% inhibition	
Tomato	61.04 ± 3.02 mg GA/g	82.78% inhibition	
Cherry	2.9 ± 0.1 mg GA/g	170 ± 20 µmol/g	(Serra et al. 2010)
Zapote	358.12 ± 1.16 mg GA/g	8.9 ± 0.26 µg/mL	(I. Cerón 2013)

2.2.2. Ultrasound assisted extraction

Ultrasound assisted extraction (UAE) is an environmentally friendly, efficient process with low application cost and equipment requirement due to the simplicity of method development (Mazvimba et al. 2012). The process consists on the transmission of the sound through a medium, generating the vibration of the molecules. Ultrasound is applied in solid or liquid media using a gas or liquid as a fluid. The UAE presents a variety of uses including cleaning, sterilization, acceleration of chemical reactions, pretreatment, oxidation, extraction, etc (Bendicho and LAvilla 2000; Daza Serna 2015). The different processes using ultrasound have in their structure a frequency generator between 18 KHz and 100 MHz, a transducer and a reactor, as shown in **Figure 2.5** (Daza Serna 2015).

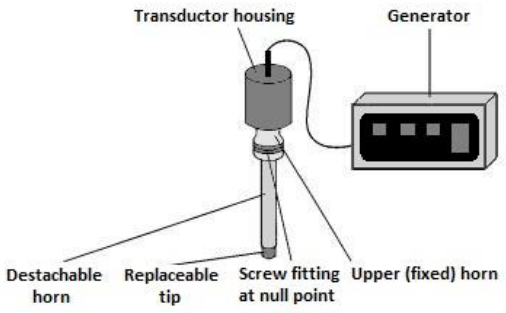


Figure 2.5. Ultrasound equipment.

The UAE presents a great potential for the polyphenolic compounds extraction due to their simplicity, high reproducibility, high efficiency and low energy consumption (Abdullah Al-Dhabia, Ponmurugana, and Maran Jeganathanb 2017). The UAE creates an acoustic cavitation effect on the solvent through an ultrasound wave. In addition, ultrasound facilitates solvent diffusion into the tissue of the residue, resulting in an increase of the contact area between the solid-liquid phases. The improvement in extraction obtained by ultrasound is mainly attributed to the effect of acoustic cavitation, produced in the solvent by the passage of an ultrasonic wave. The ultrasonic method also generates a mechanical effect, which allows a better diffusion of the solvent in the tissue and the increase of the contact surface between the solid and liquid phases. As a result, the solute diffuses rapidly

from the solid phase to the solvent (Zou et al. 2011). Through the use of UAE, different studies have been carried out to demonstrate the potential of different raw materials as shown in **Table 2.5**. Where residues from the coffee processing industry such as spent coffee grounds and coffee husk have a high content of total phenolic compounds 587.7 and 133.4 mg GA/g, respectively.

Table 2.5. Raw materials studied with UAE.

Raw material	Total Phenolic Compound	Antioxidant activity	References
Rice bran	6.35 mg GA/g	57.23 µmol/g	(Tabaraki and Nateghi 2011)
Spent coffee grounds	587.7 ± 46.6 mg GA/g	787.63 µg/mL	(Andrade et al. 2012a)
	264.1 ± 18.1 mg GA/g	1972.23 µg/mL	
Coffee husk	133.4 ± 0.6 mg GA/g	235.1 µg/mL	
	61 ± 3 mg GA/g	286.7 µg/mL	
Myrtle leaves	144.77 ± 30.23 mg GA/g	20.61 ± 1.66 µg/mL	(Dahmoune et al. 2015)
Olive leaves	45.8 mg GA/g	89.2 mg Trolox/g	(Margarita Hussam Ahmad-Qasem et al. 2013)
Orange peel	11.71 mg GA/100g		(Boukroufa et al. 2015)
Lemon peel	15.08 mg GA/g	75% inhibition	(Dahmoune et al. 2013)

2.2.3. Microwave assisted extraction

The technology of microwave assisted extraction (MAE) consists of the application of heat treatment by means of electromagnetic radiation to the sample in short time periods, which cause changes in the structure of the cell (Veggi, Martinez, and Meireles 2013). The MAE presents higher yields compared to conventional methods, presenting as disadvantages the toxic solvents used and the high temperatures required by the process to which the components to be extracted can be affected (Mazvimba et al. 2012). The equipment used to carry out the MAE uses modified microwave ovens by means of the top opening and connecting a flask with a condenser as shown in **Figure 2.6** (Peredo Luna, Palou García, and López Malo 2009).

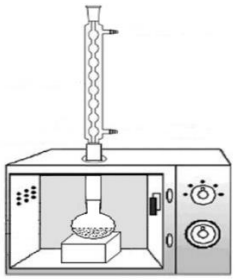


Figure 2.6. Microwave assisted extraction equipment.

Table 2.6 shows the total phenolic compounds and antioxidant activity of extracts obtained from MAE. This technology have used a wide variety of raw materials from fruits, vegetables, to agro-industrial waste to demonstrate their potential for the pharmaceutical and food industry applications.

Table 2.6. Raw materials studied with MAE.

Raw material	Total Phenolic Compound	Antioxidant activity	References
Peanut skins	144 mg GA/g	2543 µmol/g	(Ballard et al. 2010)
Tomato	997.45 mg GA/100g	251.19 µmol/g	(Hongyan Li et al. 2012)
Potato	11.00 ± 0.26 mg GA/g	95.17 ± 0.6 µmol/g	(Wu et al. 2012)
Hojas de mirto	162.49 ± 16.95 mg GA/g	16.80 ±0.29 µg/mL	(Dahmoune et al. 2015)
Hoja de eucalipto	55.26 mg GA/g	69.52 µg/g	(Bhuyan et al. 2015)
Cherry	13.78 mg GA/g	24.74 mg/g	(Simsek, Sumnu, and Sahin 2012)
Spent coffee grounds	398.95mg GA/g	90.69 % inhibition	(Pavlović et al. 2013)
Raspberry	38.57 mg GA/g	17.93 mg/g	(Teng, Lee, and Choi 2013)
Lemon peel	15.74 mg GA/g	90% inhibition	(Dahmoune et al. 2013)

2.3. Advantages and Disadvantages of Extraction Technologies

Different technologies have been studied to obtain bioactive compounds. However, each one has several advantages and disadvantages in the application. In **Table 2.7**, the most representative extraction technologies are presented for obtaining polyphenolic compounds.

Table 2.7. Comparison of some polyphenolic compounds extraction technologies.

Extraction technology	Process description	Advantages	Disadvantages	References
Solvent extraction	Selective transfer of extractives upon contact of the solid sample with the solvent. The effectiveness depends on the solubility of the solvent.	Simple process. Low power consumption.	High processing time. Unfriendly to the environment. High price.	(Plata, Kafarov, and Moreno 2009)
Mechanical extraction	Material pressure through clamps or screws, obtaining liquid extract.	Ease processing, low installation cost high performance.	High power consumption.	(U Morales, Alamilla, and Mora 2013)
Hot continuous extraction (Soxhlet)	The solid sample is deposited in a thimble which is placed in the extraction chamber of the soxhlet apparatus. The process is carried to boiling temperature with a continuous process until the sample is exhausted and extractives are obtained in the volumetric balloon.	Less solvent.	High processing time. High temperatures.	(U Morales, Alamilla, and Mora 2013)
Percolation	The solid is deposited in a cylindrical and iconic container which is moistened with the menstruum (usually alcoholic or hydroalcoholic mixture) and the product obtained by filtration or decantation.	Short extraction time.	High solvent consumption.	(U Morales, Alamilla, and Mora 2013)(Carrión and García 2010)
Steam extraction	Use of superheated or saturated steam by placing in contact with the material to be extracted, heating it until the release of the extractive by means of the volatility and leading to a stage of cooling with the water and separation of this.	Low operating cost. Simple method.	It requires long periods of time. Low yields.	(U Morales, Alamilla, and Mora 2013)(Peredo Luna, Palou García, and López Malo 2009)

Ultrasound assisted extraction	Transmission of sound through a medium by the vibration of molecules. Ultrasound is applied in solid or liquid media using a gas or liquid as a fluid.	Moderate temperatures, short process time, high efficiency, low equipment requirements, lower energy consumption and environmental friendly process.	Possible presence of cavitation phenomenon.	(Esclapez et al. 2011)
Supercritical fluids extraction	Mass transfer operation which is produced above the supercritical point of the solvent, in which the properties of the liquid and gaseous phase become similar presenting a behavior as the gases having a high diffusivity and close to the liquids by their high density allowing penetration into solid materials.	Better solubilization capacity, low temperatures, high selectivity of analytes, and reduced environmental impact.	High cost of equipment. Risks for using high pressures.	(I. Cerón 2013)
Microwave assisted extraction	Heat treatment by applying electromagnetic radiation generating heat inside the solid.	Short process time, higher yields compared to conventional methods.	Use of toxic solvents, high temperatures.	(Bin Zhang, Yang, and Liu 2008)
Molecular distillation	Simultaneous transfer of mass and heat in a closed column and in vertical position with partial separation by means of gravity.	Low operating temperatures, low residence times, high selectivity, high product purity.	High cost of the process.	(Arellano Gault 2010)(Lembke 2011)

3. AGROINDUSTRIAL RESIDUES

Colombia is a country with great biodiversity and a high agricultural production favored by the diversity of climates (Bastidas, Guerrero, and Wyckhuys 2013). The agroindustrial term as FAO defines it as "substring manufacturing activities through which raw materials and intermediate products derived from the agricultural sector are made. Therefore, agribusiness can be defined as the transformation of products from agriculture, forestry and fisheries" ("Organización de Las Naciones Unidas Para Agricultura Y La Alimentación" 2017). These products generate high amounts of agro-industrial waste, both in the harvest and in the primary processing, which have great potential in the production of value-added products. The use of these agroindustrial residues results in an improvement in the socio-economic development of the country and a better sustainable use of natural resources. The waste with large production in Colombia is mainly from coffee and fruit. Specific exotic fruits such as naranjilla, tree tomato, yellow passion fruit, purple passion fruit and sweet granadilla present a high interest in being studied and exploited to the fullest.

3.1. Coffee waste

Coffee (*Coffea sp*.) is a plant belonging to the family *Rubiaceae* (see **Table 3.1**) cultivated mainly between areas with latitudes of 25° N and 25° S (Upadhyay, Ramalakshmi, and Jagan Mohan Rao 2012). This product has an important role in the global economy, becoming one of the main exports for some countries. Actually, there are 80 varieties of identified coffee species, being the most commercialized for human consumption *Coffea canephora* or also known as *Coffea robusta* and *Coffea arabica* (Adriana Farah 2012). Colombia is a large producer of *Coffea arabica*, which has a better quality and aroma of *Coffee robusta*. Annually, around three million tons of coffee are produced in more than 60 countries. Among the main

producers are Brazil, Vietnam, Indonesia, India and Colombia (Narita and Inouye 2015; FAOSTAT 2008).

Table 3.1. Taxonomy of coffee.

Coffee	
	Family: *Rubiaceae*
	Genus: *Coffea*
	Scientific name: *Coffea arabica L.*
	Specie: *Coffea*

As it is shown in **Figure 3.1**, global coffee consumption has presented an annual increase of 2% in all continents. Europe is the continent with the highest consumption (Organization 2017). According to the ICO (International Coffee Organization), Colombia ranks third in coffee exports, and this product ranks second in national GDP after oil (Contreras-Calderón et al. 2016; International Coffee Organization 2017). Where the United States, Germany and Japan are the main countries of destination of this product (Federación Nacional de Cafeteros 2016; International Coffee Organization 2017).

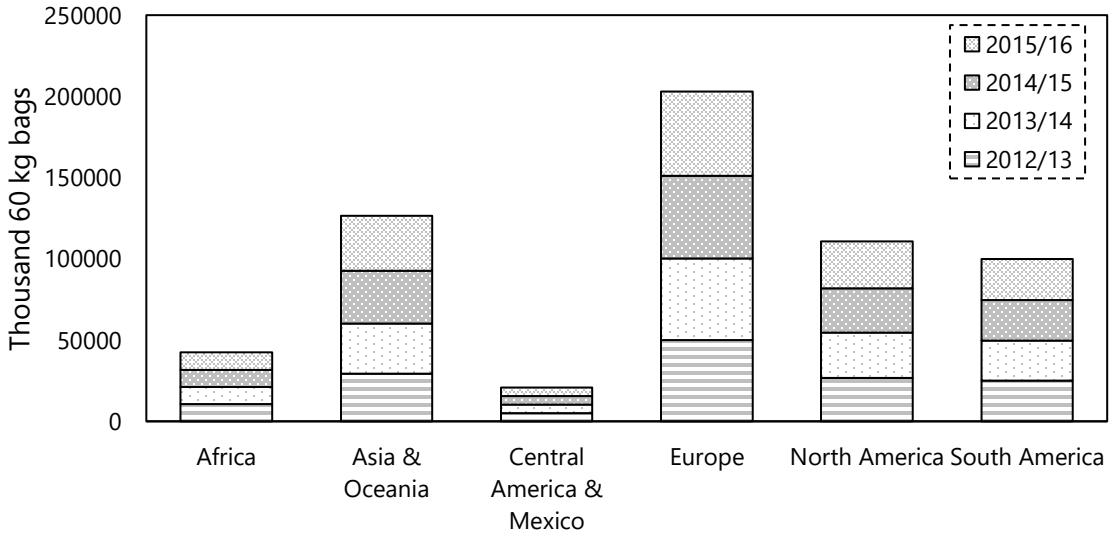


Figure 3.1. World coffee consumption in thousand 60 kg bags.

On the other hand, coffee in Colombia showed a decrease in its production before 2014. This was due to the propagation of a "rust outbreak" that affected the harvest areas. However, in 2014 there was a recovery of its production in the market, as shown in the **Figure 3.2** (Agronet 2015). At the same time, international competition was established for 2014 with 11 million bags of green coffee that were exported. This is equivalent to 13% more than in previous years ("Comportamiento de La Industria Cafetera Colombiana 2014" 2014). In 2016, Colombia had a coffee growing area of 931,750 hectares (Federación Nacional de Cafeteros 2016), achieving in the same year an export of green coffee of 12,844x103 bags of 60 kg. This high-quality coffee requires special care during the entire production process, which ranges from good sowing on fertile land to harvest and post-harvest processing. In each of these stages, large quantities of agroindustrial waste (90.5% of the total plant) are generated, which have a great potential to obtain products with high added value. Interest in the use of these wastes to obtain a large quantity of bioproducts has increased in recent years.

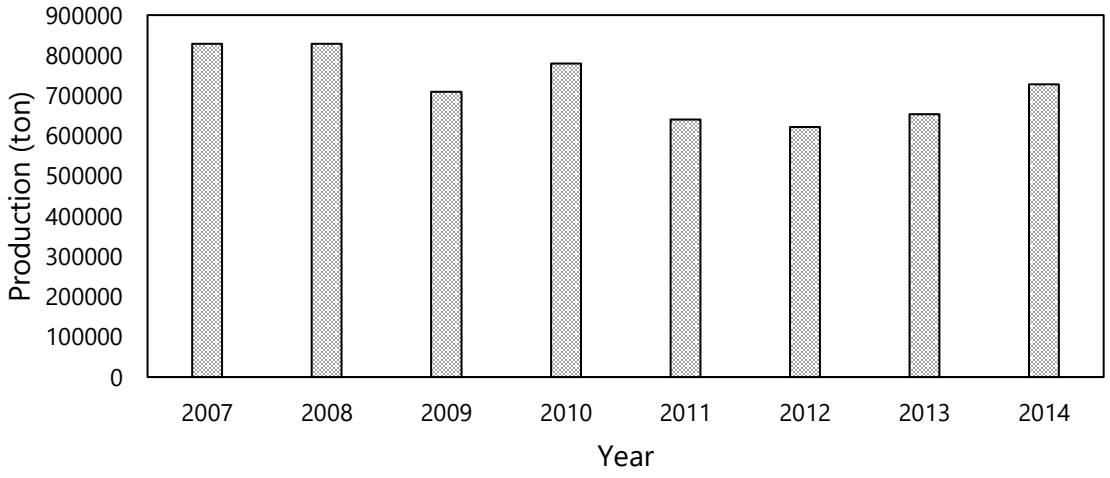


Figure 3.2. Coffee production in Colombia.

Table 3.2 shows the waste generated in the coffee production industry. Among the solid agricultural residues of the coffee process are the spent coffee grounds and coffee cut-stems. The spent coffee grounds (SCG) is obtained during the industrial processing of soluble

coffee or when the beverage is prepared from the roasted and ground grain. Normally the SCG is used as a fuel by burning it (Mussatto, Ballesteros, et al. 2011). This waste corresponds to around 10% of the weight of fresh fruit, with an oil content of 10-15% on dry basis (Rodríguez Valencia and Zambrano Franco 2010). In Colombia, an annual SCG production of 22,300 tons is estimated, mainly Arabica coffee, and mainly composed of carbohydrates, carbonaceous, lipids and nitrogen-containing compounds, among others (Karmee 2017; Rodríguez Valencia and Zambrano Franco 2010). On the other hand, the SCG is considered a promising raw material for the production of metabolites, whether in the production of biofuels, polyphenolic compounds and polyhydroxyalkanoates (PHA) (Kwon, Yi, and Jeon 2013; Mussatto, Ballesteros, et al. 2011; Obruca et al. 2014).

Table 3.2. Residues obtained in the processing of 1 kg of cherry coffee.

	Production (g)	**Process**
Fresh pulp	394	Pulped
Mucilage	216	Remove mucilage
Parchment	35	Threshing
Water	171	Drying
Volatiles	22	Torrefaction
Spent coffee grounds	104	Drink preparation

In particular, the CCS is a waste generated after the coffee harvest. This is obtained when the main stem of the coffee plant is cut at a certain height (50 cm from the ground), performing a maintenance every five years approximately. This activity is carried out in order to increase the production of coffee plantations (Castro and Montoya Restrepo 1997). The production of annual CCS in Colombia has been estimated at 3.2 tons/ha, equivalent to 0.6 kilograms of CCS per kilogram of processed coffee (Castro and Montoya Restrepo 1997; Rodríguez Valencia and Zambrano Franco 2010). **Figure 3.3** the behavior of coffee renewal during 2010-2014 is presented ("Comportamiento de La Industria Cafetera Colombiana 2014" 2014). Normally, this waste is used by the coffee producers themselves as a solid fuel for cooking food and drying the beans, or sometimes they are taken to composting. However,

CCS is a waste with great potential for value-added processes such as energy, ethanol, furfural and polyphenolic compounds (Aristizábal M., Gómez P., and Cardona A. 2015a).

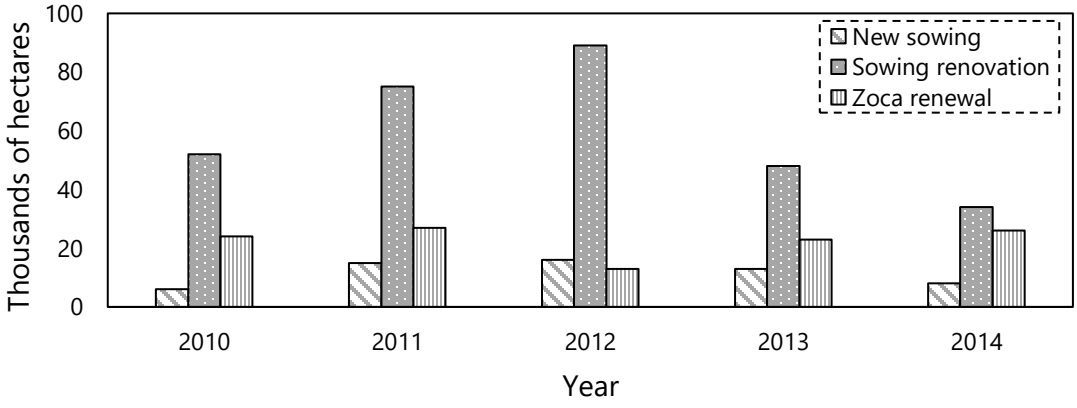


Figure 3.3. Renewed area for coffee production.

As an alternative to improve emerging technologies, interest in using SCG and CCS to obtain bioproducts has increased, leading to environmental and social change. Environmental standards for the disposal of industrial waste have become stricter, the reuse of waste can be economically viable in the agro-industrial sectors. The growing concern about these issues allows us to implement a system committed to sustainable development, bringing with it terms of bioproducts, bioenergy and bioeconomy. Additionally, this waste can become a platform product within a biorefinery (Murthy and Madhava Naidu 2012; Liu et al. 2017; Mata, Martins, and Caetano 2017; Karmee 2017).

3.2. Naranjilla Peel

The lulo or naranjilla (*Solanum quitoense*), is a fruit belonging to the *Solaneaceas* family (see **Table 3.3**), from the Andean regions of Ecuador and Colombia (J. Dávila 2015). The color of the epicarp (peel) is orange in its state of maturation. While the pulp has a yellow/green color, which contains membranous partitions (Rogério dos Santos Alves; Alex Soares de Souza 2014; Iguala et al. 2014). Additionally, *Solanum quitoense* presents a good demand in international markets (United States, Canada and European countries) as it is an exotic fruit

with high potential, presenting multiple applications for its flavor in beverages, preserves, wines and desserts, as well as its value nutritional and medicinal properties to present diuretic and toning properties (J. Dávila 2015; Tobergte and Curtis 2013).

Table 3.3. Taxonomy of naranjilla.

Naranjilla or lulo	
	Familia: *Solanaceae*
	Genero: *Solanum*
	Nombre científico: *Solanum quitoense*
	Especie: *Quitoense Lam.*

Actually, production of naranjilla predominates in Colombia and Ecuador. In Colombia, naranjilla production shows an increase as seen in the **Figure 3.4**. The departments of Huila and Valle del Cauca are the main producers (Agronet 2015; Huertas et al. 2011). The main commercialization of this product is in juice, concentrated and frozen; resulting in the residue of the peel (Medina et al. 2007). The naranjilla peel presents high potential to obtain various value added products among which you can find antioxidants, fermentation processes for production of ethanol and xylitol (J. Dávila 2015). Obtaining antioxidants from naranjilla has shown high presence, according to studies reported by Mertz et al (2009) (16.4 ± 1.3 µM/g) for the pulp and according to Dávila (2015) (0.48 µmol/g) for the peel (Mertz et al. 2009a; J. Dávila 2015). Therefore, through of non-conventional extraction processes such as supercritical fluids extraction (SFE) can be obtained antioxidants (Couto et al. 2009). On the other hand, the obtention of ethanol and xylitol can be carried out by high content of sugars in this fruit and presenting a high profitability due to the low cost of the residue coming from this (Acosta, Pérez, and Vaillant 2009).

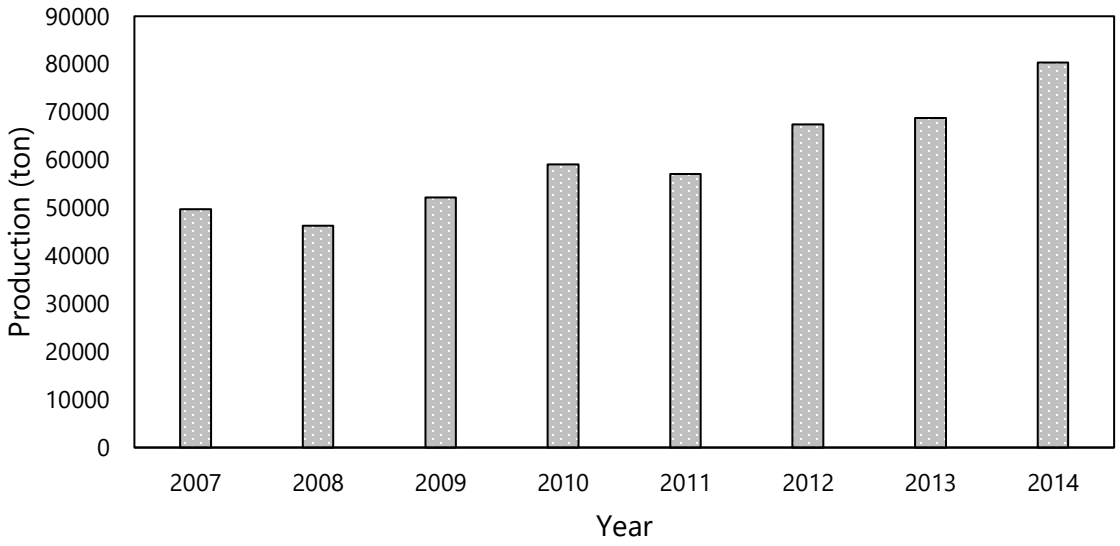


Figure 3.4. Production of naranjilla in Colombia.

3.2. Tomato tree

The tomato tree or also known as tamarillo (*Cyphomandra betacea Sendt)* is an exotic fruit native to the Andes of the *Solanaceae* family (Mutalib et al. 2016). Actually, there are about 20 species of tomato tree fruit identified, whose tree has a height between 2-3 m with a life time of 5-12 years. This grows in temperate and cold climates (2000-2400 MASL) (Biodiversity 2013), and its fruit presents an ovoid shape in most species. The largest producer and distributor of tree tomato worldwide is New Zealand. Meanwhile, in the Andes region Colombia and Ecuador are the largest growers. It has a high nutritional importance due to its antioxidant content, identified in the color of the fruit (Mutalib et al. 2017). Usually within the polyphenolic compounds of this fruit are the carotenoids, flavonoids and anthocyanins. In addition, this fruit prevention of cardiovascular disease, cancer, arthritis and delay aging (Hassan and Bakar 2013; Vasco, Ruales, and Kamal-eldin 2008; I. Cerón, Higuita, and Cardona 2011). However, despite being a raw material with a high content of polyphenolic compounds, it can not be used directly in extraction processes, because it may affect food safety (Chacón Pérez, Restrerpo Serna, and Cardona Alzate 2017). For this reason,

studies have focused on the use of tree tomato peel to obtain these compounds, determining a greater presence than in the same pulp (Mandal and Ghosal 2012).

Table 3.4. Taxonomy of tree tomato.

Tamarillo or Tomato tree	
	Family: *Solanaceae*
	Genus: *Cyphomandra*
	Scientific name: *Cyphomandra betacea*
	Specie: *Cyphomandra betacea Sendt*

3.3. Passion fruit

Colombia is a country with great diversity of exotic fruits, which have presented an increase in production in recent years. Among these fruits with high boom are the family of *Passifloraceae*, commonly known as "fruits of passion", of which about 500 species have been identified. The yellow passion fruit (*Passiflora edulis*) is the most representative among this family, followed by sweet granadilla (*Passiflora ligularis*) and purple passion fruit (*Passiflora pinnatistipula*). These fruits are shown in the **Figure 3.5** (Viganó and Martinez 2015).

Figure 3.5. *Passifloras*: a) yellow passion fruit, b) purple passion fruit, c) sweet granadilla.

The fruits of the *Pasifloras* present an elliptical and globose shape with a thick and hard peel. It grows on a perennial and woody vine with a productive commercial life of about three and a half years (Inc. 2017). Passion fruits are cultivated in most cases in seeds to prevent the spread of diseases in crops. These fruits have wide applications in the food industry as shown

in **Figure 3.6** either for the preparation of beverages and bakery products for their tropical flavor, aroma and color. At the same time, they are used in pharmaceutical preparations because of the high content of polyphenolic compounds they present (da Silva et al. 2013; Inc. 2017). *Passiflora edulis* is also used by leaves in European and American countries for tea preparation because of its anti-inflammatory potential, preparation of sedatives or tranquilizers (Coleta et al. 2006).

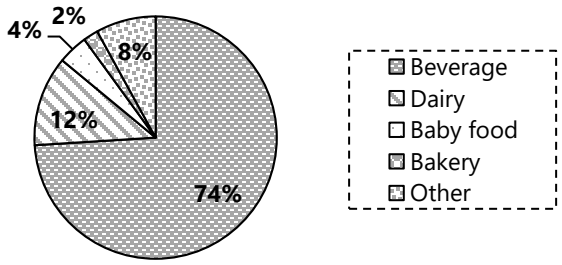


Figure 3.6. Passion fruit applications.

Passifloras present a high demand both in the national and international markets, due to their organoleptic and nutritional properties (Miranda et al. 2015). These fruits are produced in countries mainly from South America as shown in the **Table 3.5** (Miranda et al. 2015), being cultivated in the world approximately of 805,000 tonnes/year (Arias Suarez, Ocampo Pérez, and Urrea Gómez 2014). However, Colombia is the country with the largest species of *Passifloras* (around 135), cultivated mainly in temperate climate, due to the low production of fruits in very warm climates and damages of the vines in cold or icy climates (Inc. 2017).

Table 3.5. Countries producing *Passifloras*.

Specie	Yellow passion fruit	Purple passion fruit	Sweet granadilla
Producing countries	Brazil, Bolivia, Colombia, Ecuador, Peru, Venezuela, Australia, New Zealand, Israel, Hawaii	Brazil, Colombia	Chile, Mexico, Colombia, Bolivia, Peru, United States, India

The production of yellow passion fruit, purple passion fruit and sweet granadilla has increased since the year 2011. Where yellow passion fruit has the highest production followed by sweet granadilla. Even so, it should be noted that the purple passion fruit, despite not presenting a high production as evidenced by **Figure 3.7** is one of the most exported fruits in Colombia along with bananas (Agronet 2015; Miranda et al. 2015). The high demand and production is due to the fact that it presents a continuous harvest during the 12 months of the year. At national level, Cundinamarca, Boyaca and Huila are the largest producers of this fruit (Bastidas, Guerrero, and Wyckhuys 2013).

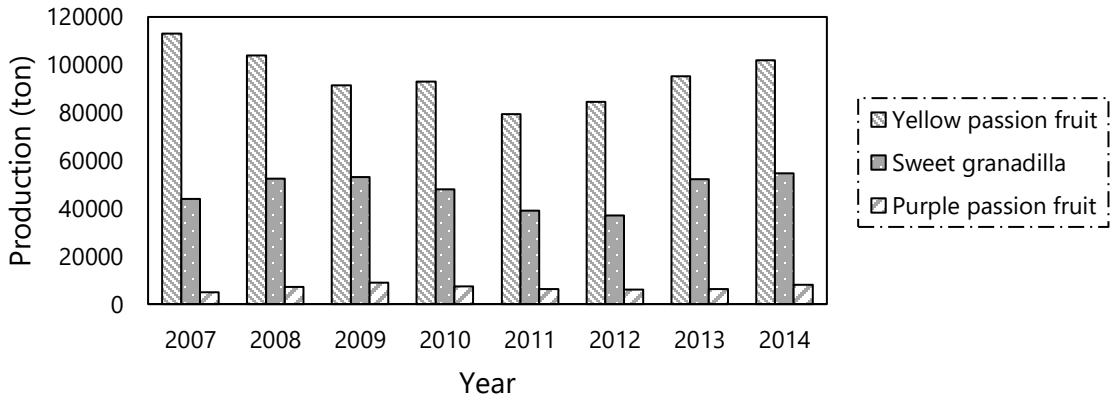


Figure 3.7. *Passiflora* production in Colombia.

3.4. Olive Waste

The olive tree (Olea europaea L.) is a fruit tree grown in different parts of the world. Actually around 8 million hectares are cultivated (Conde et al. 2009). From this tree is obtained the virgin olive oil, which is a product with high demand for its health benefits (Zbidi et al. 2009). In addition, it is the second most important product of the agro-industrial sector in Europe. The production of olive oil leaves a large amount of waste. For this crop, the olive leaves, the olive pruning and olive pomace have considered as promising residues to produce bioactive compounds. In the case of olive pruning, approximately 3 tons per hectare of crop are obtained (Conde et al. 2009), being mainly studied for obtaining energy. On the other hand, the olive leaves, the olive pomace and olive pruning are residues rich in polyphenolic

compounds. From these residues, different studies have showed the presence of compounds with high antioxidant and anticancer capacity such as oleuroperin, luteolin, hydroxytyrosol, tyrosol and apigenin (Margarita Hussam Ahmad-Qasem et al. 2013; Margarita H. Ahmad-Qasem et al. 2014; Čepo et al. 2017).

Table 3.6. Taxonomy of olive tree.

Olive tree	
	Family: *Oleaceae*
	Genus: *Olea*
	Scientific name: *Olea europaea*
	Specie: *O. europaea*

4. METHODOLOGY

The objective of this work was mainly to demonstrate the influence of non-conventional extraction technologies in obtaining polyphenolic compounds. For this, a great variety of raw materials were used, performing experimental and simulation procedures. In the experimental part were carried out physicochemical characterizations and polyphenolic compounds extraction. This last through UAE, SFE, solvent extraction and Soxhlet extraction. In addition to the extracts obtained, analyzes of antioxidant activity and determination of polyphenolic compounds were carried out. While in the case of the simulation, an analysis of pre-feasibility was carried out, either in stand-alone processes or biorefineries. For this, energy, economic and environmental analyzes were carried out.

EXPERIMENTAL PART

4.1. Raw materials and reagents

The raw materials used for this work were: spent coffee grounds, coffee cut-stem, naranjilla peel, tree tomato peel, passion fruits, and olive residues. The spent coffee grounds was obtained from a coffee machine (Grecas Nacional Coffee - model 1100), from which it was removed every two hours. The coffee cut-stems were obtained in the Caldas region. In the case of naranjilla peel and tree tomato peel were obtained through of manual separation of the pulp. The fruit of these was obtained in the Caldas region (5° 03'58 "N 75° 29'05" W), Colombia. On the other hand, yellow passion fruit, purple passion fruit and sweet granadilla were obtained in the Tolima region (4° 26'00 "N 75° 14'00" W). From these fruits the pulps were used, which were manually separated from the peel and the seeds. In this work have been used 3 raw materials related to the olive all originating in the province of Jaén in

Andalusia (Spain). Olive tree pruning (OTP) was obtained directly from the field by collecting the crushed material in an olive grove in the town of Cambil (Jaén). The olive leaf (OL leaf) came from the mill "S.C.A. Cambil Olive Oil Union ", Cambil (Jaén). Where it was separated from the olive by means of a pneumatic separator. This OL was washed with water at room temperature to remove dirt (traces of dirt, etc.). The OTP and the OL were allowed to air dry and then crushed with a mesh size of 1 cm to homogenize them. The third material was the olive pomace (olive pomace, OP) that comes in the form of pellets and was contributed by the extractor of marc "Oleocastellar, S.A.U.", Castellar (Jaén). All materials were stored at room temperature.

In the physicochemical characterization of the raw material, reactive grade sodium chlorite, sulfuric acid, sodium hydroxide, 96% acetic acid (MOL LABS), acetone (Panreac), ethanol 96% (Sigma-Aldrich) and distilled water were used. For the polyphenolic compounds extraction, carbon dioxide and ethanol 60% were used. In the quantification of polyphenolic compounds, anhydrous sodium carbonate (Panreac), gallic acid (Sigma-Aldrich), Folin-Ciocalteu 1N reagent (Sigma-Aldrich), 2,2-diphenyl-1-picrylhydrazyl (DPPH), chlorogenic acid standards, were required. Chlorogenic acid, ferulic acid, vanillin, quercetin, vanillic acid, caffeic acid purchased from Sigma-Aldrich, methanol (Dispoalkyme) and HPLC grade water.

4.2. Characterization of raw materials

The physicochemical characterization of raw materials was performed in triplicate. Moisture, extractives, ash, holocellulose, cellulose and lignin were determined according to international standards and methods for lignocellulosic waste.

4.2.1. Moisture content

The samples previously dried in an oven were determined moisture content using a Shimadzu moisture balance MOC - 120H equipment, as shown in the **Figure 4.1**. For this, 0.5 g of the raw materials were taken, placed in the moisture balance and obtained its value by increasing the temperature.

Figure 4.1. Moisture balance.

4.2.2. Extractives content

The determination of the extractive content was carried out using the method established by Han and Rowell (Han and Rowell 1997). The method required 8 g of raw material, which were deposited in a thimble (previously heavy). It was then introduced to the Soxhlet extraction unit (Schott Duran, Main, Germany) as shown in **Figure 4.2**. As the first part of the extraction 250 mL of distilled water was used, for 24 hours. Subsequently, the thimble was dried in an oven (Thermolab, Maharashtra, India) at 105°C for 24 hours and placed in the desiccator for 60 minutes.

Figure 4.2. Extraction assembly.

Then, the second part was made using 250 mL of ethanol, for 24 hours at boiling temperature. Finally the thimble with the sample was dried, taken to the desiccator and weighed. The calculation of the content of extracts it was performed by Equation 1. Where, $W_{f,1}$ is the weight of the sample after extraction and $W_{i,1}$ is the initial weight of the sample.

$$\%\,\text{Extractives} = 100 - \left(\frac{W_{f,1}}{W_{i,1}}\right) \times 100 \qquad \text{Equation (1)}$$

4.2.3. Ash content

The determination of ash content in biomass was performed by the NREL/TP 510-42622 standard (Sluiter et al. 2008). The dried sample was taken 500 mg and deposited in a crucible pre-weighed and oven dried.

Figure 4.3. Equipment of determination of ash content.

The sample as shown in **Figure 4.3** were incinerated into a muffle by the programming shown in **Table 4.1**. Once the cycle, the sample in the crucible was placed in a desiccator for 30 min and subsequently weighed.

Table 4.1. Ramp sequence for ash determination.

	Tm (min)	Ts (min)	Sv (°C)
1	12	10	105
2	30	15	250
3	180	17	575
4	1	10	105
5	0	0	0.1

The ash content was obtained by Equation 2. Where, $W_{f,2}$ is the final weight of the sample after the incineration and $W_{i,2}$ is the initial weight of the sample.

$$\%\,\mathrm{Ash} = \left(\frac{\mathrm{W_{f,2}}}{\mathrm{W_{i,2}}}\right) \times 100 \qquad \text{Equation (2)}$$

4.2.4. Hollocelulose content

The holocellulose content was obtained according to ASTM Standard D-1104 (Han and Rowell 1997). Initially, 2.5 g of the final sample of extractives were taken in a 250 mL Erlenmeyer flask. To each flask were added 80 mL of distilled water and capped with an inverted Erlenmeyer flask of 100 mL as shown in **Figure 4.4**. The flasks were brought to a bath at 70°C and 0.5 mL of acetic acid and 1 g of sodium chlorite were added. Every 60 min were added 0.5 mL of acetic acid and 1 g of sodium chlorite for 6 hours. After this time, the samples were allowed to react for 24 hours in the bath at 70°C.

Figure 4.4. Assembly for determination of holocellulose content.

Subsequently, the flasks were removed from the bath and cooled to room temperature. The samples were filtered with hot distilled water to remove the odor and yellow color they had. After they were washed with 20 mL of acetone and brought to the oven until constant weight. The holocellulose content was calculated with Equation 3. Where, $W_{f,3}$ is the final weight of the sample and $W_{i,3}$ is the initial weight of the sample.

$$\%\,\text{Holocellulose} = \left(\frac{W_{f,3}}{W_{i,3}}\right) \times 100 \qquad \text{Equation (3)}$$

4.2.5. Cellulose content

The sample obtained after the procedure holocellulose. From these are taken 2 g into a 250 mL Erlenmeyer flask and covered as shown in **Figure 4.5**. They were added 10 mL of NaOH at 17.5% to each sample, stirred and kept in a water bath at 20°C. At 5 min intervals 5mL of 17.5% NaOH was added over 45 min.

Figure 4.5. Assembly of cellulose content.

Subsequently the samples were allowed to stand for 30 min and 33 mL of distilled water was added to each. Samples were allowed to stand for 1 hour, filtered and washed with 100 mL of 8.3% NAOH. Washing was continued with distilled water and 15 mL of 10% acetic acid. Again distilled water was added until the acid was removed. The obtained solid sample was taken to the oven until constant weight obtaining. Finally the sample was left in the desiccator for one hour and weighed. The cellulose content procedure was carried out according to ASTM Standard D-1104 (Han and Rowell 1997). Equation (4) was used to calculate cellulose content. Where, $W_{i,4}$ is the initial weight of the sample taken from the holocellulose and $W_{f,4}$ is the final weight obtained after the completion of the cellulose content process.

$$\%\,\text{Cellulose} = \left(\frac{W_{f,4}}{W_{i,4}}\right) \times 100 \qquad \text{Equation (4)}$$

4.2.6. Lignin content

The lignin content was determined using the initial sample obtained after the extractive process. They were taken 200 mg of sample and deposited in an test tube, adding 2 mL of 72% H_2SO_4 (w/w). The test tube with the respective sample is brought to a water bath at 30°C for 60 min as shown in **Figure 4.6.** After the time they are removed and added to each 56 mL of distilled water.

Figure 4.6. Assembly of lignin content measuring.

The samples vessel was autoclaved at 121°C, 15 psi for 60 min. The samples were filtered, washed with hot water and brought to the oven at 60°C until constant weight was obtained. This procedure was performed according to the TAPPI T222 standard (Han and Rowell 1997).

The lignin content was determined by the Equation 5. Where, $W_{f,5}$ is the final weight of the sample and $W_{i,5}$ is the initial weight of the sample.

$$\%\,\text{Lignin} = \left(\frac{W_{f,5}}{W_{i,5}}\right) \times 100 \qquad \text{Equation (5)}$$

4.3. Polyphenolic compounds extraction

The extraction of polyphenolic compounds was carried out using two conventional technologies (Soxhlet extraction and solvent extraction) and two non-conventional (ultrasound assisted extraction and supercritical fluids extraction). The procedures for each of these technologies are described below:

4.3.1. Soxhlet extraction

The sample was deposited in a porous (thimble) vessel and placed in a Soxhlet apparatus. The extraction was carried out by means of a solid-liquid ratio 1:25 during 6 hours. Performing of the process is made at a constant reflux, which flows through the thimble obtaining the bioactive extracts.

4.3.2. Solvent extraction

The sample was disposed in a recipient with ethanol 60% in a 20:1 solvent-solid ratio (%v/w). The procedure was carried out during 8 hours at constant temperature (25 °C ± 2 °C) and 300 rpm. Then, the liquid fraction was separated by filtration.

4.3.3. Ultrasound assisted extraction

The pre-dried raw materials were brought into contact with the solvent, using a solvent-sample ratio of 20/1 (v/w). The solutions were subjected to direct sonification as illustrated

in **Figure 4.7**, using the UP50H Ultrasound Processor (Hielscher Ultrasound Technology). Variations of temperature and solvent were made for the operating conditions (Saleh et al. 2016). Finally, the mixtures were carried filtration for removal of suspended particles (Hui Li, Chen, and Yao 2005). The extracted extractives were stored in amber containers at a temperature of 0 - 4°C.

Figure 4.7. Ultrasound assisted extraction equipment.

4.3.4. Supercritical fluid extraction

Supercritical fluid extraction (SFE) was carried out in the supercritical reactor made of stainless steel material (see **Figure 4.8**). The equipment has a capacity of 254 mL and a maximum pressure of 350 bars. It is conditioned with CO_2 as solvent during 1 hour, thus avoiding degradation of the components and increasing the performance of the process. The process was carried out with the pressure and temperature evaluated theoretically, without affecting the degradation of the phenolic compounds due to its high thermal sensitivity. The obtained extracts are stored in amber containers at a temperature of 0 - 4°C for later analysis with spectrophotometric and chromatographic techniques.

Figure 4.8. Supercritical fluid equipment.

4.4. Determination of Polyphenolic Compounds

Extracts obtained were analyzed by determining content of total polyphenolic compounds, antioxidant activity and HPLC for determination of compounds.

4.4.1. Total phenolic compounds

The Folin-Ciocalteu method detects phenolic groups found in the extracts. This is done in the absence of light due to the photosensitivity of the reagents. For this method, a calibration curve was prepared at different dilutions of the stock solution, taking 1.25 g of gallic acid and dissolving it in 80% ethanol in a 250 mL volumetric flask. From this solution different concentrations were prepared by the use of a 50 mL volumetric balloon.

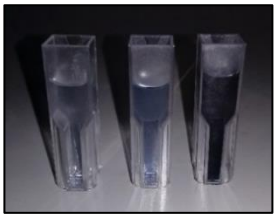


Figure 4.9. TPC determined by Folin-Ciocalteu.

In the analysis of the obtained extract were taken 100 µL and mixed with 1600 µL of distilled water, stirring for 30 seconds. Then 100 µL of Folin-Ciocalteu 1N phenol reagent was added, shaking the solution formed and allowed to equilibrate for 5 minutes. Subsequently, 200 µL of carbonate 20% (Na_2CO_3) was added. The obtained solution was mixed and allowed to stand in a dark place for 2 hours, obtaining the samples from **Figure 4.9.** The samples are brought to a spectrophotometer and measured at a wavelength of 765 nm (Rover and Brown 2013).

4.4.2. Antioxidant activity

The DPPH method consists of measuring in terms of hydrogen donation or the ability to capture free radicals. The methodology consisted of the use of 150 µL of the dilution of the extracted sample (see **Figure 4.10-a**) and 2,850 µL of DPPH reagent. The solution was stirred using a vortex for 30 seconds. Subsequently, the sample was stored in a dark place for 60

minutes (see **Figure 4.10-b**). Finally, the absorbance was recorded at a wavelength of 515 nm (I. Cerón 2013; Brand-Williams, Cuvelier, and Berset 1995).

a) b)

Figure 4.10. Samples for determination of antioxidant activity: a) diluted sample, b) final samples of DPPH analysis.

The antioxidant activity was calculated using Equations 6 - 8:

$$\%Ihnibition = \left(1 - \frac{Abs_{final}}{Abs_{white}}\right) \times 100 \qquad \text{Equation (6)}$$

$$EC_{50}\left(\frac{mL\ solution}{mL\ extract}\right) = \left(\frac{50 - Intercept}{slope}\right) \qquad \text{Equation (7)}$$

$$EC_{50}\left(\frac{mg}{mL}\right) = \left(\frac{1}{IC_{50\left(\frac{mLsolution}{mLetract}\right)}}\right)\left(\frac{mass_{(mg)}}{Volumen_{(mL)}}\right)_{Trolox} \qquad \text{Equation (8)}$$

4.4.3. HPLC

The HPLC System consists of an LC-2010A HT (SHIMADZU), with a UV-visible detector, a quaternary pump, a vacuum degasser and an automatic counter which is observed in **Figure 4.11**. The chromatographic separation was performed on a C18 column with dimensions of 150 mm x 4.6 mm and a particle diameter of 5 µm.

Figure 4.11. HPLC equipment.

4.4.3.1. Chlorogenic acid content

Separation of the chlorogenic acid required an elution gradient with acetic acid 0.5% v/v (A) methanol (B), a temperature of 25°C, a flow of 0.7 mL/min and a wavelength of 310 nm. Chlorogenic acid presented an elution profile in which solvent B started at a concentration of 10% for 15 min, increasing its concentration to 30% at 25 min (Q. Zhang et al. 2007).

4.4.3.2. Ferulic acid content

Ferulic acid was determined by the use of an elution gradient with acetic acid 0.5 v/v (A) methanol (B), a temperature of 25°C, a flow rate of 0.7 mL/min and a wavelength of 280 nm. The elution profile used started with 20% of the concentration of solvent B for 4 min. Then the concentration was increased to 45% until 12 min. Finally the concentration of B increases to 80% up to 25 min (X. Li et al. 2007).

4.4.3.3. Vanillin content

Vanillin determination was performed by a gradient elution with acetic acid 0.01% v/v (A) and methanol (B). The elution profile started with 60% B and 40 A for 5 minutes. Then, the B concentration was decreased to 50% and A increased to 60% at 7 minutes. Subsequently, B reached a concentration of 100% up to 14 min, holding it for 4 min. Finally, the concentration decreased to 60% B at 19 min. The vanillin separation used a flow of 1 mL/min, a temperature of 25°C and a wavelength of 270 nm (Y.-H. Li, Sun, and Zheng 2004).

4.4.3.4. Quercetin, caffeic acid, vanillic acid content

The determination of these compound were carried out by a flow of 1 mL/min, at a wavelength of 280 nm and a temperature of 25°C. The gradient used for the separation consisted of acetic acid 3% v/v (A) and methanol (B). The elution profile started with 100%

A; at 10 min 90% of A and 10% of B. Subsequently, at 40 min B with 70% and A with 30%. Then at 44 min 100% of A (Chen, Zuo, and Deng 2001).

4.4.3.5. Hydroxytyrosol content

The separation of hydroxytyrosol required elution gradient with 2% acetic acid (A) and methanol (B), a temperature of 25°C, a flow of 1 mL/min and a wavelength of 280 nm. The elution profile started with 95% A and 5% B, at 10 min 75% of A and 35% of B. Then at 13 min the reagent A increased to 95% and B at 5% thus remaining up to 15 min. (Smeriglio 2015).

4.5. Analysis of solubility

In order to obtain an approximation of the operating conditions in the supercritical fluid equipment (pressure and temperature), the solubility calculation of the polyphenolic compound was carried out. The properties of the mixture (CO_2-chlorogenic acid) were calculated through of the application of rules, which the properties of the mixture are related to the properties of the pure component. This last is called the mixing rule. For the determination of this solubility was required the modeling of solubility profiles. These values are calculated by solubility models reported in the literature (Huang et al. 2001; J. Moncada, Cardona, and Pisarenko 2013) and using the MATLAB ® software. Where the solubility was calculated from the main equation (Equation 9). While the Peng-Robinson state equation was used with the Stryjek-Vera modification (PRSV) and the Wong Sandler mixing rule. Additionally, some properties of chlorogenic acid were calculated. For this, the contribution method provided by Marrero-Gani was used (Equation 22 - 24) (Marrero and Gani 2001). While in the **Table 4.2** the parameters used for calculating them are shown. The equations used for this calculation are described below.

Solubility equation:

$$y_2 = \frac{P_2^S \phi_2^S}{P\bar{\phi}_2} \exp\left[\frac{V_2^S}{RT}\left(P - P_2^S\right)\right] \quad \text{Equation (9)}$$

State equation PRSV:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bv - b^2} \quad \text{Equation (10)}$$

$$a_i = 0.47724 \frac{R^2 T_{C,i}^2}{P_{C,i}} \alpha_i \quad \text{Equation (11)}$$

$$b_i = 0.0788 \frac{RT_{C,i}}{P_{C,i}} \quad \text{Equation (12)}$$

$$\alpha_i = \left[1 + k_i\left(1 - \sqrt{T_r}\right)\right]^2 \quad \text{Equation (13)}$$

$$k_i = k_0 + k_1\left(1 - \sqrt{T_r}\right)\left(0.7 - T_r\right) \quad \text{Equation (14)}$$

$$k_0 = 0.378893 + 1.4897153w - 0.173848w^2 + 0.01196554w^3 \quad \text{Equation (15)}$$

Wong-Sandler mixing rule:

$$a_m = \frac{RTQ_{WS} D_{WS}}{1 - D_{WS}} = RTD_{WS} b_m \quad \text{Equation (16)}$$

$$b_m = \frac{Q_{WS}}{1 - D_{WS}} \quad \text{Equation (17)}$$

$$D_{WS} = \frac{A_\infty^E}{cRT} + \sum_i \frac{y_i a_i}{RTb_i} \quad \text{Equation (18)}$$

$$Q_{WS} = \sum_i \sum_j y_i y_j \left(b - \frac{a}{RT} \right)_{ij}$$ Equation (19)

$$c = \frac{1}{\sqrt{2}} \ln\left(\sqrt{2} - 1\right)$$ Equation (20)

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT} \left(1 - k_{ij}\right)$$ Equation (21)

Marrero-Gani method:

$$\exp\left(\frac{T_C}{T_{C0}} \right) = \sum_i N_i T_{C1i} + \sum_j M_j T_{C2j} + \sum_k O_k T_{C3k}$$ Equation (22)

$$\left(P_C - P_{C1}\right)^{-0.5} - P_{C2} = \sum_i N_i P_{C1i} + \sum_j M_j P_{C2j} + \sum_k O_k P_{C3k}$$ Equation (23)

$$V_C - V_{C0} = \sum_i N_i V_{C1i} + \sum_j M_j V_{C2j} + \sum_k O_k V_{C3k}$$ Equation (24)

Table 4.2. Reference parameters: Marrero-Gani.

Parameter	Value	Unit
T_{C0}	231.239	K
P_{C1}	5.9827	bar
P_{C2}	0.108998	$bar^{-0.5}$
V_{C0}	7.95	cm^3/mol

4.6. Extraction kinetics of polyphenolic compounds

In the determination of extraction kinetics were used Soxhlet, solvent extraction and ultrasound assisted extraction. The concentration of polyphenolic compounds over time for each extraction process was determined by approximation of the results obtained to regression models. The results were analyzed in CurveExpert Professional software. In this program, different approach methods were analyzed considering a 95% confidence level ($P<0.05$). Obtaining predictive models for the concentration of polyphenolic compounds present in the extract. With the aim to analyze the yields that can be obtained, it is necessary to determine the extraction kinetics. In this work was considered three models to show the trend and behavior of extraction kinetics of polyphenolic compounds present. In each case was considered the technologies as solvent extraction, Soxhlet extraction and UAE. With the aim to show the extraction kinetics was employed different model that can be found in the literature. The models used in this work were presented in the **Table 4.3.** Where "y" denotes the component and the technology employed in each case given in mg/L and "x" the time of the extraction process in minutes.

Table 4.3. Mathematical models for kinetics

Model	Equation		Reference
Gaussian Model	$y = a * \exp\left(-\frac{(x-b)^2}{2c^2}\right)$	(20)	(Luca Fiori et al. 2012; L. Fiori, D. Basso, and P. Costa 2008)
Richards	$y = \frac{a}{1+\exp(b-cx)^{1/d}}$	(21)	(Tong-Jiang Xu and Yen-Peng Ting 2009)
Reciprocal Quadratic	$y = \frac{1}{a+bx+cx^2}$	(22)	(Balyan and Sarkar 2017)
Steinhart-Hart Equation	$y = \frac{1}{A+BLn(x)+CLn(x)^3}$	(23)	(Mellado et al. 2014)
Exponential Association 3	$y = a(b-\exp(-cx))$	(24)	(Adel Reyhanitabar and R.J. Gilkes 2010; Amendola D., Faveri, and G. 2010)
Rational Model	$y = \frac{a+bx}{1+cx+dx^2}$	(25)	(Mellado et al. 2014)
Weibull Model	$y = a - b * \exp(-cx^d)$	(26)	(Amendola D., Faveri, and G. 2010)
Exponential	$y = a * \exp(bx)$	(27)	(Amendola D., Faveri, and G. 2010)
Bleasdale	$y = (a+bx)^{-\frac{1}{c}}$	(28)	(Yi-Ching Cheung and Jian-Yong Wu 2013)
Heat Capacity	$y = a + bx + \frac{c}{x^2}$	(29)	(Mellado et al. 2014)
Shifted Power	$y = a(x-b)^c$	(30)	(Yi-Ching Cheung and Jian-Yong Wu 2013; Athanasia M.Goula 2013)
Modified Hoerl	$y = ab^{1/x}x^c$	(31)	(Mellado et al. 2014)
Exponential Decline	$y = q_o \exp\left(-\frac{x}{a}\right)$	(32)	(Fetkovich and Co 1980)
Farazdagui – Harris	$y = \frac{1}{a+bx^c}$	(33)	(Farazdaghi and Harris 1968)
Reciprocal Logarithm	$y = \frac{1}{a+b\,Ln(x)}$	(34)	(Mellado et al. 2014)
Ratkowsky Model	$y = \frac{a}{(1+e^{b-cx})}$	(35)	(Fetkovich and Co 1980)
DR-Hill	$y = \alpha + \frac{\theta x^n}{k^n+x^n}$	(36)	(Cui et al. 2006)
Harmonic decline	$y = \frac{q_0}{(1+x/a)}$	(37)	(Mellado et al. 2014)
Gompertz Relation	$y = ae^{-e^{b-cx}}$	(38)	(Fetkovich and Co 1980)
Vapor Pressure Equation	$y = exp\left(a+\frac{b}{x}+cln(x)\right)$	(39)	(Cui et al. 2006)

Hyperbolic decline	$y = q_o\left(1 + \frac{bx}{a}\right)^{(-1/b)}$	(40)	(Seshadri and Mattar 2010)
MMF	$y = \frac{ab + cx^d}{b + x^d}$	(41)	(Ullah 2011)
Hoerl	$y = ab^x x^c$	(42)	(Cui et al. 2006)
Saturation growth rate	$y = \frac{ax}{(b + x)}$	(43)	(Ullah 2011)
Power	$y = ax^b$	(44)	(Cui et al. 2006)

4.7. Biorefineries simulation

The simulation of each procedure described in the Aspen plus V.9.0 software was carried out, in order to determine the thermodynamic properties and mass and energy balances at each stage of the procedure. Through the obtained properties thermodynamic exergy system it was analyzed. As a next step, an economic analysis carried out with the use of the Aspen Process Economic Analyzer V.8.8 software and an environmental analysis was developed, using indicators stipulated by the Environmental Protection Agency (EPA).

4.7.3. Simulation process

The Aspen plus software (ASPEN TECNHNOLOGY INC.) was used to carry out the simulation of these processes. This generated the material and energy balances of different scenarios, giving a basis for the analysis of economics in supplies, utilities and energy requirements, among others. As an initial basis, a case of 1 tonne/h calculation was proposed, carrying out the economic and environmental analysis of products obtained from residues.

4.7.3.1. Antioxidant obtaining

For the polyphenolic compounds extraction were used a conventional technology (solvent extraction) and one non-conventional technologies (supercritical fluids extraction). The purpose of this comparison is to demonstrate the economic and environmental benefits of non-conventional technology by improving performance, selectivity and low operating costs in the extraction process.

4.7.3.1.1. Solvent extraction

The solvent extraction of polyphenolic compounds from agroindustrial residues, rich in antioxidants, consisted as a first step in the elimination of moisture by means of a dryer at

40°C. Subsequently to the dried shell its particle size (40 mesh) was reduced and taken to the extraction stage. The extraction carried out in a container used ethanol 60% in a 1:20 (w/v) solid-liquid ratio and 50°C in the process. The polyphenolic compound rich stream is finally brought to an ethanol separation stage which is reintegrated into the system as shown in **Figure 4.12**.

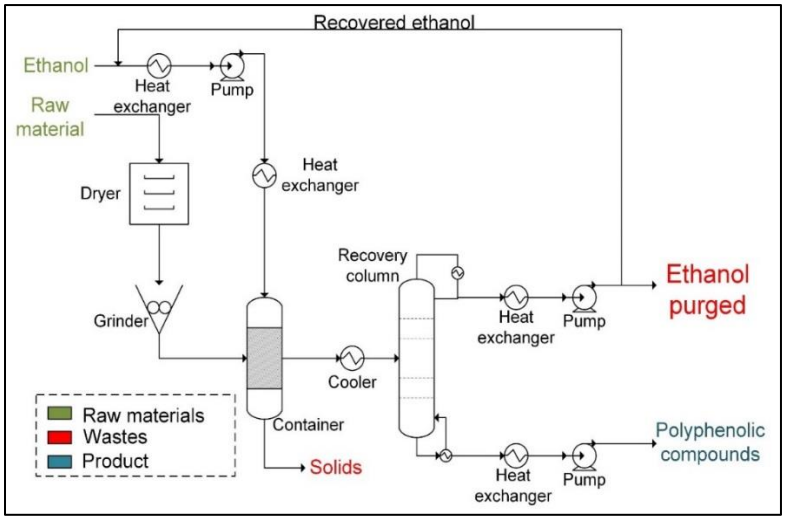


Figure 4.12. Flow diagram of solvent extraction process.

4.7.3.1.2. Supercritical fluid extraction

Each of the raw materials is brought to an initial stage of drying at 40°C. Later they are deposited in the extractor, in which carbon dioxide (CO_2) enters in supercritical conditions (300 bar and 50°C), with the first aid of a cooling of the CO_2 at -19°C and a pump which operates at 300 bars. Obtained the CO_2 in liquid state and with high pressure, the dioxide is brought to supercritical temperature (50°C) to the extractor. Additionally a co-solvent (ethanol 60%) with a 1:3 ratio, solid-co-solvent is used. After carrying out the extraction process in the extractor, the system is depressurized through the use of a valve until obtaining room temperature. The CO_2 present in the system is separated by means of a collector and recirculated in the system to reduce the costs of raw materials. Separated the carbon dioxide the current is taken to an evaporation stage with the objective of separating

the polyphenolic compounds from the ethanol, re-entering the ethanol into the system. **Figure 4.13** the supercritical fluids extraction scheme is observed.

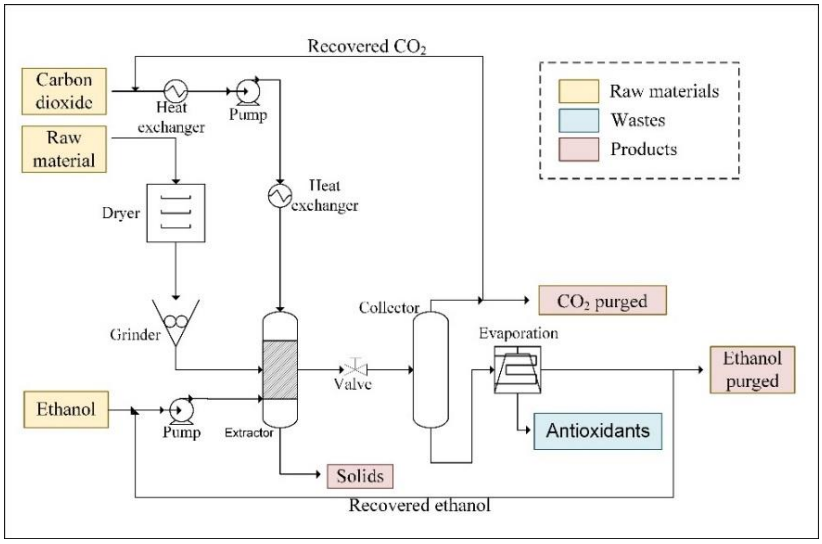


Figure 4.13. Flow diagram of SFE process.

4.7.3.2. Glucose and xylose production

The solid retrieved previously subjected to dilute acid treatment was carried out at 2% v/v. Where the kinetics used are reported by Aguilar et al (2002) (Aguilar et al. 2002). The product of this process was a xylose rich liquor, which was separated from the solids by filtration. The solid fraction was subjected to enzymatic hydrolysis in order to obtain a solution rich in glucose. The kinetics used to carry out the enzyme hydrolysis was reported by Philippidis, Smith and Wyman (1993) (Philippidis, Smith, and Wyman 1993). The resulting solution was filtered and a solution rich in glucose and a lignin rich fraction were obtained. **Figure 4.14** shows a diagram of the process described.

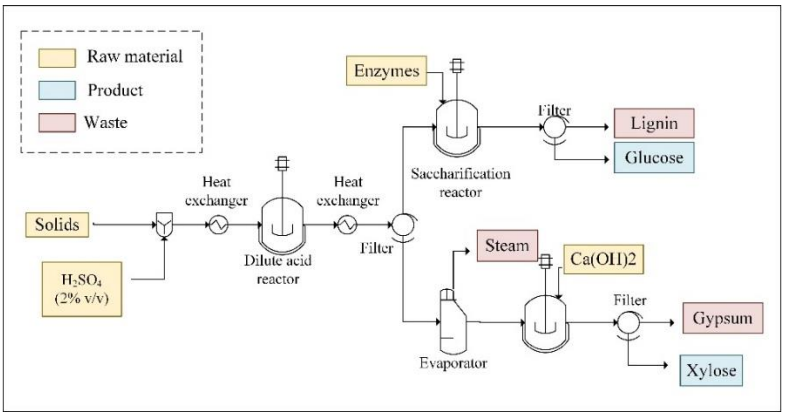


Figure 4.14. Flow diagram of glucose and xylose production.

4.7.3.3. Ethanol production

The glucose was submitted to a fermentation process to obtain ethanol based on the kinetic expressions proposed by Rivera et al (2006), using *Saccharomyces cerevisiae* as microorganism at 37ºC (Rivera et al. 2006). Afterwards, cell biomass was separated from the culture broth by centrifugation. After, the fermentation stage, the culture broth containing approximately 5 - 10% wt of ethanol was taken to the separation step, which consists of two distillation columns. In the first column, ethanol was concentrated nearly to 45 - 50% by weight. In the second column, the liquor was concentrated, until the azeotropic point (96% wt). After was employed a dehydration step with molecular sieves to obtain an ethanol concentration of 99.6% wt (Pitt, Haag, and Lee 1983). **Figure 4.15** shows how it was employed the glucose to obtain ethanol according to the process described above.

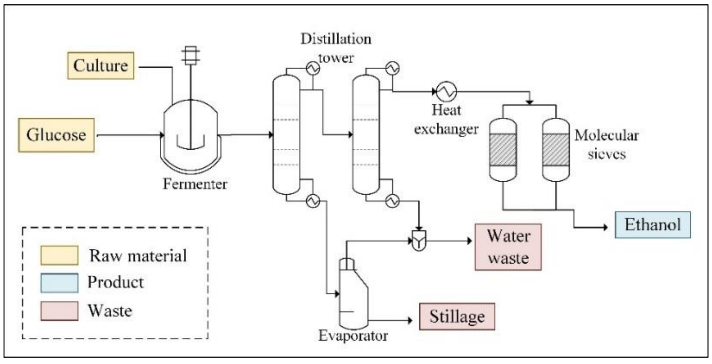


Figure 4.15. Flow diagram of ethanol production.

4.7.3.4. Xylitol production

The xylose obtained in one of the previous stages can be used to obtain xylitol by means of a fermentative process. The microorganism used in this work was *Candida parapsilosis* (Aranda-Barradas, Delia, and Riba 2000). The purification process of the xylitol was carried out by means of precipitation in the presence of ethanol in a relation 1:1 (Mussatto et al. 2014). Filtration was then carried out in order to remove precipitated xylitol. **Figure 4.16** shows how under the proposed process was obtained xylitol as a final product

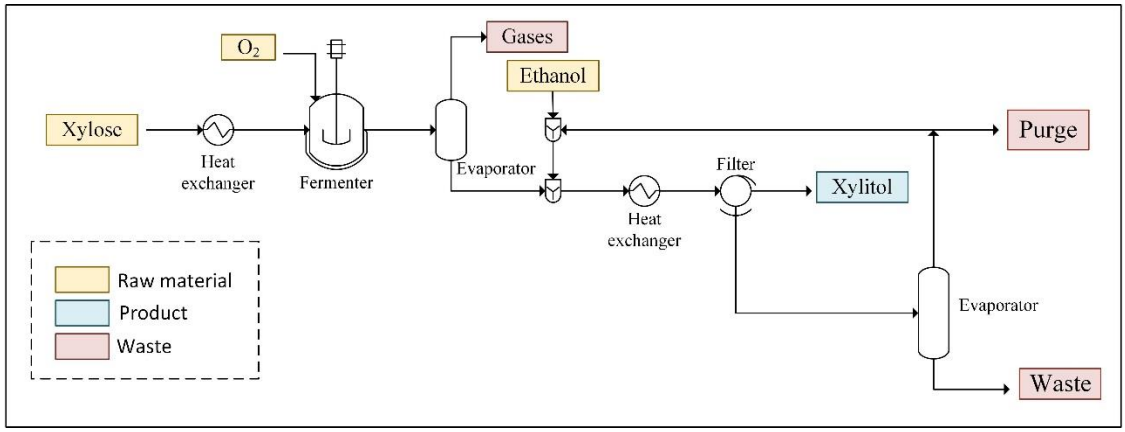


Figure 4.16. Flow diagram of xylitol production.

4.7.3.5. Cogeneration system

The lignin obtained from the solid fraction of the enzymatic hydrolysis was subjected to a gasification process. In this process, a syngas stream was obtained with a high calorific value that was used in the electricity generation through Rankine cycle (Manatura et al. 2017; Bridgwater 1995). In this case was considered the use of a turbine. Where it was fed the syngas and through process of expansion a motor was moved generating in the process electricity in potency form (see **Figure 4.17**). Also, a syngas stream was obtained with a less content of energy.

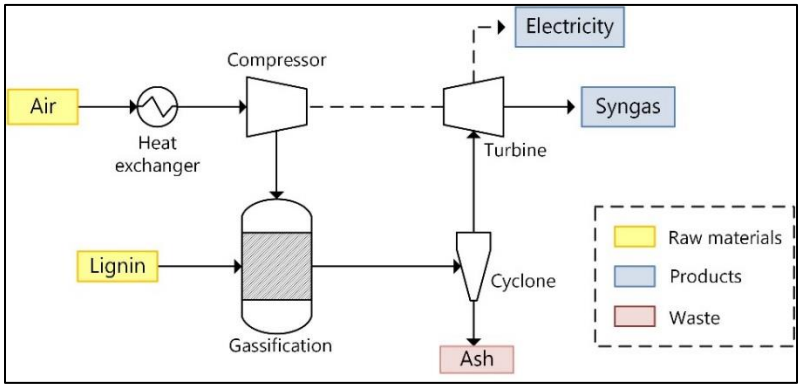


Figure 4.17. Flow diagram of cogeneration of electricity.

4.7.3.6. Furfural

Furfural was obtained through the dehydration of xylose (Cortés et al. 2013). As a first stage the xylose is taken to a reactor which operates at 170°C and 10 bars. This reactor is additionally fed the catalyst, which consists of aluminum clays and hafnium. In order to extract the furfural as it is produced, air is fed to the reactor that functions as a recovery agent (see **Figure 4.18**). For the process of recovery and purification of the furfural, the solution obtained in the reactor is sent first to a distillation train, with the objective of removing the sugars that did not react and as much water as possible. Next, a solvent extraction process with toluene is carried out. The resulting mixture is sent to a distillation process in which a furfural with a purity of 98% is obtained.

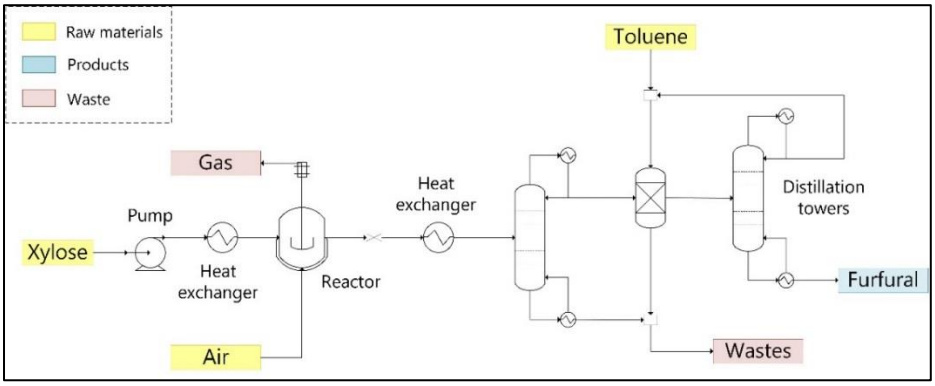


Figure 4.18. Flow diagram of furfural production.

4.7.4. Economic Assessment

The costs with high influence on the developed processes (operating costs, raw materials, general and administrative, depreciation, among others) were calculated by using the Aspen Process Economic Analyzer software (Aspen Technologies, Inc., USA). As an analysis, an evaluation time was estimated for a period of 10 years with a linear depreciation method, using a tax rate of 25% and an annual interest rate of 17% corresponding to values used in the Colombian economy. As results, the prices of each of the items were obtained in US dollars (USD) per kilogram of product. **Table 4.4** summarizes the economic data required for the analysis, such as the price of raw materials, reagents used, public services and labor wages. Additionally, the evaluation of the profitability of each of the scenarios was determined by analyzing the Net Present Value (NPV) over a 10-year period.

Table 4.4. Prices of raw materials and supplies.

	Price	Reference
Raw material		
Spent coffee grounds	0.01 USD/tonne	
Coffee cut-stems	0.05 USD/tonne	
Naranjilla peel	0.01 USD/tonne	(J. A. Dávila et al. 2014)
Tomato tree peel	0.01 USD/tonne	
Reagents		
Carbon dioxide	1.55 USD/kg	(Cerón Salazar 2013)
Ethanol	1.24 USD/kg	(Jonathan Moncada et al. 2015)
Sodium hidroxide	0.05 USD/kg	(J. A. Dávila et al. 2014)
Sulfuric acid	0.1 USD/kg	
Utilities		
Electricity	0.10 USD/kWh	(J. A. Dávila et al. 2014)
Fuel	7.21 USD/MMBTU	

Water	1.25 USD/m^3	
LP steam	1.57 USD/tonne	(Jonathan Moncada et al. 2015)
MP steam	8.18 USD/tonne	
HP steam	9.86 USD/tonne	
Operating cost		
Supervisor	4.29 USD/h	(J. A. Dávila et al. 2014)
Operator	2.14 USD/h	

4.7.5. Energy and exergy assessment

The energy is associated with the capacity that can present a body or system to perform transformations, regardless of whether these are carried out or not the process presents a change in their energy (Moran and Shapiro 2004; Dincer and Rosen 2013). Such changes can be quantified from the calculation of thermodynamic properties such as the exergy. Which from the thermodynamics point of view 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 reaches thermodynamic equilibrium with the environment (Dincer 2002; Tsatsaronis 2007). Using Aspen Plus software, it is also possible to know the total energy consumption of the equipment involved in the process. This information is used to know the distribution of energy consumption for both SE and SFE. With the aim of obtaining more information about the energy consumption took place the determination of consumption exergy using the methodology proposed by Zhang et al (2012) (Y. Zhang et al. 2012). In this work only was considered the physical and chemical exergy as a main cause of exergetic changes. The changes attributed to the physical exergy were determined from the data of enthalpy and entropy obtained in Aspen Plus.

Equation 29 presented the terms that presents a high contributions to the total value of exergy. Equations 30 and 31, show how to determine the physics and chemistry exergy, while

the Equation 31 describes the calculation of the exergy physical specific in terms of enthalpy and entropy. The value of ex_i^{ch} for each component was determined using the information reported by Rivero and Song (Rivero and Garfias 2006; Song, Shen, and Xiao 2011)

$$Ex = Ex^{ph} + Ex^{ch} \quad \text{Equation (29)}$$

$$Ex^{ph} = \sum_i n_i \, ex_i^{ph} \quad \text{Equation (30)}$$

$$ex_i^{ph} = (h_j - h_o) - T_o(s_j - s_o) \quad \text{Equation (31)}$$

$$Ex^{ch} = \sum_i n_i \left(ex_i^{ch} + RT_o Ln\left(\frac{n_i}{\sum n_i}\right)\right) \quad \text{Equation (32)}$$

4.7.6. Environmental assessment

The evaluation of the environmental impact potential (PEI) was carried out through the use of the Waste Reduction Algorithm (WAR). This software was developed by the National Risk Management Research Laboratory of the United States Environmental Protection Agency (D. Young, Scharp, and Cabezas 2000). Through the mass and energy balances of the simulation of processes carried out previously, the impacts of eight categories were calculated (gate-to-gate approach) (C. A. Cardona, Marulanda, and Young 2004). Within the analyzed categories are the Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Exposure (HTPE), Terrestrial Toxicity Potential (TTP), Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP)), Ozone Depletion Potential (ODP), Photochemical Oxidation Potential (PCOP) and Acidification Potential (AP) (D. M. Young and Cabezas 1999).

RESULTS SECTION

5. SOLUBILITY

Supercritical fluids extraction consists of three main stages. First, the matrix of the plant (or raw material) absorbs the supercritical solvent and the additional fluids are released. As a second step, the compounds obtained are dissolved from the use of a solvent. While in the third stage, the dissolved compounds are transported out of the surface of the solid. In this, diffusion is the most important transport mechanism. To improve the yield in the extraction process by SFE (obtain more compounds), the calculation of the solubility of the compound of interest is required. In this sense, the solubility of a substance in a pure supercritical fluid can be obtained from the analysis of a binary system. This system must present operating conditions close to that of the critical or near-critical region (area around the critical point of a solvent or mixture). Additionally, the solubility depends on the variation of the partial molar volumes with pressure. Based on the above, the solubility calculation of chlorogenic acid was performed, using the properties shown in **Table 5.1**. These properties were obtained from the contribution method of Marrero-Gani groups. This polyphenolic compound was selected due to its multiple applications and importance in the pharmaceutical and cosmetics industry. In addition to being a representative compound in the composition of coffee and its residues.

Table 5.1. Properties of polyphenolic compounds.

Property	Units	Chlorogenic acid
T_c	[K]	873.55
P_c	[bar]	6.00
V_c	[cm^3/mol]	481.23
w		1.02

In **Figure 5.1** the behavior of the solubility with respect to the temperature and extraction pressure is presented. For this, carbon dioxide was used as a supercritical fluid and its influence on the extraction of chlorogenic acid. For this analysis it was considered that the P>Pc and the T<TC. As a result, it was found that as the pressure increases, the chlorogenic acid becomes more soluble. From this, the possible best operating pressure is in a range of 200 - 300 bars. In addition, solubility was higher at a temperature between 40 - 50°C (317.15 - 327.15 K). This temperature is adequate not to influence the thermolability of the polyphenolic compounds, which can affect the ability to neutralize free radicals. From this, a solubility of $2.3x10^{-8}$ was obtained at 300 bars and 50°C. According to the previous analysis, it was decided to work at high pressures (P> 200 bars) and temperature of 50°C. This with the aim of preserving the antioxidant activity of the extracts to obtain and improve the yields of the process.

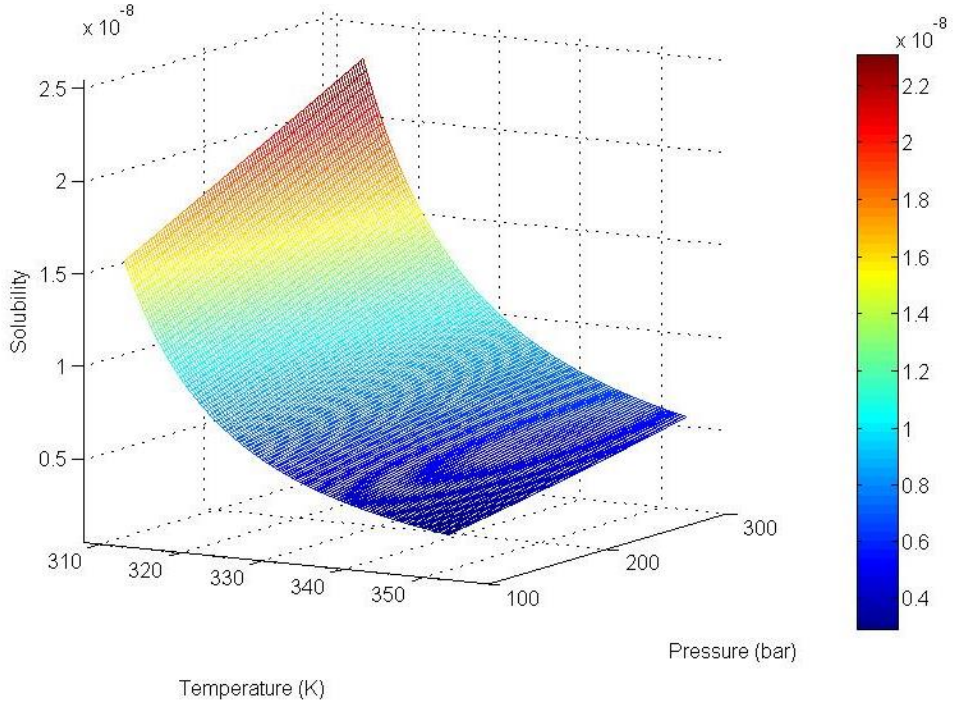


Figure 5.1. Solubility: CO2 - Chlorogenic acid.

Conclusions

The previous analysis of the solubility is of high importance due to the high precision with the experimental results obtained, thus facilitating the number of variables to be analyzed and achieving a higher concentration of polyphenolic compounds from the extracts by SFE. Additionally, the technology of supercritical fluid extraction proved to present a high potential obtaining with these different polyphenolic compounds of interest through the use of a smaller volume of solvent and time of operation.

6. SPENT COFFEE GROUNDS

The spent coffee grounds was used as raw material to obtain value-added products. In the first part of this chapter, an experimental analysis of the influence of non-conventional technologies in the polyphenolic compounds extraction was carried out. Later, in the second part, the extraction kinetics of polyphenolic compounds identified in this residue were obtained. Finally, a pre-feasibility analysis was developed through the use of biorefineries to obtain different products.

6.1. Experimental results

This study consisted of the use of the coffee waste (SCG) for the polyphenolic compounds extraction present in the waste. For this, two types of coffee waste were used: one from a coffee machine in Colombia (Homemade SCG) and another from an industry in Portugal (Indrustrial SCG). The extraction process consisted in carrying out the methodology proposed in **Figure 6.1** performing each stage in triplicate. As an initial step, the drying of the fluff at 45°C was carried out in a furnace, until a humidity of less than 10% was obtained. Subsequently, its physical-chemical composition was determined as indicated in item 5.2. Once the physical-chemical characterization was carried out, the polyphenolic compounds extraction was carried out through the application of four technologies: solvent extraction, Soxhlet extraction, UAE and SFE. Each of these technologies showed variations in operating conditions either by modifying the type of solvent (water, ethanol, ethanol 60%) and in some cases the temperature (UAE) and operating pressure (SFE) as shown in **Figure 6.1**. The objective of this part is to obtain the best extraction conditions and analysis of the influence of each of the technologies. Subsequently, each of the extracts obtained were stored in amber bottles at -4°C, for subsequent determination of polyphenolic compounds through of spectrophotometry methods.

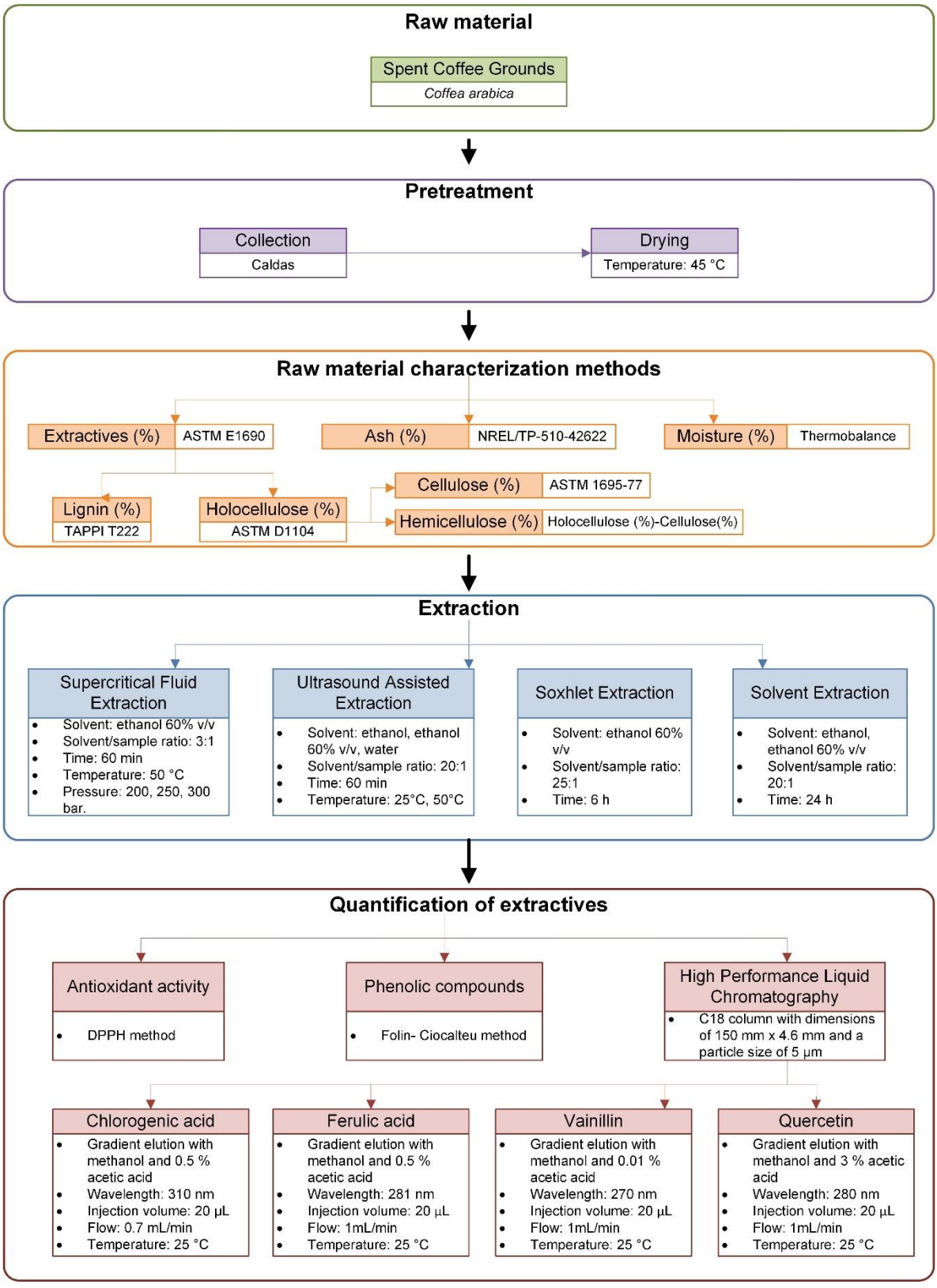


Figure 6.1. Experimental scheme of the process of obtaining extracts from spent coffee grounds.

The results of the physical-chemical composition of the SCG are shown in **Table 6.1**. These results present a high content of extracts (mainly in the Homemade SCG). The physical-chemical characterization obtained resulted in a high content of polysaccharides (cellulose and hemicellulose) representing more than 50% of the weight of the wastes. This shows a high potential for obtaining sugars and subsequent value-added product such as ethanol, acid lactic, xylitol, among others (Quintero, Moncada, and Cardona 2013a; Roukas and Kotzekidou 1998; Rao et al. 2006; Mussatto, Machado, et al. 2011). In the case of the Homemade SCG presented a value of 29.81 ± 2.09% (w/w) for hemicellulose and 22.21 ± 0.06% (w/w) for cellulose. However, for the case of hemicellulose, it was lower than that obtained from the Industrial SCG (39.93 ± 1.79% w/w), due to the greater depletion of this raw material, resulting in a lower content of extracts (6.14 ± 0.33% w/w) compared to Homemade SCG (26.51 ± 0.27% w/w). On the other hand, lignin presented a value of 20.50 ± 0.76% (w/w) and 25.16 ± 1.4% (w/w) for Homemade SCG and Industrial SCG, respectively. Where this raw material can be used for processes such as the energy generation and the production of artificial vanillin (Cardona Alzate and Sánchez Toro 2006; Araújo, Grande, and Rodrigues 2010). In the ashes case, the one coming from Industrial SCG showed a value 2.6 times higher than the Homemade SCG. Meanwhile, industrial SCG presented a content similar to that reported by Ballesteros, Texeira and Musatto (2014) in the hemicellulose and lignin (see **Table 6.1)**. This last due to the use in both cases of an industrial level SCG.

Table 6.1. Physical-chemical composition of spent coffee grounds.

	Homemade SCG	**Industrial SCG**	**Reference** (L. F. Ballesteros, Teixeira, and Mussatto 2014)
Extractives (% dw)	26.51 ± 0.27	6.14 ± 0.33	---
Holocellulose (% dw)	52.02 ± 2.03	49.89	---
Cellulose (% dw)	22.21 ± 0.06	9.96 ± 0.04*	12.40 ± 0.70*
Hemicellulose (% dw)	29.81 ± 2.09	39.93 ± 1.79	39.10 ± 1.90
Lignin (% dw)	20.50 ± 0.76	25.16 ± 1.4	23.90 ± 1.70
Ash (% dw)	0.97 ± 0.05	2.56 ± 0.13	1.30 ± 0.10

*Glucose

In **Table 6.2**, the yields of the total polyphenolic compounds analyzed from the SCG extracts are presented. The determination of the TPC in conventional technologies showed yields from 3.32 - 13.98 mg GA/g with the best values for the Homemade SCG. Where the best operating condition was with ethanol 60% as a solvent due to the improvement in the solubility of the polyphenolic compounds. However, values lower than those found in the literature were obtained. Andrade et al (2012) reported with Soxhlet extraction 119.5 mg GA/g using ethanol and 182.6 mg GA/g with ethyl acetate for 6 hours and a solid-liquid ratio 1:15 (w/v) (Andrade et al. 2012b). On the other hand, comparing the solvent extraction, it was found that the results were in the range of those reported by Mussatto et al (2011) of 2.6 - 16.2 mg GA/g using methanol as solvent, with a solid-liquid ratio 3:1 (w/v) and 90 minutes of extraction (Mussatto, Ballesteros, et al. 2011).

The UAE technology resulted in a higher content at a temperature of 50°C and 60% ethanol with 12.67 ± 0.31 mg GA/g and 10.01 ± 0.14 mg GA/g for Homemade SCG and Industrial SCG. Compared with the UAE technology also used by Abdullah et a (2017), low TPC values were obtained for the present study, because of they report concentrations of 32.81 - 36.23 mg GA/g (Abdullah Al-Dhabia, Ponmurugana, and Maran Jeganathanb 2017). In this case was used ethanol, temperatures between 30 - 50°C and a time of 25 to 45 minutes. However, Le et al (2017) reported similar values to those obtained in this work with concentrations of 13.46 mg GA/g (Le et al. 2017), using n-hexane, a 1:20 (w/v) solid-liquid ratio and room temperature during 30 min. The extracts of spent coffee grounds obtained by SFE do not show a significant change in the pressure variation. From this was obtained a better concentration at 300 bars for the Homemade SCG (1.97 mg GA/g) and 200 bars for the Industrial SCG (1.43 mg GA/g). These values obtained were low compared to those reported by Andrade et al (2012) that present a range of 24.1 - 57 mg GA/g. Nevertheless, this uses an operation time of 4.30 hours, higher than this work. Additionally, they added a separation stage of ethanol achieving with this a concentration of the extract of greater SCG (Andrade et al. 2012a).

Additionally, the results of the analysis of the antioxidant activity through the DPPH method are presented in **Table 6.2**. When comparing the antioxidant activity using conventional technologies, better results are obtained with the Sox-E with 34.29 µg/mL and 26.47 µg/mL for the Homemade SCG and Industrial SCG, respectively. On the other hand, in the non-conventional technologies, the UAE presented the highest values using as solvent water at 25°C with 27.37 ± 0.28 µg/mL for Homemade and 21.54 ± 0.18 µg/mL for Industrial SCG. As reported by Le et al (2017) (31.44 µg/mL) with SCG (Le et al. 2017). Where lower concentration values were obtained in this study, a possible consequence is the use of another solvent (hexane). In the case of the SFE EC_{50} values were obtained above 38 µg/mL and showing an increase in its composition as the pressure in the system increased. Additionally, it can be considered that the extract obtained is a product with a good antioxidant potential, competing at the same time with raw materials such as myrtle leaves (20.61 µg/mL) and eucalyptus (2.09 µg/mL) (Andrade et al. 2012a; de Campos et al. 2008; Dahmoune et al. 2015; Santos et al. 2012).

Through HPLC was evident the content of some polyphenolic compounds present in SGC extracts. In the determination of chlorogenic acid in SCG, the same trend was observed for total phenolic compounds, as evidenced in **Table 6.3**. The best concentration with UAE technology at 50°C and 60% ethanol (0.93 mg/g for the Homemade and 0.43 mg/g for the Industrial SCG). According to the values reported by Abdullah et al (2017), the content of chlorogenic acid ranges between 0.49 - 1.31 mg/g using this same technology, with ethanol, temperatures between 30 - 50°C and a time between 25 to 45 minutes (Abdullah Al-Dhabia, Ponmurugana, and Maran Jeganathanb 2017). This showed that to the conditions worked a high extraction of chlorogenic acid was obtained. In SE the chlorogenic acid content presented the highest value with 0.54 mg/g (ethanol 60%) for the Homemade SCG. This value is in the range of that reported by Musatto et al (2011) (0.37-1.39 mg/g) (Mussatto, Ballesteros, et al. 2011).

Table 6.2. TPC and antioxidant activity of extracts from spent coffee grounds.

Technology		TPC		DPPH	
		Homemade SCG	Portugal SCG	Homemade SCG	Industria SCG
		(mg GA/g)	(mg GA/g)	EC_{50} (µg/mL)	EC_{50} (µg/mL)
SE	W	5.73 ± 0.44	4.07 ± 0.21	7.29 ± 0.19	5.18 ± 0.09
	EtOH	4.30 ± 0.30	3.32 ± 0.09	8.47 ± 0.36	7.29 ± 0.22
	EtOH 60%	8.99 ± 0.07	6.35 ± 0.20	12.87 ± 0.25	8.85 ± 0.15
Sox-E	W	9.62 ± 0.53	7.04 ± 0.17	17.36 ± 0.34	16.43 ± 0.18
	EtOH	9.04 ± 0.28	7.62 ±0.13	21.64 ± 0.22	17.29 ± 0.11
	EtOH 60%	13.98 ± 0.09	11.32 ± 0.27	34.29 ± 0.52	26.47 ± 0.20
UAE	W-25°C	4.75 ± 0.38	3.12 ± 0.20	27.37 ± 0.28	21.54 ± 0.18
	W-50°C	7.00 ± 0.40	4.76 ± 0.18	10.09 ± 0.26	13.65 ± 0.08
	EtOH-25°C	4.73 ± 0.13	3.78 ± 0.17	4.64 ± 0.42	5.89 ± 0.05
	EtOH-50°C	6.24 ± 0.39	4.69 ± 0.15	14.54 ± 0.57	15.48 ± 0.09
	EtOH 60%-25°C	9.57 ± 0.21	7.37 ± 0.37	25.83 ± 0.30	9.48 ± 0.19
	EtOH 60%-50°C	12.67 ± 0.31	10.01 ± 0.14	10.94 ± 0.55	7.59 ± 0.13
SFE	200 bar	1.92 ± 0.03	1.43 ± 0.07	38.45± 0.62	39.59 ± 0.29
	250 bar	1.96 ± 0.05	1.13 ± 0.08	50.37± 0.18	49.54 ± 0.31
	300 bar	1.97 ± 0.00	1.06 ± 0.05	63.39 ± 0.53	52.43 ± 0.37

Furthermore, SCG showed ferulic acid content, presenting similar values to Grapefruit (0.32 mg/g) and sugar beet (0.25 mg/g) using Soxhlet extraction (Gorinstein et al. 2001; Mattila and Hellström 2007). While it showed values equal to tomato (0.01 mg/g), avocado (0.01 mg/g) and potato (0.01 mg/g) (Periago et al. 2002; Mattila and Hellström 2007). Meanwhile, in the quantification of ferulic acid content by UAE values were obtained from 0.01-0.22 mg/g, with 60% ethanol as the best solvent. Among the polyphenol compounds analyzed, vanillin presented the highest content with 2.50 mg/g for the Homemade SCG with UAE 50°C and ethanol 60%. This compound present in the market higher costs than the vanillin obtained in a synthetic way. However, in the Industrial SCG only presence was present through Soxhlet with ethanol 60% (0.01 mg/g).

Quercetin is the most representative compound of flavonoids. This compound has many therapeutic uses such as: anti-inflammatory, antioxidants, antihistamines, treatments for cancer, allergies, asthma, urticarial, antidiabetics, treatments for rheumatoid arthritis. Besides that it brings color in fruits, flowers and vegetables (Carrión and García 2010). The SCG extracts demonstrated the presence of quercetin. In this case, the best concentration were obtained with ethanol with 0.09 and 0.19 mg/g with SE and Sox-W, respectively. Quercetin showed its best concentration at the level of all the technologies at operating conditions different from the other polyphenolic compounds analyzed with 0.13 mg/g (Homemade SCG) using ethanol as solvent and at 50°C. In addition, SCG showed that it has a higher quercetin content than raw materials such as apple (0.12 mg/g), raspberry (0.03 mg/g) and blackberry (0.03 mg/g) (Sultana and Anwar 2008; Häkkinen et al. 1999).

Two other compounds identified were vanillic acid and caffeic acid, with the highest values in the Industrial SCG using Soxhlet technology (60% ethanol) with 0.18 mg/g and 0.15 mg/g for vanillic acid and caffeic acid, respectively. While with Homemade SCG in the case of vanillic acid was obtained to 0.13 mg/g with Soxhlet extraction (60% ethanol) and for caffeic acid to 0.07 mg/g with SFE at 200 bars.

Using the SFE technology, the identified polyphenolic compounds were: chlorogenic acid, ferulic acid, vanillin, caffeic acid and vanillic acid as shown in **Table 6.3**. These compounds were expressed in mg per g of sample. As a result it was obtained that the compound with the highest concentration was vanillin (in the case of the Homemade SCG) with to 0.32 mg/g. While the chlorogenic acid which is reported in the literature for a high presence in the coffee waste, presented to 0.22 mg/g. The analyzed compounds had a higher concentration with a pressure of 200 bars. Comparing with results found in literature, chlorogenic acid presented values similar to those reported by Andrade et al (2012) with 0.19 mg/g with SFE and 200 bars (Andrade et al. 2012a).

Table 6.3. Content of polyphenolic compounds from spent coffee grounds.

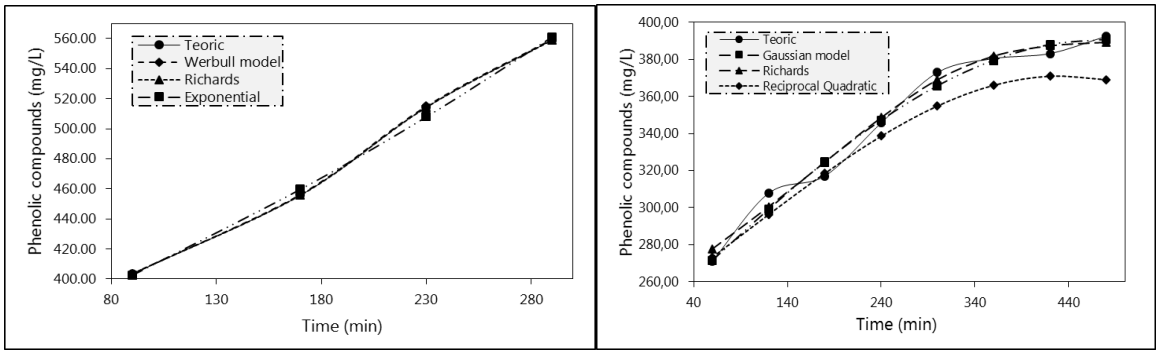
		Homemade SCG						Industrial SCG					
		Chlorogenic acid	Ferulic acid	Vanillin	Quercetin	Vanillic acid	Caffeic acid	Chlorogenic acid	Ferulic acid	Vanillin	Quercetin	Vanillic acid	Caffeic acid
		(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)
SE	W	0.21±0.03	0.01±0.00	0.31±0.03	0.03±0.01	0.04±0.00	0.01±0.00	0.19±0.01	0.70±0.02	NR	0.07±0.00	0.08±0.00	0.02±0.00
	EtOH	NR	0.02±0.00	0.14±0.01	0.09±0.01	NR	NR	0.03±0.00	0.01±0.00	NR	0.07±0.00	NR	NR
	EtOH 60%	0.54±0.02	0.15±0.00	0.57±0.01	0.01±0.00	0.06±0.01	0.03±0.00	0.25±0.02	0.57±0.03	NR	0.08±0.00	0.14±0.01	0.08±0.00
Sox	W	0.56±0.01	0.22±0.01	0.94±0.03	0.01±0.00	0.08±0.00	0.03±0.00	0.28±0.02	0.60±0.04	NR	0.03±0.00	0.11±0.00	0.10±0.01
	EtOH	0.18±0.03	0.11±0.01	0.68±0.01	0.19±0.02	0.02±0.00	0.02±0.00	0.17±0.01	0.32±0.02	NR	0.11±0.01	0.04±0.00	0.01±0.00
	EtOH 60%	0.63±0.01	0.28±0.02	1.21±0.01	0.02±0.00	0.13±0.01	0.06±0.00	0.35±0.02	0.65±0.05	0.01±0.00	0.04±0.00	0.18±0.01	0.15±0.01
UAE	W-25°C	0.05±0.00	0.01±0.00	0.33±0.02	NR	0.04±0.00	0.02±0.00	0.09±0.01	0.78±0.04	NR	0.09±0.00	0.06±0.00	0.02±0.00
	W-50°C	0.52±0.03	0.08±0.00	0.50±0.03	0.02±0.00	0.07±0.01	0.04±0.00	0.21±0.01	0.46±0.06	NR	0.02±0.00	0.07±0.00	0.04±0.00
	EtOH-25°C	NR	0.02±0.00	0.13±0.00	0.05±0.03	0.01±0.00	NR	0.12±0.03	0.01±0.00	NR	0.12±0.01	NR	NR
	EtOH-50°C	0.01±0.00	0.05±0.00	0.29±0.02	0.13±0.01	0.02±0.00	0.01±0.00	0.27±0.01	0.01±0.00	NR	0.16±0.01	NR	NR
	EtOH 60%-25°C	0.50±0.03	0.15±0.02	1.92±0.02	0.02±0.00	0.07±0.00	0.04±0.00	0.39±0.02	0.70±0.02	NR	0.97±0.03	0.21±0.01	0.12±0.01
	EtOH 60%-50°C	0.93±0.01	0.22±0.02	2.50±0.04	0.02±0.00	0.24±0.04	0.05±0.01	0.43±0.01	0.10±0.1	NR	0.50±0.03	0.11±0..01	0.06±0.00
SFE	200 bar	0.22±0.01	0.08±0.00	0.32±0.01	NR	0.08±0.01	0.07±0.00	0.16±0.02	0.07±0.01	NR	NR	0.11±0.01	0.09±0.01
	250 bar	0.18±0.01	0.04±0.00	0.25±0.01	NR	0.02±0.00	0.01±0.00	0.09±0.01	0.03±0.00	NR	0.01±0.00	0.08±0.00	0.03±0.00
	300 bar	0.14±0.00	0.04±0.00	0.23±0.01	NR	0.02±0.00	0.01±0.00	0.13±0.02	0.04±0.00	NR	0.02±0.00	0.02±0.00	0.01±0.00

6.2. Extraction kinetics of polyphenolic compounds from Homemade SCG

Operating conditions such as time, solvent, solvent-liquid ratio, temperature, among others, affect the performance in obtaining polyphenolic compounds. For this reason, according to the results obtained, an adjustment was made to each of the technologies with the best solvent analyzed (ethanol 60%), obtaining the mathematical models with the best correlation factor for the extracts from the homemade SCG.

6.2.1. Total phenolic compounds

The TPC presents different yields depending on the technology used. In this sense, technologies such as solvent extraction, Soxhlet extraction and UAE are some of the alternatives available. **Figure 6.2** shows the concentration of TPC as a function of time. In the results obtained from the analyzed samples, it can be observed that the UAE presents a shorter operating time. This technology can achieve a concentration of phenolic compounds of 650.45 mg GA/L in a time of 60 min. While the solvent extraction has a concentration of 392.50 mg GA/L in a time of 480 min. Finally, the Soxhlet extraction has a value of 559.09 mg GA/L in 290 min. These results demonstrate the efficiency of the UAE, which using less operation time. Subsequently, the parameters were found for the equations that best describe the phenomenon involved in the extraction processes analyzed. In the **Table 6.4** was shows the parameters found for each case. From the information presented in this table, the different models for each case were plotted. At the same time it is possible to observe the difference that present each one with the other models and with the experimental data.



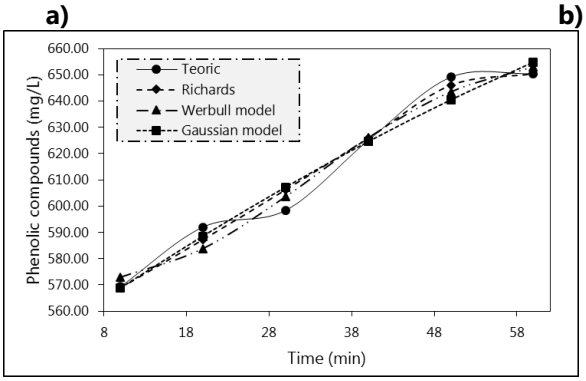


Figure 6.2. Model adjustment for TPC from SCG. (a) Solvent extraction. (b) Soxhlet extraction. (c) UAE.

Table 6.4. Parameters for mathematic models of TPC from SCG.

Technology	Model	r^2	Parameters			
			a	b	c	d
Solvent	Gaussian Model	0.9842	3.91.E+2	4.79.E+2	4.94.E+2	
	Richards	0.9857	3.90.E+2	6.56	2.08.E-2	1.52.E+1
	Reciprocal Quadratic	0.9839	3.99.E-3	-6.30.E-6	6.92.E-9	
Soxhlet	Weibull	0.9999	5.83.E+2	1.90.E+2	5.20.E-8	3.09
	Richards	0.9970	5.59.E+2	8.39.E+1	2.98.E-1	1.71.E+2
	Exponential	0.9955	3.47.E+2	1.66.E-3		
UAE	Richards	0.9825	6.50.E+2	2.92.E+2	5.61	1.76.E+3
	Weibull	0.9730	6.58.E+2	8.69.E+1	6.42.E-5	2.62
	Gaussian Model	0.9661	7.03.E+2	1.28.E+2	1.82.E+2	

6.2.2. Chlorogenic acid

Among the phenolic compounds analyzed in SCG, chlorogenic acid can be found. In the three technologies analyzed, the best yields were obtained in UAE. While solvent extraction and Soxhlet have similar values. A concentration of chlorogenic acid of 46.53 mg/L can be obtained by UAE. While with solvent extraction and with Soxhlet it is possible to obtain concentrations of 24.87 and 25.22 mg/L, respectively. The above can be seen by comparing **Figure 6.3, b** and **c**. Likewise, the predictive models that show the adjustments are presented.

The models that best fit for solvent extraction are those of Steinhart-Hart, Exponential Association 3 and Rational. For the Soxhlet extraction are the Weibull, Bleasdale and Steinhart-Hart models. Finally, for the UAE there are the models of Heat Capacity, Shifted Power and Modified (see **Table 6.5**).

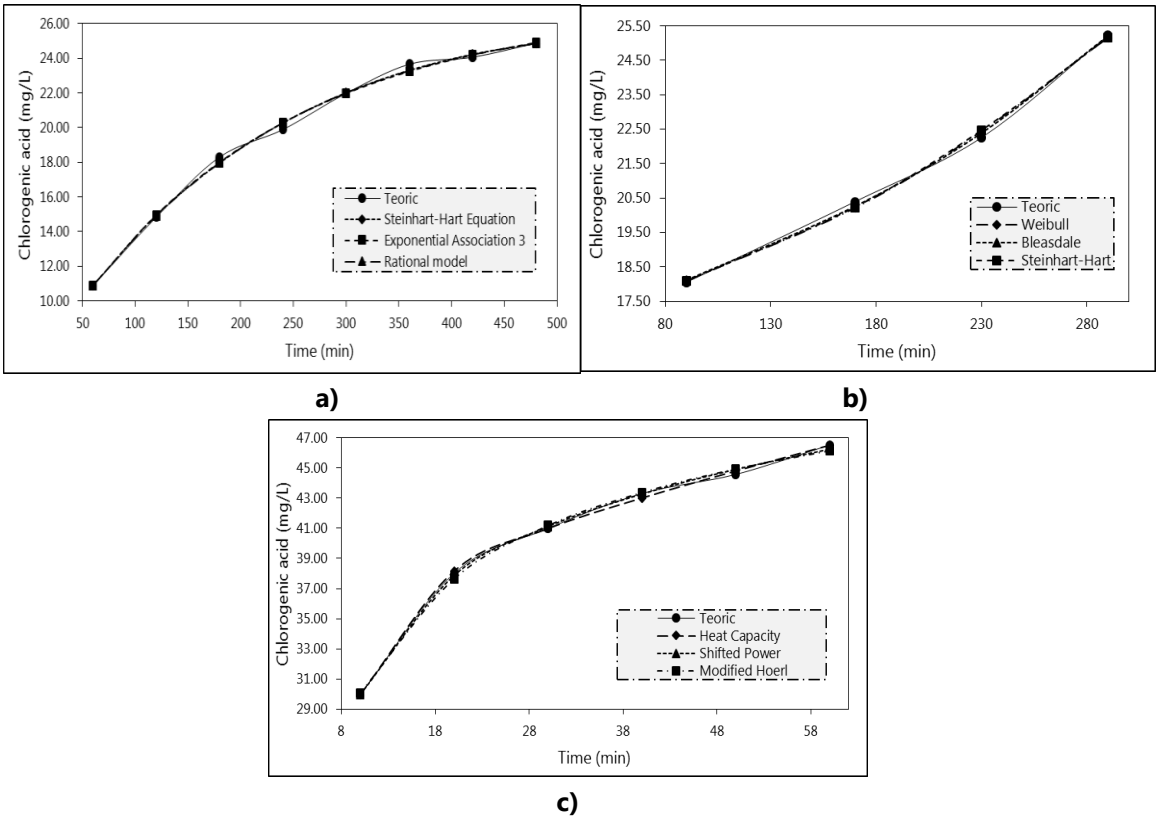


Figure 6.3. Model adjustment for the chlorogenic acid from SCG. (a) Solvent extraction, (b) Soxhlet extraction, (c) UAE.

Table 6.5. Parameters for mathematic models of chlorogenic acid from SCG.

Technology	Model	r^2	Parameters			
			a	b	c	d
Solvent	Steinhart-Hart Equation	0.9975	3.34.E-1	-6.80.E-2	5.38.E-4	
	Exponential Association 3	0.9974	2.16.E+1	1.25	4.86.E-3	
	Rational Model	0.9974	5.61	1.12.E-1	2.13.E-3	1.59.E-6
Soxhlet	Weibull	0.9973	2.44.E+2	2.27.E+2	1.33.E-6	1.80
	Bleasdale	0.9986	1.13.E-2	-1.97.E-5	1.61	
	Steinhart-Hart Equation	0.9972	-1.37.E-2	2.54.E-2	-4.96.E-4	
UAE	Heat Capacity	0.9990	3.72.E+1	1.60.E-1	-8.82.E+2	
	Shifted Power	0.9987	2.68.E+1	7.76	1.38.E-1	
	Modified Hoerl	0.9974	3.46.E+1	3.54.E-2	8.42.E-2	

6.2.3. Ferulic acid

For this compound the technology that provides a more efficient extraction in terms of yields is Soxhlet extraction. With this technology a concentration of up to 11.42 mg/L can be obtained. While with solvent extraction and UAE are achieved concentrations of 8.49 and 10.85 mg/L, respectively (see **Figure 6.4**). In the **Table 6.6** the mathematical model used for the adjustment in each of the technologies is presented. For the case of solvent extraction, the Vapor Pressure, Modified Hoerl and Gompertz Relation models are presented. In the Soxhlet extraction the models analyzed are those of Weibull, Rational Model and Harmonic Decline. Finally, for UAE, the Exponential Decline, Farazdaghi-Harris and Steinhart-Hart models are presented.

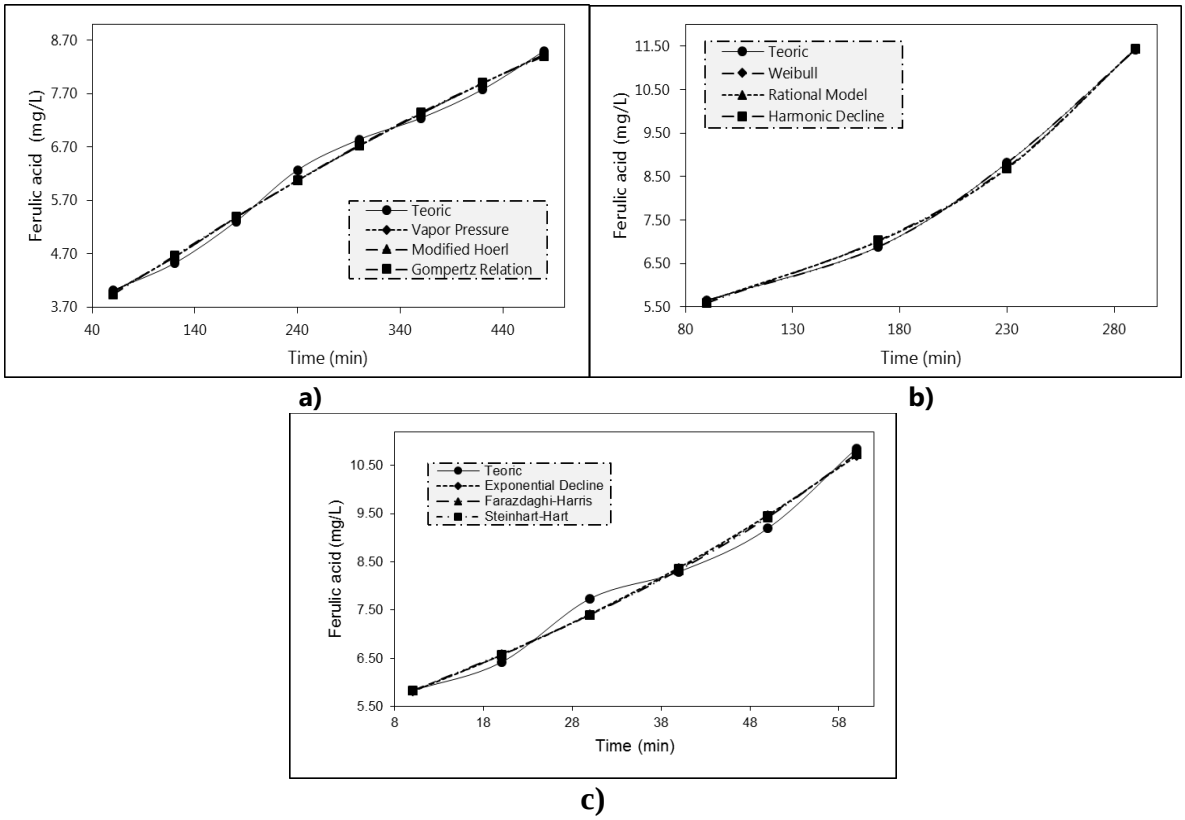


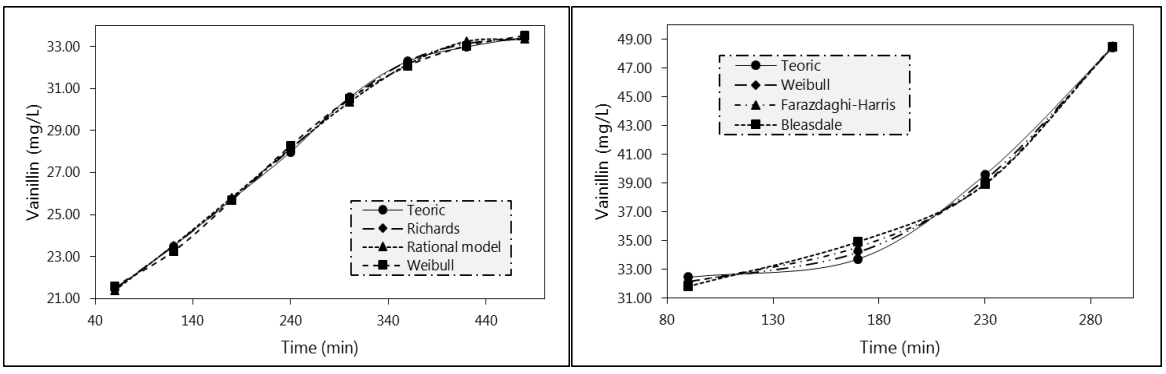
Figure 6.4. Adjustment of models for the extraction of ferulic acid from SCG: a) Solvent extraction, b) Soxhlet extraction, c) UAE**.**

Table 6.6. Parameters for mathematic models of ferulic acid from SCG.

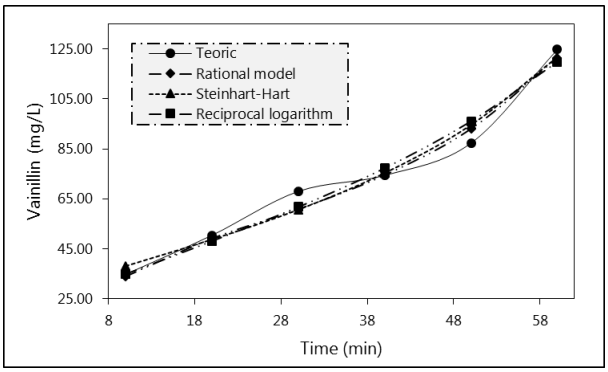
Technology	Model	r^2	Parameters				
			q_0	a	b	c	d
Solvent	Vapor Pressure Model	0.99444		-1.36	2.79E+1	5.57E-1	
	Modified Hoerl	0.99444		2.56E-1	1.31E+12	5.57E-1	
	Gompertz Relation	0.99444		1.17E+1	2.56E-1	2.84E-3	
Soxhlet	Weibull model	0.999900		1.85E+1	1.30E+1	1.45E-8	3.10
	Rational model	0.998212		9.35E+3	4.15E+3	9.31E+2	1.95
	Harmonic Decline	0.998212	4.55	-4.81E+2			
UAE	Exponential Decline	0.986251	5.14	-8.20E+1			
	Farazdaghi-Harris	0.987763		2.03E-1	-6.53E-3	6.91E-1	
	Steinhart-Hart Equation	0.987182		1.79E-1	5.07E-3	-1.55E-3	

6.2.4. Vanillin

Among the polyphenolic compounds, vanillin was found which can be observed in **Figure 6.5** with the selected predictive models. For solvent extraction the best fit was with Richards Model with a correlation coefficient of 0.9996. While for the Soxhlet extraction, Weibull model presented a value of 0.9972. From UAE, vanillin showed a concentration at the end of the extraction process of 124.78 mg/L. Where over time it showed a behavior with adjustment to the mathematical models of Rational model (r^2 = 0.9818), Steinhart-Hart (r^2 = 0.9733) and Reciprocal logarithm (r^2 = 0.9684). The values of the parameters found by the selected models are shown in **Table 6.7**.



a) **b)**



c)

Figure 6.5. Adjustment of models for vanillin extraction from SCG: a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 6.7. Parameters for mathematic models of vanillin from SCG.

Technology	Model	r^2	Parameters			
			a	b	c	d
Solvent	Richards model		3.34E+1	9.30	2.64E-2	1.74E+1
	Rational Model		1.94E+1	-1.15E-2	-2.18E-3	2.02E-6
	Weibull Model		3.38E+1	1.28E+1	6.80E-6	2.14
Soxhlet	Weibull model	0,9972	7.25E+1	4.05E+1	2.65E-11	4.18
	Farazdaghi -Harris	0,9924	3.17E-2	-3.92E-9	2.62	
	Bleasdale	0,9856	2.77E-7	-8.49E-10		
UAE	Rational Model	0.9818	-2.24E+7	6.30E+6	1.33E+5	-1.41E+3
	Steinhart-Hart Equation	0.9733	3.88E-2	-4.55E-3	-1.74E-4	
	Reciprocal logarithm	0.9684	5.46E-2	-1.13E-2		

6.2.5. Quercetin

Another polyphenolic compound observed during the extraction processes was quercetin. This compound obtained a yield of 0.01 and 0.02 mg/g with solvent extraction and Soxhlet using 60% ethanol, respectively. The content accumulated over time is presented in **Figure 6.6**. In addition to the selected mathematical models: Ratkowsky Model, Gaussiano Model and Richards for solvent extraction and Weibull and DR-Hill for Soxhlet extraction. Finally, using UAE a concentration of quercetin of 1.06 mg/L was achieved; in which the behavior of quercetin shown in **Figure 6.6** presented as the best adjustments the models of Heat

Capacity, Shifted Power and Rational Model. For each of these models, the equation parameters and correlation values shown in **Table 6.8** were obtained.

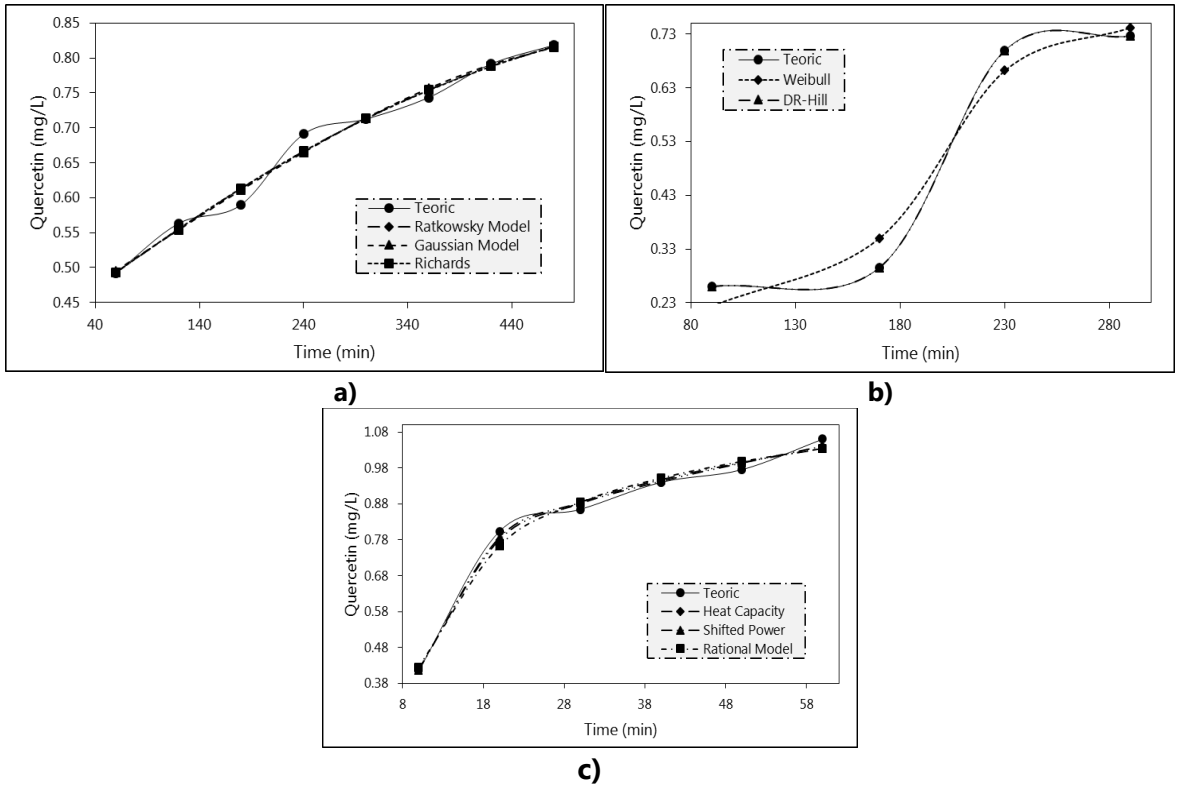


Figure 6.6. Adjustment of models for the extraction of quercetin from SCG: a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 6.8. Parameters of mathematics models of quercetin from SCG.

Technology	Model	r^2	Parameters			
			a	b	c	d
Solvent	Ratkowsky Model	0.9857	9.20E-1	1.32E-1	4.58E-3	
	Gaussian Model	0.9851	8.32E-1	5.86E+2	5.16E+2	
	Richards model	0.9857	9.31E-1	-2.86E-1	4.23E-3	7.21E-1
Soxhlet	Weibull Model	0.9688	7.43E-1	5.22E-1	3.41E-15	6.24
	DR-Hill	0.9999	2.60E-1[a]	4.67E-1[b]	1.75E+1[c]	1.96E+2[d]
UAE	Heat Capacity	0.9929	8.04E-1	4.15E-3	-4.27E+1	
	Shifted Power	0.9929	5.25E-1	9.74	1.73E-1	
	Rational Model	0.9864	-3.79E+6	6.25E+5	5.83E+5	-6.88E+2

[a]alpha, [b]tetha, [c]eta, [d]kappa

6.3. Biorefinery from spent coffee grounds

Whit the aim to use the compounds present in the SCG were performed simulations in the Aspen Plus software. Where the physicochemical composition shown in the **Table 6.1** was taken as a basis for the selection of the products. For this, the level of complexity was increased, proposing four scenarios (see **Table 6.9**). Antioxidants, ethanol, xylitol and energy cogeneration were proposed as products. Where the obtaining of antioxidants was carried out through of supercritical fluids extraction (using the performance shown in **Table 6.2**) to 200 bars. While the cogeneration of energy was made from the gasification technology.

Table 6.9. Schemes for obtaining products from SCG.

Scenarios	Products
Scenario 1	Antioxidants
Scenario 2	Antioxidantes + ethanol
Scenario 3	Antioxidants + ethanol + xylitol
Scenario 4	Antioxidants + ethanol+ xylitol + cogeneration of energy

In **Figure 6.7** shows the block diagram of the stage 4 (greater complexity of this analysis). Finally, each scenario was evaluated energy, economically and environmentally. In addition, it was made a variation in the costs of raw materials and products. The latter to analyze the influence of these prices on the net present value of each scenario.

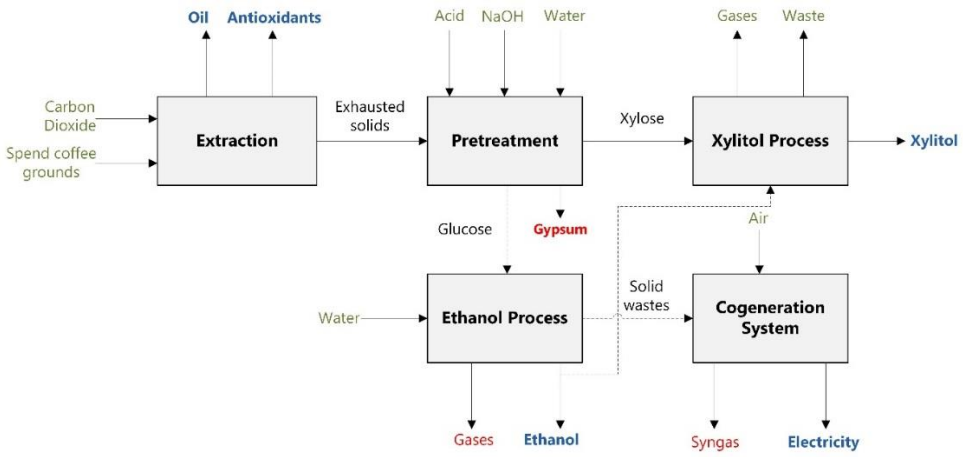


Figure 6.7. Scheme of biorefinery from SCG.

As results were obtained the yields present in the **Table 6.10**. These results show a high potential for SCG to obtain value-added products. From these values we can observe a high yield of syngas, product obtained in the energy cogeneration process. This yield (0.803 kg/kg SCG) in addition to being high for the composition of lignin, is also due to the ratio of air used in the feed of the gasifier. On the other hand, the yields of ethanol and xylitol are shown in the **Table 6.10**, products obtained from glucose and xylose.

Table 6.10. Yields of product from SCG.

Product	Yield
Antioxidants	0.013*
Xylose	0.202*
Glucose	0.216*
Ethanol	0.110**
Xylitol	0.119*
Syngas	0.803*
Electricity	0.125***

* kg product per kg raw material, ** L product per kg raw material and *** KW per kg raw material.

Energetic analysis

In this analysis, two points of view were considered. In first place, an energetic and exergetic evaluation were carried out step by step and in second place, all the steps were considered at the same time. The steps considered in the present work were selected according to obtaining a value-added product or in the case of an intermediary for a subsequent step. Based on the above, **Table 6.11** presents the five steps of the process considered and the corresponding energy and exergy values, as well as this table present the overall energy consumption and exergy of the process.

Table 6.11. Energy and exergy for a biorefinery from SCG.

Process step	Energy		Exergy	
	kW	Percent	kW	Percent
Extraction	110.61	0.38	52.34	0.85
Sugars	15,939.23	54.72	1,823.54	29.73
Ethanol	3,056.75	10.49	848.08	13.83
Xylitol	8,382.55	28.78	1,638.69	26.72
Cogeneration	1,639.00	5.63	1,770.56	28.87
Global	29,128.14	100.00	6,133.21	100.00

The energy consumption of a process is constituted by all the energy necessary to carry out the different transformations in which a change in temperature or pressure was required. The greatest contribution to energy consumption in many processes is through temperature changes. In order to be able to change the temperature of a fluid, it is necessary to supply or remove energy (depending on the case, heating or cooling) through the use of utilities such as steam or cooling water. When a process employs pressures different to atmospheric pressure, the energy in the form of power is used to carry out the pressure change represents a percentage to be considered in an energy balance. This is case of process steps such as extraction and cogeneration, which energy in the form of power represents 25.28% and 8.11% of the total energy of each step, respectively. Steps such as the obtaining of sugars, ethanol, xylitol and cogeneration, have higher percentages of energy used in cooling processes (51.49, 63.68, 53.20 and 53.03% of the total of each step, respectively). These values can be explained due to in these stages temperatures are used above the ambient and subsequently it is required to decrease the temperature to continue with the process. For the extraction step the percentage of energy required for cooling (21.92% of total energy required for this step) was lower than the heating step (52.80% of total energy required for this step) due to the energy required for the solvent (CO_2) to get to the extraction temperature (50°C). On the other hand, given the pressure at which the extraction was carried out, it was possible to use moderate temperatures. In total, a total of 104,777.47 KJ per kg of raw material was required for the use of SCG as raw material under the biorefinery concept through which the products presented in the methodology section are obtained.

This energy comprises both energy in the form of power and energy supplied in the form of utilities (steam and water) for heating and cooling processes.

For the exergy a global value of 6,133.21 kW (1.71E-3 kJ/kg) was presented for the proposed biorefinery. This value is given by the difference between the raw material exergy (SCG) and the output streams and the increase or decrease of the process exergy. Given the characteristics and operating conditions of the extraction step, this is the only stage of the process in which exergy is being generated. However, due to the design of the process this exergy was not exploited in subsequent steps. On the other hand, steps such as obtaining sugars, ethanol, xylitol and cogeneration, showed a decrease in exergy. Where the sugar stage showed the greatest decrease due to prolonged operating time and significantly higher temperatures than the standard. The decrease of exergy in the other steps was caused by the irreversibilities of the processes used in this work. For the extraction, sugar production, ethanol, xylitol and cogeneration steps, a percentage distribution of the exergy of 0.85, 29.73, 13.83, 26.72 and 28.87% was presented, respectively. Then, it is possible to identify that the zones in which the greatest irreversibilities are present including sugar production and cogeneration. While processes such as component extraction do not present significant changes in the balance of exergy. In thi sense, the exergy of the products did not present great differences with respect to the products and the energy used in the process.

Economic analysis

The increased complexity of a biorefinery is an attractive alternative for reducing production costs. However, it is not always an effective proposal, since it depends to a large extent on the performance of the products obtained, the energy consumption and the reagents required for its production. For this reason, four scenarios were proposed in which an increase in the level of products obtained was carried out, resulting in the production cost of each of these in the **Table 6.12**. The total costs of production were lower in scenario 4

with 0.65 USD/kg. This last due to the addition of a high yield product such as syngas. Since this product does not require a complex process for its production.

Table 6.12. Costs of obtaining value-added products from SCG.

Item	Scenario 1		Scenario 2		Scenario 3		Scenario 4	
	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)
Raw materials cost	0.74	54.24	1.34	43.94	0.63	32.04	0.19	29.35
Utilities cost	0.02	1.26	0.88	28.88	0.61	31.08	0.19	28.81
Operating labor cost	0.04	2.73	0.03	0.91	0.02	0.99	0.01	1.00
Plant overhead	0.04	2.59	0.02	0.80	0.02	0.79	0.01	0.84
Operating charges	0.01	0.68	0.01	0.23	4.87E-3	0.25	1.6E-3	0.25
Maintenance cost	0.03	2.46	0.02	0.69	0.01	0.59	4.38E-3	0.67
General and administrative cost	0.07	5.12	0.18	6.04	0.10	5.26	0.03	4.87
Depreciation expense	0.42	30.91	0.57	18.52	0.57	28.99	0.22	34.19
Total	1.36	100	3.05	100	1.96	100	0.65	100

The Net Present Value (NPV) was evaluated in each of the scenarios over a period of 10 years. As a result, the behavior of each of the scenarios was obtained in **Figure 6.8**. The best recovery of the investment was obtained in scenario 3 and 4 after one year. While scenario 1 showed a recovery at three years. However, of all the scenarios evaluated, scenario 2 presented only losses over the years evaluated. This due to the low yield in the obtaining of ethanol and the high energy consumption required by the distillation towers for their separation and purification.

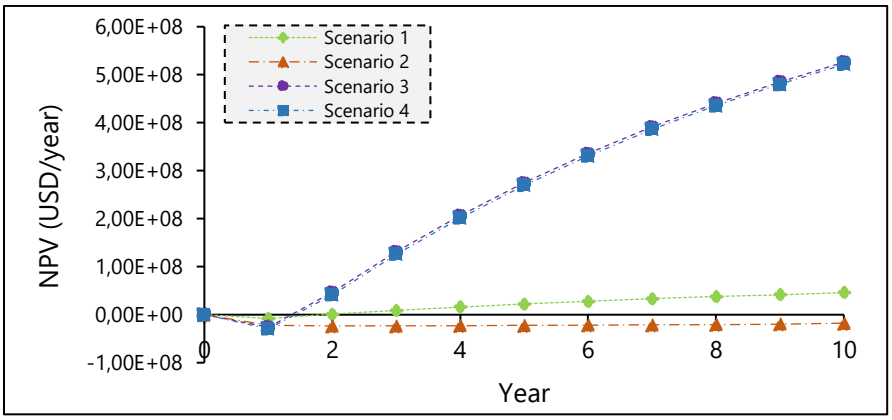
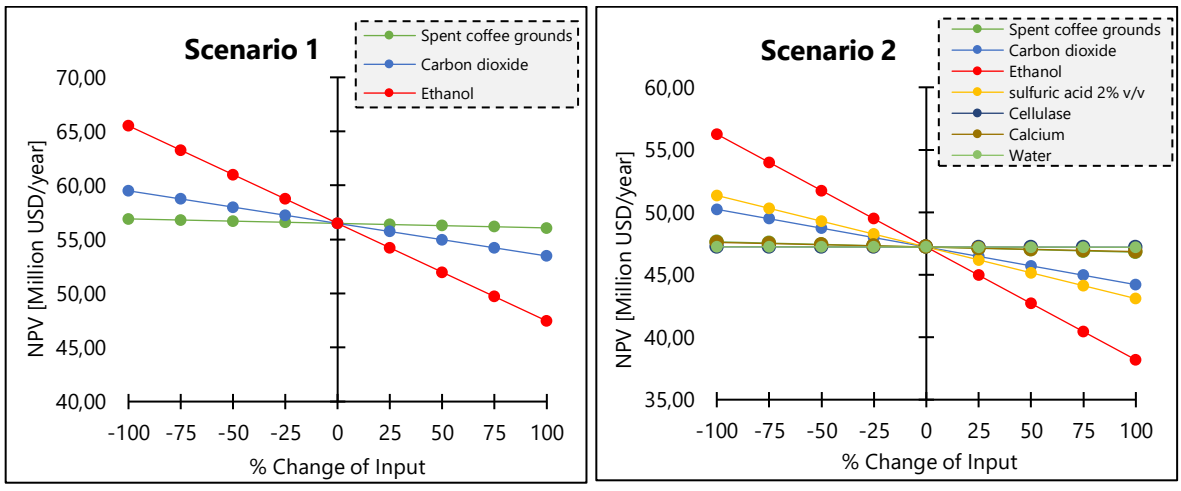


Figure 6.8. Net present value of processes from SCG.

To each of the proposed scenarios, a sensitivity analysis was carried out on the cost of acquisition of the raw materials and cost of sale of the products. In the variation of raw material costs (**Figure 6.9**) it was observed that in all scenarios ethanol was the one that had the greatest influence in the NPV. This is mainly due to its requirement in the SFE process. However, it should be noted that this technology uses a lower amount of solvent compared to the conventional technologies used. On the other hand, the SCG did not show a significant variation in these processes, showing the advantages of the use of an agroindustrial waste. While in the costs of calcium, cellulase, sulfuric acid and carbon dioxide there is a small influence on the recovery of the investment. The latter due to the low volume required and the purchase price. Additionally, this analysis showed that each of the proposed scenarios are profitable, even when the cost of raw materials is increased to 100%.



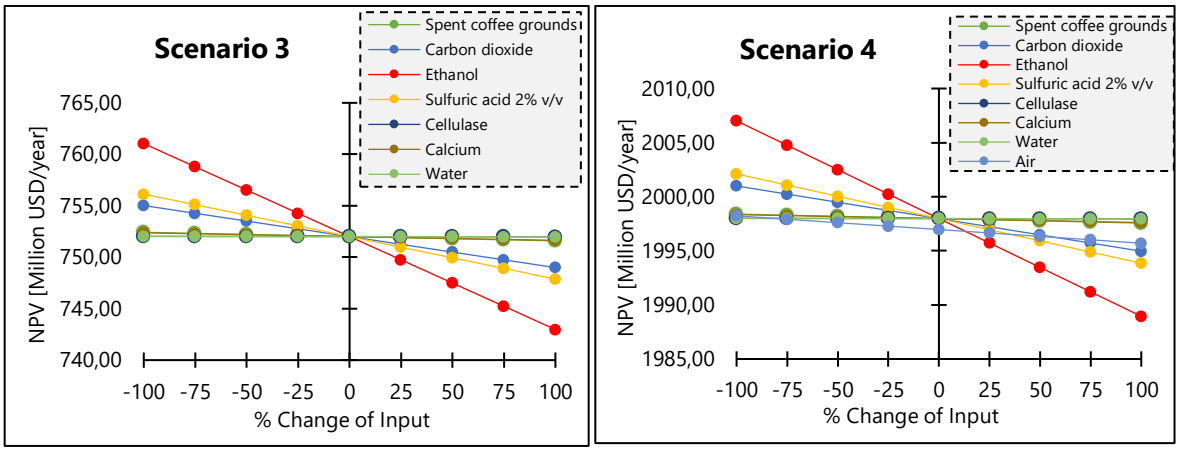
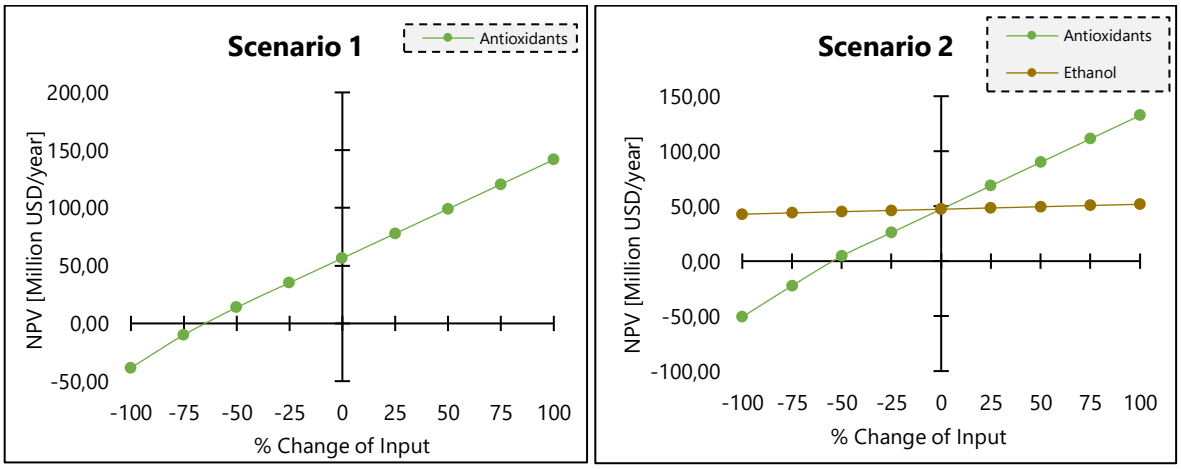


Figure 6.9. Influence of the cost of raw materials in the NPV from scenarios from SCG.

The variation in the cost of the products showed a greater influence in the NPV, in comparison with the costs of raw materials as shown in the **Figure 6.10**. In the case of scenarios 1 and 2, there is no recovery of investment when the costs of antioxidants decrease by 50%. While in the other scenarios it does not present affectation due to its low performance compared to other products. As for scenario 3, xylitol causes the greatest impact in the analysis, even if its value is reduced by 100%, it does not have a negative impact on the process. Finally, scenario 4, when presenting a great variety of products, does not affect the process. However, syngas and xylitol present the greatest variations in the NPV, due to their high selling costs in the market. This analysis shows that these products have a high pre-feasibility in the development at industrial level.



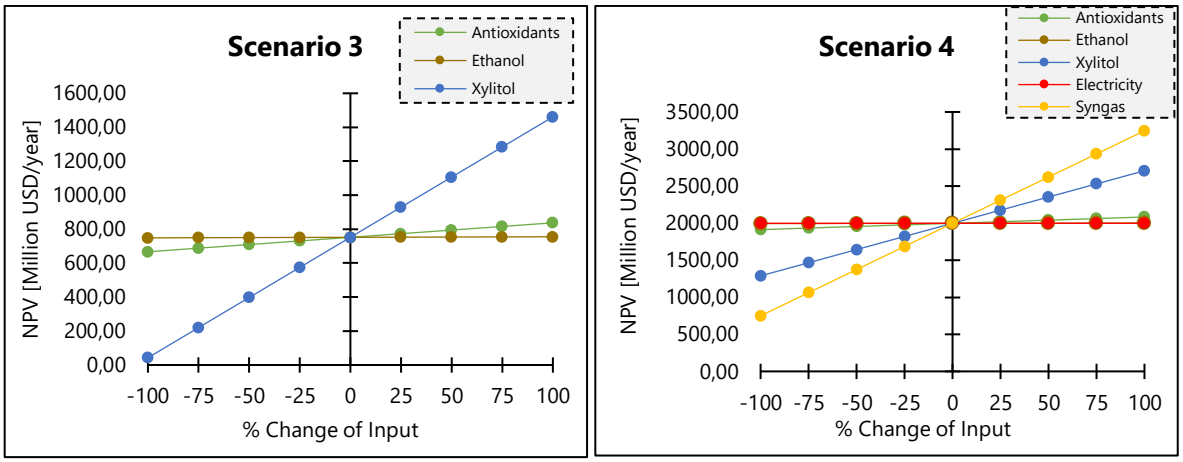


Figure 6.10. Influence of the cost of products in the NPV from scenarios from SCG.

Environmental analysis

The selection of the products to be obtained in a biorefinery is an influential factor especially in the environmental impact. Where, through the Environmental Impact Potential defined as the effect that a chemical would have on the environment if it is emitted, it is obtained by means of a compatibility analysis in the production area; that is, in the product life cycle through a door-to-door analysis. Thus, in scenario 4 that considers the production of energy presents a higher environmental impact to the other scenario due to the pollution produced by the release of synthesis gas without any suitable treatment, or if necessary be used to obtain other value-added products. Additionally, environmental impact categories such as HTPE, PCOP showed a decrease in all the scenarios evaluated, with their lowest values in scenario 2 and 3. While in the HTPI and TTP categories scenario 4 presented an increase in the potential for environmental impact. On the other hand, the scenarios evaluated had no impact on the ODP, but showed their greatest effect on the acidity potential (AP), due to the gases released into the atmosphere.

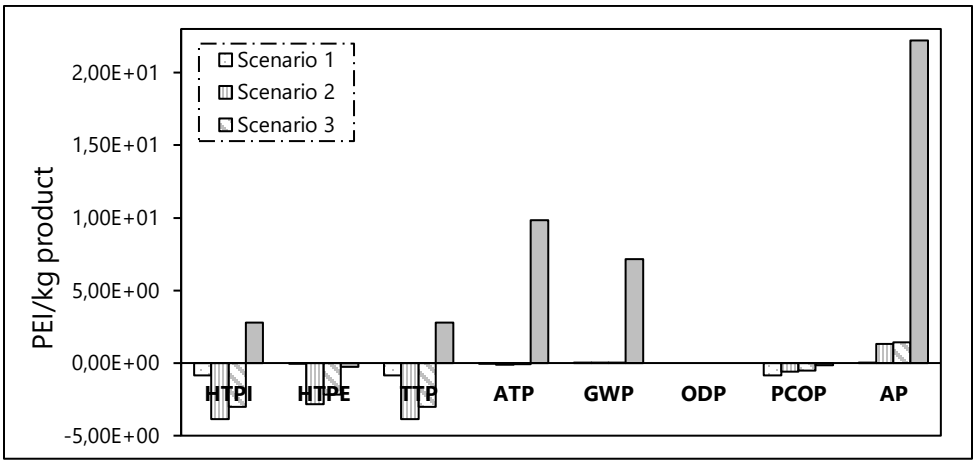


Figure 6.11. Potential environmental impact of products from SCG.

7.4. Conclusions

After analyzing the different variables proposed for obtaining polyphenolic compounds was obtained that in conventional technologies, Soxhlet extraction presents the best yields over the solvent extraction method, with shorter operating times. However, one of the disadvantages may lie in the use of a greater amount of solvent, making it a more expensive process and causing greater environmental damage. For this reason, solvent extraction is the most used and studied in conventional methods.

The operating conditions in the polyphenolic compounds extraction showed that through ultrasound assisted extraction, a higher yield was presented at 50°C and with 60% ethanol as a solvent. In addition, it proved to be a technology with high potential, requiring less operating time than traditional methods, and increasing selectivity in the process. On the other hand, the use of agroindustrial waste is an industrially promising option since it would add value during the processes and would present better use and less environmental pollution.

The use of computational tools for the development of pre-feasibility analysis showed a positive analysis from SCG as a raw material. With an increase of the NPV in the majority of the cases when increasing the level of complexity. This is due to the greater use of the raw

materials of the process and the performance of each product. On the other hand, the environmental analysis showed an opposite behavior, where when requiring less reagents, there was a lower potential environmental impact.

7. COFFEE CUT-STEMS

The coffee cut-stems (CCS) market a waste that has not been studied to obtain antioxidants. For this reason, the objective of this chapter in its first part was to demonstrate the potential of this waste in polyphenol compounds extraction processes. Additionally, various extraction technologies were used. Where to each of the technologies (solvent extraction, Soxhlet extraction, UAE and SFE) were analyzed different operating conditions (solvent, temperature or pressure). The second objective was to obtain the extraccion kinetics of different polyphenolic compounds. This kinetic was obtained from the best operating conditions previously found. Where this kinetic obtained through adjustments of mathematical models is very useful for modeling and scaling in industrial processes. The third objective was to carry out the energy, economic and environmental analysis of various products based on CCS. To carry this out, simulations were developed based on the concept of increasing complexity (adding products). This objective was to show the prefeasibility of the use of coffee cut-stems to obtain value-added products.

7.1. Experimental results

The experimental methodology for obtaining polyphenolic compounds from coffee cut-stems is shown in **Figure 7.1**. Initially in the pre-treatment stage, the use of CCS as a raw material required a wash to eliminate the remains of dirt and impurities. Then it was cut into 0.5 cm wide rings and dried in an oven at 45°C. It was then reduced in size by grinding. Finally, the sample is taken to 20 to 80 mesh vibrating screens (J. Dávila 2015), using for experiments only those with a particle diameter of 2 mm (40 mesh). The physicochemical characterization of the CCS was carried out as a second stage. While in the third stage was carried out the processes of extraction through four technologies. To each of these was

made a variation of operating conditions, whether solvente, temperature or pressure. The extracts stored at -4°C and in amber bottles were analyzed for the determination of polyphenolic compounds. For this, the method of determination of antioxidant activity (DPPH method), total polyphenolic compounds (Folin-Ciocalteu method) and HPLC were used.

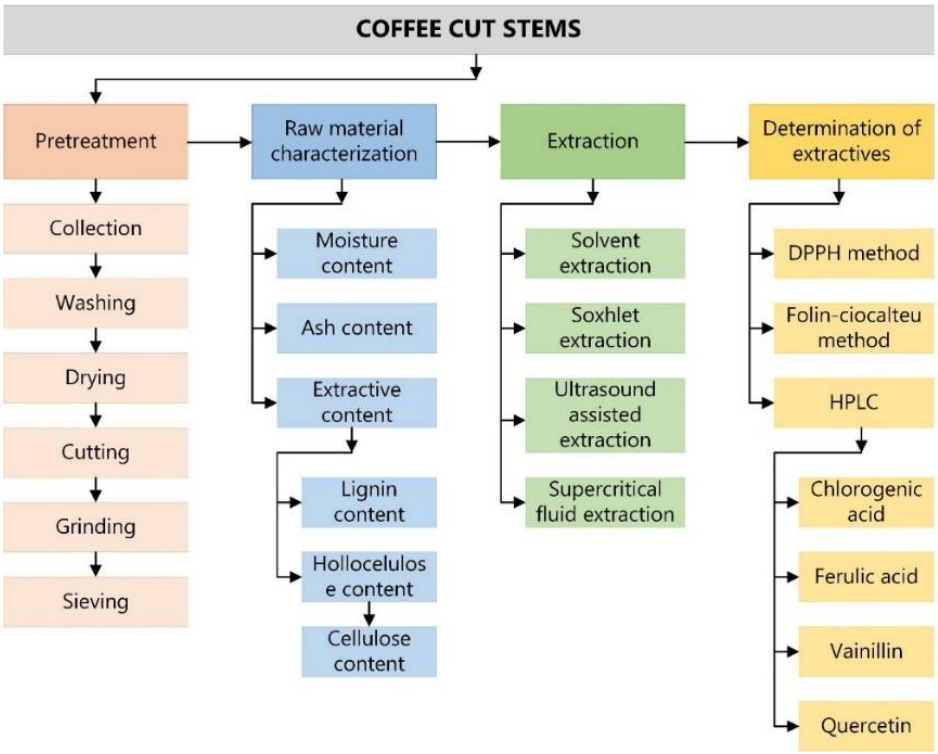


Figure 7.1. Experimental diagram from coffee cut-stems.

Table 7.1 shows the coffee cut-stems characterization on a dry basis for each of the evaluated components (extractive, cellulose, hemicellulose, lignin and ash). Cellulose (hexoses) and hemicellulose (pentoses) representing 49.46 and 16.75%, respectively. From these sugars can be obtained through of pretreatments such as acid hydrolysis, alkaline, among others. In addition, in the case of cellulose, an enzymatic saccharification stage is added (Y. H. P. Zhang 2008). These obtained sugars can be used for the production of xylitol, ethanol, furfural, butanol, lactic acid, PHB, among others (Y. H. P. Zhang 2008; Quintero, Moncada, and Cardona 2013b; Min et al. 2011; Hung et al. 2015). Lignin covered a relatively high percentage (26.28%), which makes it a profitable raw material for use in energy

generation processes such as gasification, direct combustion, pyrolysis and synthetic vanillin production processes (Abdullah and Sulaiman 2013; Walton, Mayer, and Narbad 2003). The percentage of extractives corresponding to 6.37% makes it a relatively promising raw material for obtaining polyphenolic compounds. The results of the physicochemical characterization of the coffee zone, presented results similar to those reported by Aristizabal, Gómez and Cardona (2015) in cellulose and ash (Aristizábal M., Gómez P., and Cardona A. 2015b). While in the composition reported by Triana et al (2011) presented a high variation in each of the components evaluated, with a very low content of extracts (1.62%) (Triana et al. 2011). These differences in composition may be due to the origin of the coffee cut-stems in each of the studies.

Table 7.1. Physicochemical composition of coffee cut-stems.

Components	This work	Reference (Aristizábal M., Gómez P., and Cardona A. 2015b)	Reference (Triana et al. 2011)
Extractives (%wt dry)	6.37 ± 0.21	14.18	1.62
Holocellulose (%wt dry)*	62.43 ± 0.31	74.4	44.34
Cellulose (%wt dry)	49.46 ± 0.28	40.39	31.06
Hemicellulose (%wt dry)	16.75 ± 0.59	34.01	13.28
Lignin (%wt dry)	26.28 ± 1.50	10.13	44.73
Ash (%wt dry)	1.14 ± 0.02	1.27	0.88

The determination of the concentration of total polyphenolic compounds was carried out by the Folin-Ciocalteu method, which detects the phenolic groups present in the extracts. The results of the TPC of the extraction from coffee cut-stems are presented in **Table 7.2**. In this analysis, the best yields were obtained from UAE. However, although the SFE did not present the best values, it is a technology that requires a low volume of solvent, which can make it a more profitable technology. On the other hand it was observed that non-conventional technologies can compete with conventional technologies which require more time for their development. In the UAE was possible to demonstrate that temperature is a variable with little influence in obtaining these compounds from coffee cut-stems, obtaining a range of

2.08 -2.86 mg GA/g at 25°C and 2.66 - 3.01 mg GA/g at 50°C. Additionally, it could be observed that from the three solvents used for the extractions, the ethanol 60% obtained the best concentrations (2.86 - 3.01 mg GA/g), followed by water (2.77 - 2.81 mg GA/g) and finally ethanol (2.08 - 2.66 mg GA/g). Therefore, it was determined that the lowest conditions obtained in this work for obtaining polyphenolic compounds from coffee cut-stems are using ethanol 60% and an extraction temperature of 50°C (3.01 ± 0.07 mg GA/g). In the case of SFE, it showed the highest concentration at 300 bars with 2.20 ± 0.01 mg GA/g. This result showed the behavior mentioned above in the solubility analysis.

The coffee cut-stems are a raw material that does not present studies in the production of polyphenolic compounds. For this reason, the results obtained were compared with other coffee residues and some wood residues. The CCS showed a lower concentration compared to other residues from coffee cultivation and processing using UAE. Where from SCG Al-Dhabi et al (2017) reported 6.20 mg GA/g at 40°C for 25 min (Al-Dhabi, Ponmurugan, and Maran Jeganathan 2017). While from coffee husk Andrade et al (2012) determined a TPC content of 61 mg GA/g with hexane and a solid-liquid ratio 1:30 (w/v) at room temperature for 2 hours (Andrade et al. 2012a). On the other hand, comparing the TPC obtained from the CCS extract with other wood residues, it was determined that this raw material also presents a low content of TPC. Where Ghitescu et al (2015) used spruce bark and ethanol 50%, in a solid-liquid ratio 1:10 (w/v), making temperature variations and extraction time, reporting TPC concentrations from 5.51 to 13.32 mg GA/g (Ghitescu et al. 2015); obtaining the best values at 60°C and 60 min. Other wood raw materials such as *Pinus radiata* bark presented 599 mg GA/g according to data reported by Aspé and Fernandez (2011) (Aspé and Fernández 2011). This demonstrate that the CCS present a low yield to obtain these value-added compounds.

The results of the analysis of the antioxidant activity are presented in **Table 7.2**. The conventional extractions showed the best yields with ethanol with 7.21 ± 0.23 and 8.25 ± 0.20 µg/mL for SE and Sox-E. Even so, the SFE showed the best of all the evaluated

technologies with a range of 8.38 - 9.48 µg/mL. This technology showed that it can compete with traditional technologies just by applying one hour of operation. On the other hand, the influence of both the temperature and the solvent used through of UAE could be evidenced. From these experimental results it was observed that a greater EC_{50} was present at 50°C with ethanol as a solvent (6.64 ± 0.18 µg/mL). While water and ethanol 60% were used, there was greater antioxidant activity at 25°C with 3.65 ± 0.12 µg/mL and 5.32 ± 0.23 µg/mL, respectively. On the other hand, the antioxidant activity of CCS extracts was relatively low, compared with other coffee residues. Where the spent coffee grounds can be presented according to data reported by Andrade et al (2012) of up to 787.63 µg/mL. While the coffee husk up to 235.1 µg/mL through of UAE with ethanol as solvent (Andrade et al. 2012a). This variation may additionally be due to Andrade et al (2012) used a higher solid-liquid ratio (1:30 w/v) and double the operating time to that of this study.

Table 7.2. Polyphenolic compounds content and antioxidant activity from the CCS extracts.

Technology	Solvent	TPC (mg/g)	DPPH EC_{50} (µg/mL)
SE	W	2.32 ± 0.02	5.28 ± 0.17
	EtOH 60%	2.43 ± 0.03	7.03 ± 0.27
	EtOH	2.17 ± 0.06	7.21 ± 0.23
Soxhlet	W	3.01 ± 0.03	6.52 ± 0.26
	EtOH 60%	3.12 ± 0.04	7.16 ± 0.19
	EtOH	2.81 ± 0.07	8.25 ± 0.20
UAE	W-25°C	2.77 ± 0.00	3.65 ± 0.12
	W-50°C	2.81 ± 0.00	3.03 ± 0.08
	ETOH 60%-25°C	2.86 ± 0.16	5.32 ± 0.23
	ETOH 60%-50°C	3.01 ± 0.07	5.02 ± 0.15
	EtOH-25°C	2.08 ± 0.01	6.21 ± 0.25
	EtOH-50°C	2.66 ± 0.12	6.64 ± 0.18
SFE	200 bar	2.01 ± 0.04	8.38 ± 0.27
	250 bar	2.14 ± 0.02	9.07 ± 0.24
	300 bar	2.20 ±0 .01	9.48 ± 0.31

In the quantification of polyphenolic compounds present in coffee cut-stems extracts through UAE, presence was obtained in most cases of ferulic acid, vanillin, quercetin and vanillic acid as seen in

Table 7.3. The chlorogenic acid was a compound that only showed presence when the UAE was performed with ethanol 60% and 50°C (0.01 ± 0.002 mg/g). While ferulic acid showed its highest composition with ethanol 60% (0.05 - 0.06 mg/g) and water (0.04 - 0.05 mg/g), with a minimum variation with the change in temperature. Quercetin was the compound with the highest concentration among those analyzed with up to 0.37 ± 0.03 mg/g with ethanol at 50°C. Another compound with a high presence was vanillin, which in the case of water and ethanol 60% did not present great variations. However, the same trend did not occur with ethanol, which showed a change from 0.11 to 0.17 for 25 and 50°C, respectively. Meanwhile caffeic acid and vanillinic acid showed similar concentrations in each of the variables analyzed, except when only ethanol was used.

These results demonstrated the presence of various polyphenol compounds from CCS. This raw material can compete in the market and does not affect food safety. Where in ferulic acid concentration has similar values with vegetables and fruits such as broccoli (0.04 mg/g), tomato (0.01 mg/g) and raspberry (0.02 mg / g) (Mattila and Hellström 2007; Periago et al. 2002; Häkkinen et al. 1999). In addition, quercetin has higher values than fruits such as blueberry (0.16 mg/g) and apple (0.12 mg/g) (Häkkinen et al. 1999; Sultana and Anwar 2008).

Table 7.3. Polyphenolic compounds content from CCS extracts.

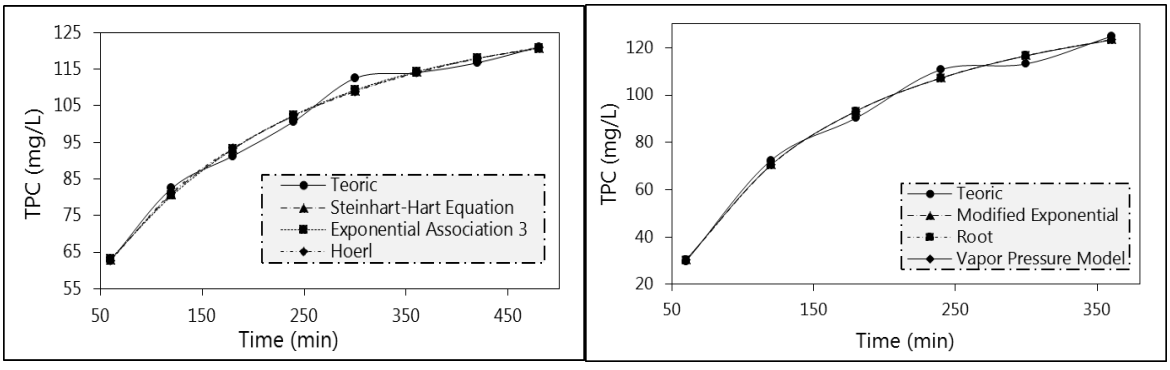
Technology		Chlorogenic acid (mg/g)	Ferulic acid (mg/g)	Vanillin (mg/g)	Quercetin (mg/g)	Vanillic acid (mg/g)	Caffeic acid (mg/g)
SE	W	NR	0.02±0.00	0.12±0.02	0.08±0.01	NR	NR
	EtOH 60%	NR	0.04±0.00	0.14±0.01	0.32±0.01	0.02±0.00	0.01±0.00
	EtOH	NR	0.01±0.00	0.11±0.01	0.30±0.02	0.01±0.00	NR
Soxhlet	W	0.01±0.00	0.06±0.00	0.22±0.01	0.15±0.02	0.02±0.00	0.02±0.00
	EtOH 60%	0.02±0.00	0.08±0.01	0.25±0.02	0.41±0.02	0.09±0.01	0.05±0.00
	EtOH	NR	0.03±0.01	0.20±0.02	0.37±0.02	0.03±0.00	0.02±0.00
UAE	W-25°C	NR	0.05±0.00	0.20±0.00	0.10±0.01	0.02±0.00	0.01
	W-50°C	NR	0.04±0.00	0.19±0.02	0.21±0.02	0.01±0.00	NR
	ETOH 60%-25°C	NR	0.05±0.00	0.21±0.01	0.35±0.05	0.01±0.00	0.02±0.00
	ETOH 60%-50°C	0.01±0.00	0.06±0.00	0.21±0.01	0.34±0.03	0.03±0.00	0.01±0.00
	EtOH-25°C	NR	0.01±0.00	0.11±0.01	0.28±0.03	NR	NR
	EtOH-50°C	NR	0.02±0.00	0.17±0.01	0.37±0.03	0.01±0.00	NR
SFE	200 bar	0.01±0.00	0.01±0.01	0.11±0.02	0.21±0.01	0.05±0.00	NR
	250 bar	0.01±0.00	0.02±0.01	0.09±0.01	0.22±0.01	0.02±0.00	NR
	300 bar	0.02±0.00	0.02±0.01	0.08±0.01	0.25±0.03	NR	0.03±0.00

7.2. Extraction kinetics for coffee cut-stems extracts

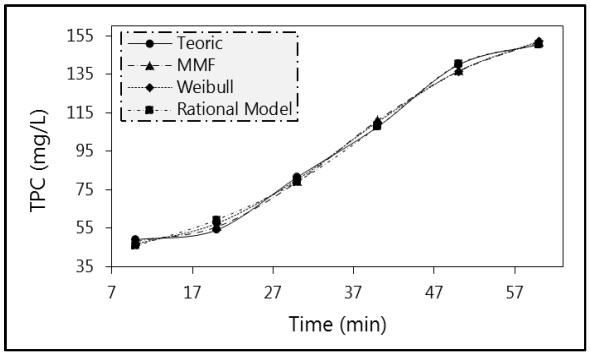
The kinetics of a process has great importance in the prediction of the results and processes of simulation. Where the latter can be used for the study of the technical, environmental and economic feasibility of the study process. To obtain a kinetic model should be used experimental data which can be adjusted both to existing kinetic models such as mathematical models. This work presents experimental data adjustment to different mathematical models. Used data correspond to data scale laboratory in processes of polyphenolic compounds extraction from coffee cut-stems through solvent extraction, Soxhlet extraction and UAE.

7.2.1. Total phenolic compounds

In order to compare the results obtained with UAE, was carried out a solvent extraction (SE) and Soxhlet extraction. When its compare the relationship time - concentration of TPC was obtained that the concentration obtained with SE at 60 min (62.64 mg GA/L) can be obtained around of 20 min with UAE. When UAE takes a time of 60 min of operation the concentration of TPC is 150.5 mg GA/L. The concentration to 480 min of SE presents significant differences with this value. With it at this time, it was possible to obtain a concentration of 121 mg GA/L. While with Soxhlet extraction was obtained at 6 hours 124.8 mg GA/L. In the **Figure 7.2** the extraction behavior is shown from the extraction of CCS. Also in the **Table 7.4** the parameters of mathematical adjustments obtained for each technology are presented.



a) b)



c)

Figure 7.2. Adjustment of models for TPC from SCG: a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 7.4. Parameters for mathematic models of TPC from CCS.

	Model	r^2	Parameters			
			a	b	c	d
SE	Steinhart-Hart Equation	0.9921	4.90E-2	-9.25E-3	6.96E-5	
	Exponential Association 3	0.9919	8.85E+1	1.45	5.17E-3	
	Hoerl	0.9919	1.15E+1	9.99E-1	4.21E-1	
Sox-E	Modified Exponential	0.9936	1.63 E+2	-1.01E+2		
	Root	0.9936	1.63E+2	1.82E-44		
	Vapor Pressure Model	0.9936	5.11	-1.01E+2	-1.87E-3	
UAE	MMF	0.9964	4.78E+1	1.78E+6	1.72E+2	3.91
	Weibull	0.9960	1.60E+2	1.15E+2	2.03E-5	2.88
	Rational Model	0.9954	3.69E+1	-2.71E-1	-2.81E-2	2.29E-4

8.2.2. Ferulic acid

The behavior of the ethanol 60% extractions of ferulic acid for UAE, SE and Soxhlet are shown in **Figure 7.3**. Where the parameters obtained from these for the extraction kinetics of each of the models are provided in the **Table 7.5**. Concentrations of ferulic acid obtained with solvent extraction at 60 and 480 min were 1.08 and 2.26 mg/L, respectively. In the case of Soxhlet extraction, there was an increase in ferulic acid concentration from 0.37 at 60 min to

3.2 mg/L at 360 min. While those obtained with ultrasound assisted extraction to 10 and 60 min corresponded to 1.33 and 3.42 mg/L, respectively.

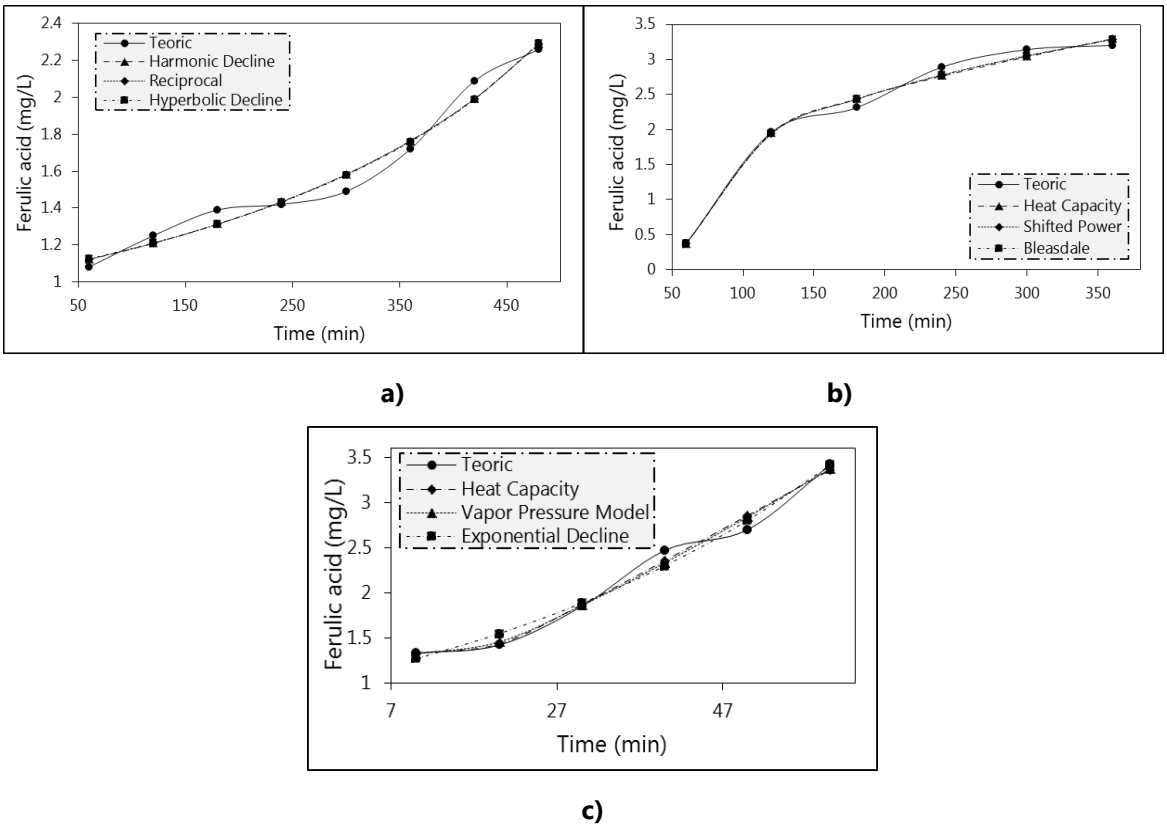


Figure 7.3. Adjustment of models for ferulic acid from CCS: a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 7.5. Parameters for mathematic models of ferulic acid from CCS.

	Model	r^2	Parameters				
			q_0	a	b	c	d
SE	Harminic Decline	0.9740		-8.83E+2			
	Reciprocal	0.9740		9.57E-1	1.08E-3		
	Hyperbolic Decline	0.9741		-9.15E+2	1.09		
Sox-E	Heat Capacity	0.9908		1.93	3.95E-3	-6.48E+3	
	Shifted Power	0.9925		5.02E-1	5.96E+1	3.29E-1	
	Bleasdale	0.9925		-7.37	1.24E-1	-3.04	
UAE	Heat Capacity	0.9875		2.67E-1	5.13E-2	5.49E+1	
	Vapor Pressure Model	0.9872		-4.02	1.50E+1	1.22	
	Exponential Decline	0.9711	1.04	-5.05E+1			

8.2.3. Vanillin

For vanillin presented significant differences between the data obtained from SE, Soxhlet and UAE (see **Figure 7.4**). With SE at 60 min was obtained a concentration of 3.54 mg/L. While UAE at 10 min concentration was 2.35 mg/L. At the end of the process with SE concentration was 7.05. Meanwhile when ends UAE, after 60 min, the concentration of vanillin was 10.54 mg/L. On the other hand, the Soxhlet extraction showed a concentration of up to 10.02 mg/L at 360 min. This value showed a small difference with respect to the UAE. As for the mathematical models used and the parameters are presented in the **Table 7.6**. For the SE, Heat Capacity, Rational and Hoerl models were used. In the Soxhlet extraction, the Heat Capacity, Shifted Power and Natural Logarithm models were used. While from the UAE the Gaussian, Hyperbolic Decline and Shifted Power models were used.

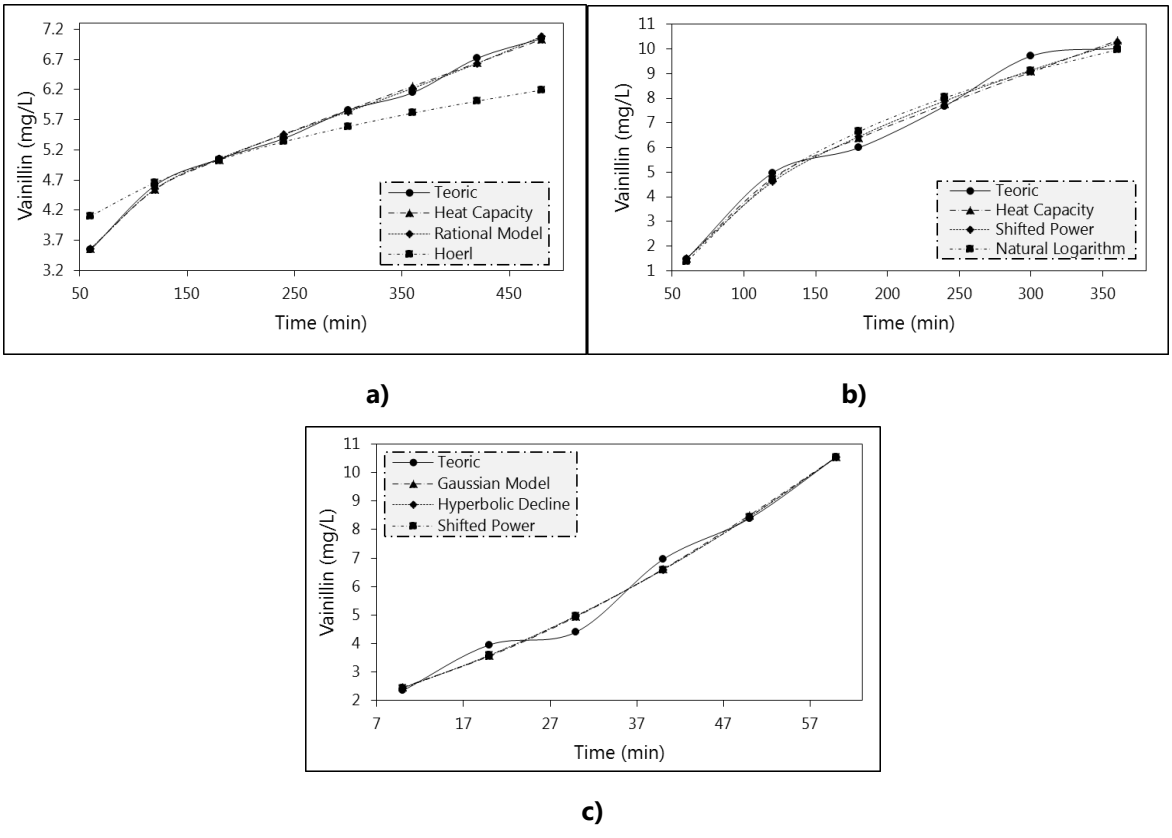


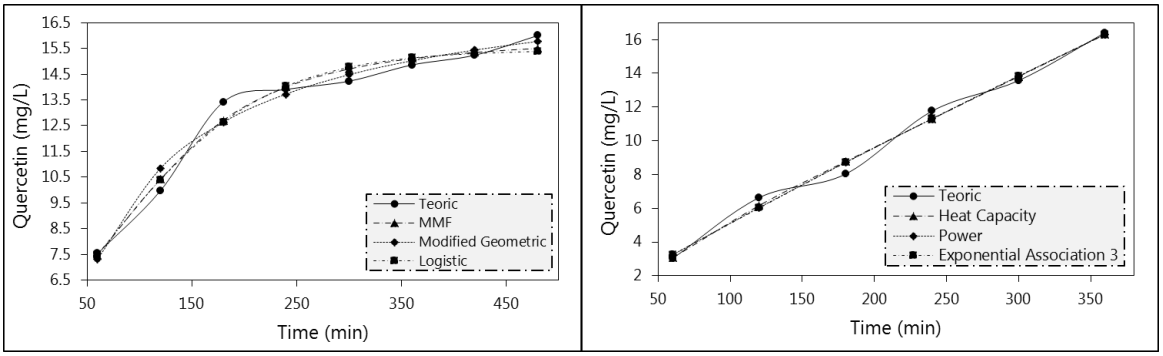
Figure 7.4. Adjustment of models for vanillin from CCG a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 7.6. Parameters for mathematic models of vanillin from CCS.

	Model	r^2	Parameters				
			q_0	a	b	c	d
SE	Heat Capacity	0.9971		3.97	6.39E-3	-2.89E+3	
	Rational Model	0.9976		-1.63E+6	8.80E+4	1.78E+4	-1.23E+1
	Hoerl	0.9914		1.28	1.00	2.51E-1	
Sox-E	Heat Capacity	0.9860		2.94	2.08E-2	-9.69E+3	
	Shifted Power	0.9859		4.98E-1	5.18E+1	5.27e-1	
	Natural Logarithm	0.9805		-1.83e+1	4.18		
UAE	Gaussian Model	0.9875		1.74E+1	1.12E+2	5.14E+1	
	Hyperbolic Decline	0.9874	1.52	-1.87E+1	-4.79E-1		
	Shifted Power	0.9874		7.21E-4	-3.91E+1	2.09	

8.2.4. Quercetin

For quercetin concentrations with SE at 60 and 480 min corresponded to a 7.54 and 16 mg/L, respectively. For this polyphenolic concentrations obtained from the use of the UAE were 2.51 mg/L to 10 min and 17.32 mg/L to 60 min. In the case of the Soxhlet extraction, up to 16.41 mg/L was obtained at 360 min. Comparing the results obtained from each method its can see the advantages of the UAE. Not only present higher concentrations of polyphenolic compounds, also the time of extraction decreases considerably. Each of these technologies presented the behavior shown in **Figure 7.5**. The kinetic parameters shown in the **Table 7.7** were obtained from these graphs.



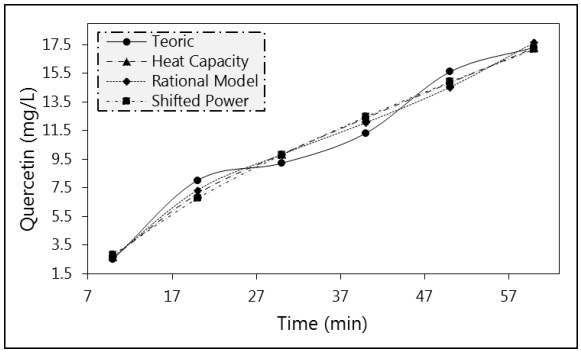


Figure 7.5. Adjustment of models for quercetin from CCG a) Solvent extraction, b) Soxhlet extraction, c) UAE.

Table 7.7. Parameters for mathematic models of quercetin from CCS.

	Model	r^2	Parameters			
			a	b	c	d
SE	MMF	0.9787	6.25	1.31E+5	1.59E+1	2.40
	Modified Geometric	0.9724	1.88E+1	-1.39e+1		
	Logistic	0.9738	1.55E+1	2.33	1.31E-2	
Sox-E	Heat Capacity	0.9914	1.42	4.14E-2	-2.98E+3	
	Power	0.9905	7.95E-2	9.04E-2		
	Exponential Association 3	0.9903	9.37E+1	1.00	5.18E-4	
UAE	Heat Capacity	0.9790	2.92	2.40E-1	-2.67E+2	
	Rational Model	0.9816	-1.49E+7	1.98E+6	2.04E+5	-1.77E+3
	Shifted Power	0.9816	1.09	6.06	6.91E-1	

8.3. Biorefinery from Coffee Cut-Stems

In biorefineries, the products that can be obtained from of the phisicochemical composition of CCS are biofuels, bioenergy, biomaterials, biomolecules, chemical products and food products (see **Table 7.8**) (Jonathan Moncada, El-Halwagi, and Cardona 2013). The lignocellulosic components of CCS allow some of these products to be extracted or obtained by biochemical, chemical, physical and thermochemical methods (Aristizábal M., Gómez P., and Cardona A. 2015a; García et al. 2017). By chemical or enzymatic pretreatments of CCS, it is possible to obtain fermentable C_5 and C_6 sugars, such as xylose and glucose, from hemicellulose and cellulose, respectively. The remaining component of the waste matrix

(lignin) can be used for the production of energy or syngas by a thermochemical system such as gasification, or it can be used together with polysaccharides to obtain polyphenolic compounds.

Table 7.8. Schemes for obtaining products from CCS.

Scenarios	Products
Scenario 1	Antioxidants
Scenario 2	Antioxidants + glucose + xylose
Scenario 3	Antioxidants + ethanol + xylose
Scenario 4	Antioxidants + ethanol + furfural
Scenario 5	Antioxidants + ethanol + furfural + syngas+ electricity

Based on the above, 5 scenarios were proposed as shown in the **Table 7.8**. Where, to these schemes was carried out a pre-feasibility analysis (energy, economically and environmentally). In the **Figure 7.6**, the scheme of scenario 5 is shown, which covers the largest number of products obtained in this work.

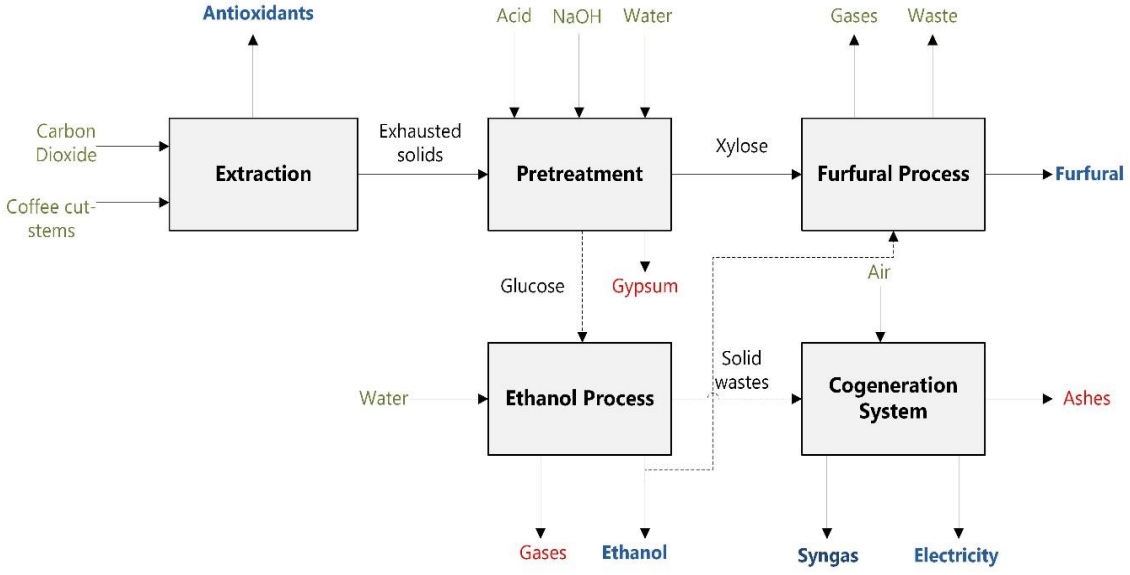


Figure 7.6. Scheme of biorefinery from CCS.

As a result of the simulations the yields shown in **Table 7.9** were obtained. These showed a high yield of syngas and glucose (from which ethanol was obtained). From these it was demonstrated that the coffee market is a raw material with high potential for obtaining these products. While the antioxidants presented a very low yield.

Table 7.9. Yields of products from CCS.

Product	Yield
Antioxidants	0.002*
Xylose	0.121*
Glucose	0.476*
Ethanol	0.242**
Furfural	0.060**
Syngas	0.952*
Electricity	0.148***

* kg product per kg raw material, ** L product per kg raw material and *** KW per kg raw material.

Energetic analysis

The determination of the exergy in a process and especially in complex processes such as biorefineries allows us to infer from the phenomenon that occurs step by step. In this work it was considered the use of CCS as a promising material for obtaining different value-added products under a biorefinery scheme. In order to demonstrate the feasibility of using the concept of biorefinery, five main processing steps were considered. In these steps final or intermediate products were obtained for subsequent processes. For each of the steps the total energy and exergy was determined. The results of these calculations are presented in **Table 7.10**. Similarly, this table shows the percentage distribution of the energy and energy consumption of the process per step and as a biorefinery.

Table 7.10. Energy and exergy values for each step of the biorefinery from CCS.

Process step	Energy		Exergy	
	kW	Percent	kW	Percent
Extraction	1,232.76	0.42	8,547.70	17.15
Sugars	80,144.29	27.26	11,731.42	23.53
Ethanol	15,244.31	5.18	3,425.90	6.87
Furfural	183,149.09	62.29	16,261.91	32.62
Cogeneration	14,267.82	4.85	9,880.28	19.82
Global	294,038.28	100.00	49,847.22	100.00

Among the steps analysed, the step that presented the highest energy consumption was the production of furfural followed by sugar production. In order to obtain furfural in this work, it was considered that the process was carried out at high temperatures and pressures significantly higher than the atmospheric. These operating conditions require high energy consumption to be achieved. Likewise, during the furfural purification step it was necessary to use distillation trains with high energy consumption in order to achieve an adequate separation. Although this was not significantly different in terms of energy required in the cooling and heating processes (50.71 and 49.28%, respectively). Similar situation can be seen in the extraction step in which both heating and cooling presented the same percentage of energy (44.33%). Where the remaining energy was required in the form of potency. However, this power could only be used to condition the raw material for extraction. Due to a consecutive process, it was not possible to use this energy for other purposes (either the conditioning of other materials in subsequent steps or to supply the requirements of some equipment). For sugar production, ethanol and the cogeneration process, the energy used for cooling (51.14%, 63.90% and 53.84%, respectively) was more valuable than the energy used for heating (48.86%, 36.10% and 38.12%, respectively). Under a biorefinery scheme it was necessary to use 211,538.33 kJ per kg of raw material. While the value obtained for the exergy was 3.41E-4 kJ per kg of raw material.

Given the characteristics of the different steps of the biorefinery at each step, an increase in exergy was evident. Steps such as getting furfural and sugars, presented a significant

contribution from the increase in exergy in the system by the energy requirements presented. As can be seen in the **Table 7.10**, these two steps of the process are those that presented the highest energy consumption (27.26 and 62.29% for sugars and furfural, respectively). From these results it is possible to observe the relationship between energy and exergy. Likewise, we can also observe the importance of these analyses to identify the zones of the process in which the highest energy consumption is presented and how these are related to the changes that occur within the process.

Economic analysis

In the economic analysis the total costs of production of each scenario shown in the **Table 7.11** were obtained. These costs showed their highest percentage in the purchase of raw materials. However, the CCS showed a very low value. While the cost was mainly attributed to the use of ethanol and toluene in some processes. On the other hand, the highest total costs were observed in scenarios 1 and 4. The latter due to the low yield of antioxidants and furfural from the CCS. While scenario 5 presented the lowest value, obtaining a total of five products (antioxidants, ethanol, furural, syngas and electricity).

Table 7.11. Costs of obtaining value-added products from CCS.

Item	Scenario 1		Scenario 2		Scenario 3		Scenario 4		Scenario 5	
	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)
Raw materials cost	6.11	82.77	2.03	66.90	1.23	61.37	5.16	71.77	1.31	70.71
Utilities cost	0.69	9.33	0.71	23.58	0.50	24.79	1.58	21.98	0.42	22.49
Operating labor cost	0.04	0.58	0.01	0.34	0.01	0.21	0.01	0.10	0.02	0.10
Plant overhead	0.08	1.08	0.03	1.02	0.03	1.42	0.04	0.62	0.01	0.68
Maintenance cost	0.01	0.15	0.05	1.61	0.05	2.39	1.58	1.10	0.02	1.19
General and administrative cost	0.07	1.01	0.03	1.04	0.03	1.51	0.05	0.68	0.01	0.74
Depreciation expense	0.37	5.08	0.17	5.50	0.16	8.20	0.27	3.75	0.08	4.09
Total	7.38	100	3.03	100	2.01	100	7.18	100	1.85	100

In the **Figure 7.7** the results of the evaluation of the NPV of each scenario in a period of 10 years are shown. In this analysis it was possible to observe only a recovery of capital in

scenarios 2, 3, 4 and 5. While in scenario 2, where it was only obtained antioxidants showed losses during this process, mainly due to the low yield of this product. Additionally, it was observed that when the composition of CCS was harvested (obtaining more products), the highest value of NPV was presented. In addition to being influenced by the yields and prices of the products obtained.

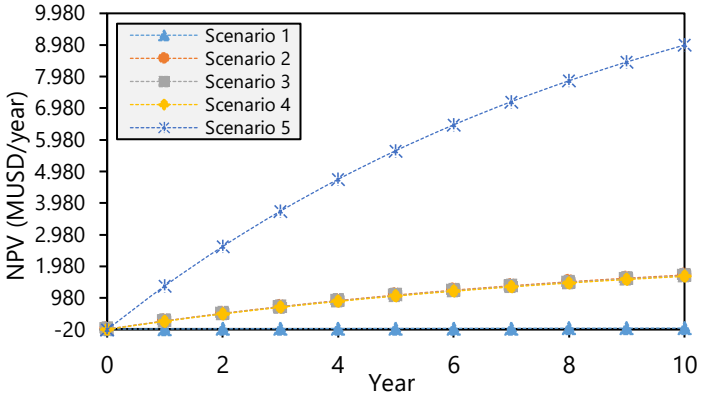


Figure 7.7. Net present value of processes from CCS.

The recovery of capital can also be affected by the variance of the costs of raw materials and products in the market. For this reason, an analysis was carried out varying the prices of raw materials and products from -100% to 100% of its current sale. The change of costs of the raw materials with respect to the net present value of the processes is shown in **Figure 7.8**. Scenario 1 was the only one that showed a loss in the process if it were to increase the price of ethanol by more than 50%. While the CCS market and the carbon dioxide even with the great change, the investment in the system was always recovered. As for scenarios 2, 3 and 4, there was a greater recovery of the system. The latter due to the high yields of the added products compared to scenario 1 where the antioxidants have a low yield. Scenario 5 presented an NPV in the same range as scenario 1. However, they had never lost in the process, even though when the toluene raw material with greater influence increased its cost to 100%. On the other hand, in scenarios 1, 2 and 3, ethanol presented the greatest influence due to the extraction process. While scenarios 4 and 5 were more affected by the cost of toluene, the raw material required in the process of obtaining furfural.

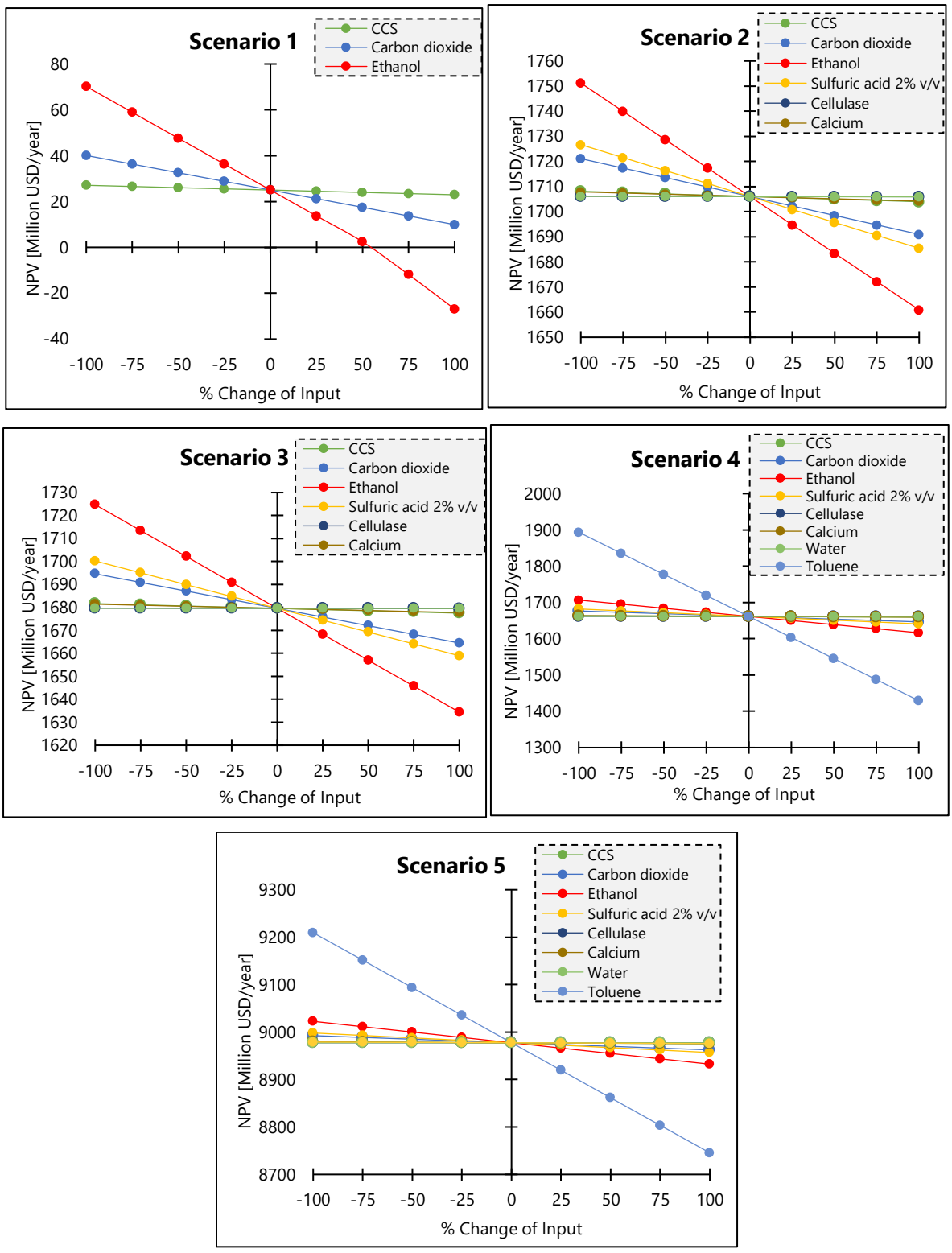
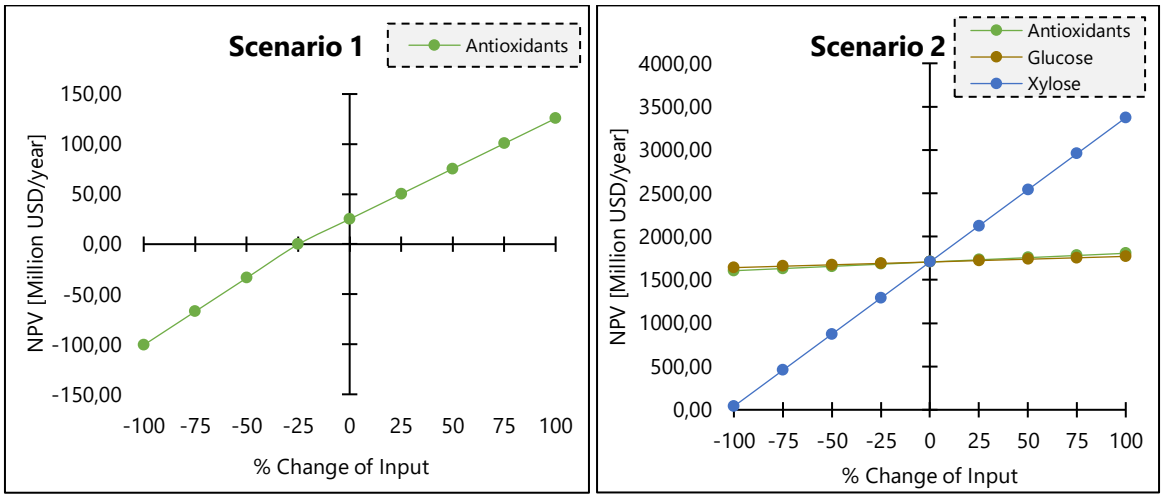


Figure 7.8. Influence of the cost of raw materials in the NPV from scenarios from CCS.

The variation of product costs is shown in **Figure 7.9**. Where it is observed that the cost of the products causes a big change in the net present value of each scenario. Scenario 1 evidenced a negative behavior of NPV by decreasing the price of the antioxidant from 25%. This result is also influenced by the low yield of this product from CCS. While in scenario 2, which is additionally obtained glucose and xylose NPV is affected by the cost of xylose. However, this price did not show a negative behavior throughout the evaluated input change. In the same way, scenario 3 presented the same behavior as in scenario 2. The latter due to the low yield of glucose and ethanol in the process, and because xylose is a product with high cost in the market. On the other hand, the price of furfural caused a high impact on the NPV of scenario 4, being a product with uses for the manufacture of plastics, solvent for lubricating oils or base for insecticides, among others. Finally, in scenario 5 the variation of the price of the syngas from -100% to 100% produces an NPV of 20 to 16,000 million USD per year, respectively.



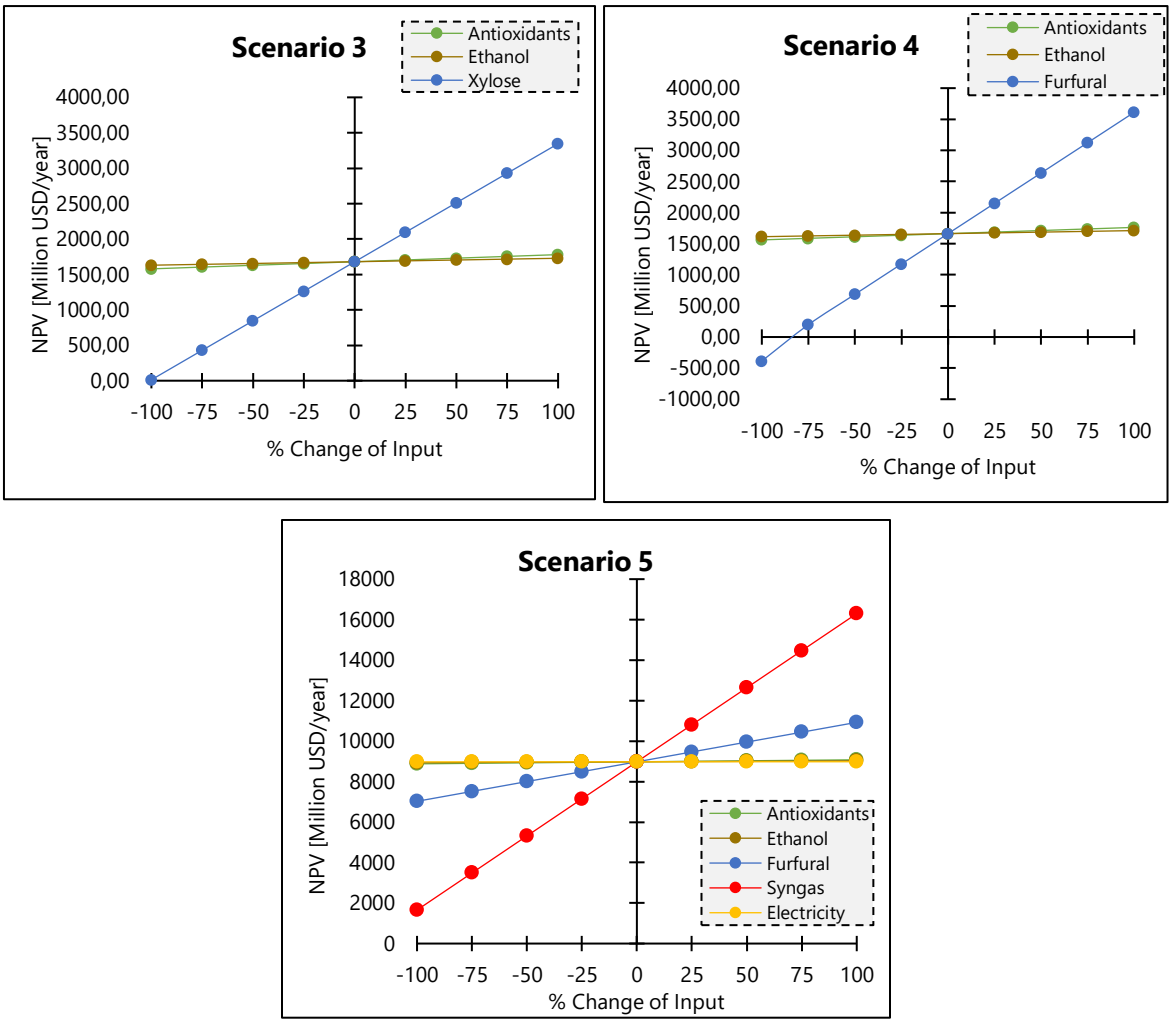


Figure 7.9. Influence of the cost of products in the NPV from scenarios from CCS.

Environmental analysis

From the analysis of the proposed scenarios, the environmental impact was obtained. In the **Figure 7.10** the potential of environmental impact generated by each scenario is observed. These diagrams show each of the catagorias evaluated. In this analysis it was observed that scenario 1 had the lowest environmental impact. This due to the low requirement of reagents for its development. On the other hand, the use of a reagent with high toxicity such as toluene and the low yield of furfural was the main cause of scenario 4 showing the highest PEI per kilogram of product. In the analysis of each one of the categories, it was obtained that in the HTPI, TTP and PCOP there was a decrease in all the scenarios. While the GWP,

ODP and AP showed a small affectation from these processes. This is due to the production and use of some gases (such as CO_2, CO, CH_4, among others) and acid solutions (sulfuric acid).

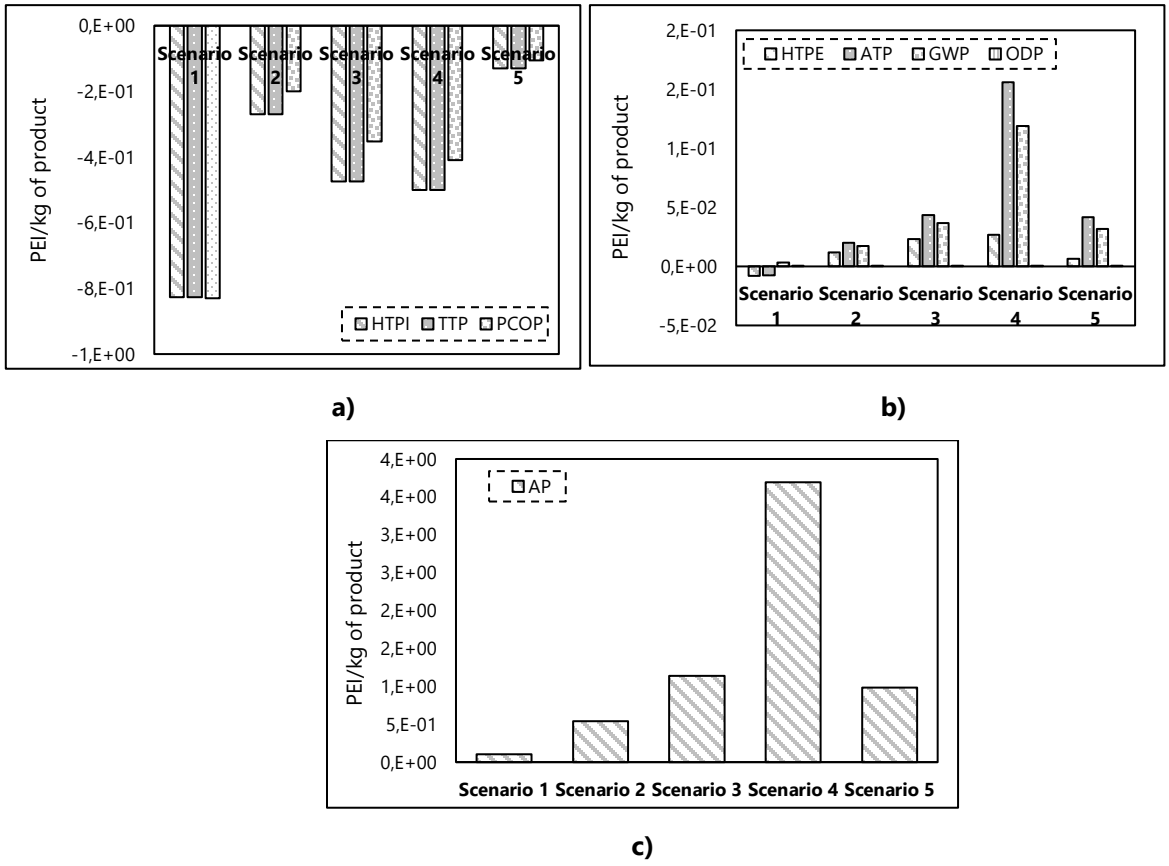


Figure 7.10. Potential environmental impact scenarios from CCS: a) HTPI, TTP, PCOP; b) HTPE, ATP GWP and ODP; c) AP.

Conclusions

Coffee cut-stems are presented as a promising alternative for use in processes for obtaining of polyphenolic compounds. First, this material presents no risk to food security since it is obtained as a residue of the process of renewal of coffee cultivation. Secondly, from this material it is possible to obtain similar of polyphenolic compounds concentrations such as the acid ferulic and quercetin to which can be obtained through the use of fruits and vegetables.

Solvent and the temperature used in the extraction process have a key role since it is possible to obtain different concentrations from variations in the solvent and temperature. This is the case of solvents such as ethanol, ethanol 60% and water, where concentrations most high is obtained at a temperature of 50° C 2.66, 2.81 and 3.01 mg GA/g, respectively. Thus showing that for the of polyphenolic compounds extraction from coffee cut-stems, solvent that allows to obtain the higher concentrations is the ethanol 60%.

The adjustment of mathematical models the extraction is a powerful tool for the study of the potential that presents material in processes of polyphenolic compounds extraction. These models can be used to determine the feasibility that presenting the material to be submitted to these processes. In addition, this models can be used for the simulation of the process in order to obtain information more detailed on the properties of the process and carry out analysis more rigorous as the economic and environmental analysis.

The pre-feasibility analsis from CCS showed that it is not economically profitable to obtain only antioxidants from these raw material. Therefore, it is necessary to obtain additional products. This in order to improve the process in general.

8. NARANJILLA PEEL

The naranjilla peel has a high potential in obtaining polyphenolic compounds according to research reported in literature (Gancel et al. 2008; Acosta, Pérez, and Vaillant 2009). For this reason, this work focuses on obtaining these compounds from the application of extraction technologies. This chapter is divided into three main parts. In its first part, the analysis of the influence of non-conventional technologies in the polyphenolic compounds extraction. For this, technologies such as UAE and SFE were compared to conventional technologies such as solvent extraction and Soxhlet extraction. Additionally, in some of these technologies the variation of solvent was evaluated (UAE, Solvent, Soxhlet). While in others the operating temperature (UAE) and pressure (SFE). In the second part, the extraction kinetics of TPC and some identified polyphenolic compounds were obtained. This was done for the UAE, solvent extraction and Sohxlet extraction, with the best operating conditions previously obtained. In the last part of this chapter, the concept of biorefinery was implemented. Where an additional product was obtained in each scenario based on the physicochemical composition of the naranjilla peel. As an analysis, energy, economic and environmental results of each process were carried out.

8.1. Experimental results

The pre-treatment of the naranjilla peel consisted of cutting manually, separating the peel from the pulp. The cover was washed to remove traces of impurities and dried at 45°C for 24 hours. Subsequently, the naranjilla peel was crushed and sieved, using only the 40 mesh particle size samples for the experimental analysis. Finally, the sample was stored at -4°C to avoid degradation. Subsequently, the analysis consisted in the determination of moisture content, ash, extractives, lignin and holocellulose (cellulose and hemicellulose). The next step

was the UAE, SFE, solvent extraction and Soxhlet extraction. Where to the extractions were made variations of operating conditions. Finally, DPPH, Flolin-Ciocalteu and HPLC methods were used to determine polyphenolic compounds present. The general scheme of experimental procedure is shown in the **Figure 8.1**.

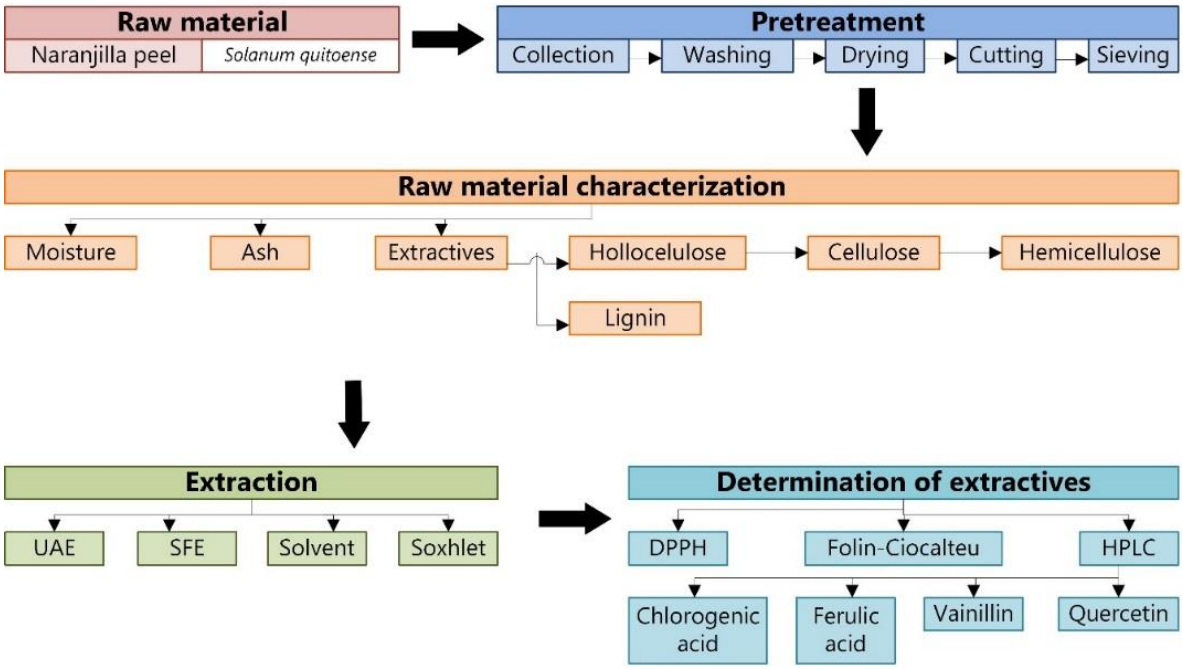


Figure 8.1. Experimental diagram of obtaining from naranjilla peel.

In the realization of the characterization of the naranjilla peel, the amount of extractives (soluble components), holocellulose, cellulose, lignin and ash was determined, showing the results in **Table 8.1**. The results show that this raw material has high cellulose contents and hemicellulose with 29.66 and 17.46, respectively. On the other hand, ash presented a percentage of 3.53 of the total agroindustrial waste. While the extractives obtained the highest percentages with 32.67. Comparing the results of this work with the physicochemical composition provided by González et al (2016), a percentage of holocellulose was obtained in the range of what was reported (44-57 % dw) (González Velandia et al. 2016). While lignin and cellulose had a smaller composition, which can be attributed to the origin of the naranjilla peel in each study.

Table 8.1. Physicochemical composition of the naranjilla peel.

	This work	**Reference** (González Velandia et al. 2016)
Extractives	32.67 ± 0.61	
Holocellulose	47.11 ± 5.97	44 - 57
Cellulose	29.66 ± 1.26	39 - 46
Hemicellulose	17.46 ± 5.95	
Lignin	16.99 ± 1.19	26 - 29
Ash	3.53 ± 0.29	

The determination of the TPC showed a concentration between 2.42 - 15.79 mg GA/g from naranjilla peel extracts as shown in **Table 8.2**. The technologies of SE and Sox-E presented the highest values with ethanol 60% as solvent with 11.18 ± 0.10 mg GA/g and 15.79 ± 0.41 mg GA/g, respectively. While the solvent that presented the lowest solubility with the naranjilla peel was ethanol with 7.60 ± 0.07 mg GA/g for the SE and 12.72 ± 0.07 mg GA/g for the Sox-E. On the other hand, by extraction with non-conventional technologies, the best concentrations were obtained with UAE (6.21 - 12.06 mg GA/g). However, the SFE despite the low concentration obtained (2.42 - 2.75 mg GA/g), uses a very low volume of solvent, being more friendly to the environment.

Additionally, analysis by UAE determined the best operating conditions from ethanol 60% (12.06 ± 0.06 mg GA/g), followed by water at 50°C (10.36 ± 0.01 mg GA/g) and ethanol at 50°C (10.15 ± 0.02 mg GA/g). This demonstrated the influence of at temperature in obtaining phenolic compounds to obtain better results at 50°C than at 25°C. In the case of SFE, there were no significant differences in the 200, 250 and 300 bars extractions. However, values of up to 2.75 ± 0.10 mg GA/g were obtained through of 300 bars. Therefore Soxhlet extraction followed by UAE presented the best performance of the process. However, on an industrial scale, only the application of the UAE is possible, demonstrating that non-conventional technologies can replace solvent extraction, which is the most widely used worldwide.

According to literature data, using as raw material peel, placental and naranjilla pulp Gancel et al (2008) reported 15.59 mg GA/g, 6.05 mg GA/g and 10.08 mg GA/g, respectively (Gancel et al. 2008). These extracts were obtained by extraction with solvent, obtaining in the case of the peel values higher than those of this work, which may be due to the use of another solvent (acetone 70%) and greater volume of solvent (solid-liquid ratio 1:40 w/v). When naranjilla peel was used as raw material, higher TPC values were found than those found in the literature based on naranjilla pulp. Where Mertz et al (2009) reported a TPC of 6.50 mg GA/g from the pulp using acetone 70% (solid-liquid ratio 1:30 w/v) for 15 minutes (Mertz et al. 2009b). Moreno, Ortiz and Restrepo (2014) obtained up to 3.2 mg GA/g at 50°C with a ratio 1:20 (w/v) for 30 minutes (Moreno, Ortiz, and Restrepo 2014). Demonstrating that the naranjilla peel has a better TPC content than the pulp, which can be used without affecting food safety.

The results of the determination of the antioxidant activity by means of the DPPH method are presented in **Table 8.2**. From these results, it was observed that the SFE presents the highest EC_{50} of all the analyzed technologies. In which by using 300 bars as operating pressure values of up to 1600 µg/mL were obtained. The Soxhlet extraction was the second best technology in antioxidant activity through the use of water as a solvent (1150 µg/mL). While in the case of the UAE the influence of the temperature presented the same behavior of the results of TPC, with the best results at 50°C (770 - 1320 µg/mL). As for the solvent in the same way as Sox-E, the water showed the highest EC_{50} (1320 µg/mL). In the case of antioxidant activity, results similar to those reported in the literature were obtained. Where Gancel et al (2008) reported by means of solvent extraction an EC_{50} of 1100 µg/mL using the peel, 380 µg/mL with the placental and 870 µg/mL with the pulp (Gancel et al. 2008). The little difference is due to the use of another solvent (acetone). However, in this work, solvents were used that caused a lower impact on the environment.

Table 8.2. TPC and antioxidant activity from naranjilla peel.

Technology		TPC (mg/g)	DPPH (µg/mL)
SE	EtOH	7.60 ± 0.07	530
	EtOH 60%	11.18 ± 0.10	890
	W	9.50 ± 0.48	1020
Sox-E	EtOH	12.72 ± 0.07	540
	EtOH 60%	15.79 ± 0.41	1020
	W	13.66 ± 0.16	1150
UAE	EtOH-25°C	6.21 ± 0.36	560
	EtOH-50°C	10.15 ± 0.02	770
	EtOH 60%-25°C	10.01 ± 0.02	980
	EtOH 60%-50°C	12.06 ± 0.06	1050
	W-25°C	9.56 ± 0.04	1270
	W-50°C	10.36 ± 0.01	1320
SFE	200 bar	2.42 ± 0.05	1400
	250 bar	2.59 ± 0.08	1430
	300 bar	2.75 ± 0.10	1600

Among the polyphenolic compounds identified in the extracts of naranjilla peel were found (see

Table 8.3): chlorogenic acid, ferulic acid, quercetin, vanillinic acid and caffeic acid. Chlorogenic acid showed its highest concentration using UAE with ethanol 60% -50°C (3.11 ± 0.08 mg/g) and 25°C (2.74 ± 0.02 mg/g). For ferulic acid, Soxhlet extraction provided the highest concentration with ethanol 60% and ethanol with 1.21 ± 0.01 mg/g and 1.19 ± 0.01 mg/g, respectively. For the case of quercetin, Sox-E also obtained the highest concentration (0.58 ± 0.02 mg/g with water and 0.49 ± 0.02 mg/g with 60% ethanol). While the UAE was the non-conventional technology with the highest concentration of quercetin (0.45 ± 0.02 mg/g).

Vanillic acid obtained up to 0.58 ± 0.03 mg/g with Sox-E. However, from the SFE similar concentrations were obtained with 0.57 - 0.54 mg/g; without significant differences when increasing the pressure. Likewise, caffeic acid presented the best concentrations with Soxhlet extraction. However, this technology requires a high volume of solvent to obtain high concentrations of polyphenolic compounds. Additionally, it was observed that the compounds identified had the lowest concentrations in most cases through the use of solvent extraction; technology that is used at the industry level and demonstrating that it can be replaced by non-conventional technologies such as the UAE and SFE.

Other authors also reported the presence of polyphenolic compounds in the naranjilla peel and pulp. Mertz et al (2009) reported the presence of chlorogenic acids: monocaffeoyl quinic acid (1.06 mg/g) and diffeoyl quinic acids (0.054 mg/g) in the naranjilla (Mertz et al. 2009b); in which the first showed values in the range found in this work. In the same way, Gancel et al (2008) reported the presence of some polyphenolic compounds in extracts of naranjilla peel (CGA, kaempferol, lutein and rutin) (Gancel et al. 2008). On the other hand Diaz (2012) identified the presence of flavonoids (0.27 - 0.36 mg/g) (Díaz Navarrete 2012). Other compounds determined in other studies identify the presence of carotenoids (lutein and zeaxanthin), flavonoids, tannins and phenols (Murillo, Meléndez-Martínez, and Portugal 2010).

Table 8.3. Polyphenolic compounds content from naranjilla peel.

Technology		Chlorogenic acid (mg/g)	Ferulic acid (mg/g)	Quercetin (mg/g)	Vanillic acid (mg/g)	Caffeic acid (mg/g)
SE	EtOH	0.79 ± 0.04	0.22 ± 0.03	0.10 ± 0.01	0.06 ± 0.01	0.03 ± 0.00
	EtOH 60%	1.32 ± 0.03	0.16 ± 0.01	0.04 ± 0.00	0.15 ± 0.01	0.08 ± 0.00
	W	1.56 ± 0.07	0.67 ± 0.02	0.25 ± 0.02	0.16 ± 0.01	0.09 ± 0.01
Sox-E	EtOH	0.98 ± 0.06	1.19 ± 0.01	0.40 ± 0.02	0.12 ± 0.01	0.08 ±0.00
	EtOH 60%	1.98 ± 0.06	1.21 ± 0.01	0.49 ± 0.02	0.58 ± 0.03	0.35 ± 0.02
	W	1.28 ± 0.02	0.17± 0.02	0.58± 0.02	0.43 ± 0.03	0.19 ± 0.01
UAE	EtOH-25°C	1.02 ± 0.04	0.33 ± 0.03	0.06 ± 0.00	0.07 ± 0.00	0.04 ± 0.00
	EtOH-50°C	1.28 ± 0.03	0.30 ± 0.05	0.18 ± 0.01	0.18 ± 0.01	0.10 ± 0.01
	EtOH 60%-25°C	2.74 ± 0.02	0.61 ± 0.01	0.33 ± 0.02	0.40 ± 0.03	0.23 ± 0.02
	EtOH 60%-50°C	3.11 ± 0.08	0.55 ± 0.02	0.45 ± 0.02	0.53 ± 0.03	0.28 ± 0.02
	W-25°C	0.97 ± 0.04	0.18 ± 0.04	0.04 ± 0.00	0.16 ± 0.01	0.09 ± 0.01
	W-50°C	1.04 ± 0.04	0.16 ± 0.06	0.17 ± 0.01	0.29 ± 0.02	0.16 ± 0.01
SFE	200 bar	1.17± 0.02	0.12 ± 0.02	0.02 ± 0.01	0.57 ± 0.04	0.21 ± 0.02
	250 bar	1.18± 0.02	0.011 ± 0.01	0.02± 0.01	0.54 ± 0.03	0.23 ± 0.01
	300 bar	1.22 ± 0.03	0.08± 0.02	0.03 ± 0.01	0.53 ± 0.03	0.26 ±0.02

8.2. Extraction kinetics from naranjilla peel

The adjustment of experimental data to mathematical models not only provides a tool for predicting the behavior of the experiment based on an independent variable such as time, but can also be used in other areas such as process simulation. From the implementation of mathematical models such as kinetics in simulation processes it is possible to predict the behavior of the reaction or extraction. In addition, these simulations can be used to perform technical, economic, environmental and energy analyses that allow the evaluation of the feasibility of the process and determine its viability. In processes that can be carried out using different technologies, the determination of kinetics is very important when evaluating and comparing each technology from the simulation of them. Technologies such as SE, Sox-E and UAE, where each of these presents different behaviors, can be used in polyphenolic compound extraction processes.

8.2.1. Total phenolic compounds

Figure 8.2 shows the behavior of each of these technologies according to the extraction time for TPC. In this figure it is possible to appreciate the experimental data obtained in the present work (teoric) which were used in the adjustment to mathematical models. Given the characteristics of the extraction process for each technology, the three models that presented the best adjustment were selected. **Table 8.4** shows the parameters corresponding to each mathematical model as shown in **Figure 8.2** for each technology. **Table 8.4** also shows the correlation coefficients for each mathematical model used. Comparing the data obtained from conventional and non-conventional technologies, it is possible to observe the advantage of using the last ones. Not only do it reduce the operating time considerably, it also allows a higher concentration of polyphenolic compounds to be obtained. Thus, for the naranjilla peel case as raw material under conventional technologies, concentrations of 474.77 and 508.94 mg/L can be obtained for SE and Sox-E, respectively. While by using a non-conventional technology such as UAE it was possible to obtain a

concentration of 603.18 mg/L TPC in a time of 60 min. Although Sox-E can produce a higher concentration of polyphenolic compounds than SE (428.13 mg/L and 508.94 mg/L for Sox-E and SE respectively at 360 min). This technology uses a higher amount of solvent. It also requires a continuous supply of energy given the operating conditions, i. e. in terms of energy consumption, this technology has a higher consumption to carry out the evaporation of the solvent.

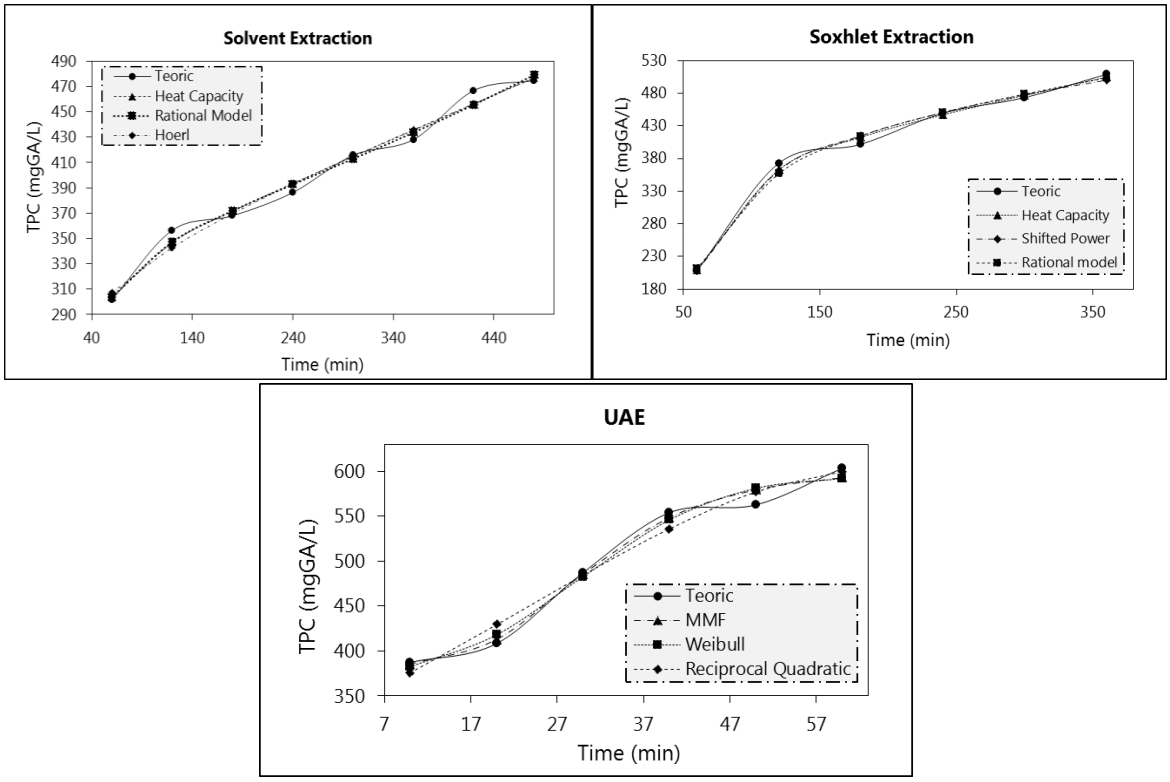


Figure 8.2. Adjustment of models for TPC from naranjilla peel.

Table 8.4. Parameters of mathematics models of TPC from naranjilla peel.

	Model	r^2	Parameters			
			a	b	c	d
SE	Heat Capacity	0.9861	3.14E+2	3.41E-1	-1.11E+5	
	Rational Model	0.9862	-3.33E+8	3.28E+7	9.30e+4	-5.42E+1
	Hoerl	0.9815	1.85e+2	1.00	1.17E-1	
Sox-E	Heat Capacity	0.9956	3.54e+2	4.33E-1	-6.13E+5	
	Shifted Power	0.9930	1.52E+2	5.54E+1	2.08E-1	
	Rational Model	0.9913	-3.01E+9	8.93E+7	1.90E+5	-8.00E+1

	MMF	0.9884	3.83E+2	2.20E+6	6.06E+2	4.25
UAE	Weibull Model	0.9826	5.94E+2	2.18E+2	4.57E-5	2.82
	Reciprocal Quadratic	0.9711	3.06E-3	-4.31E-5	3.32E-7	

9.2.2. Chlorogenic acid

Among the polyphenolic compounds that can be found in the naranjilla peel is the chlorogenic acid. This compound can be obtained at higher concentrations by using non-conventional technologies such as UAE (155.53 mg/L). While with the use of conventional technologies such as SE and Sox-E the concentrations obtained were 66.29 and 79.20 mg/L, respectively. In other words, 134.62% more can be obtained through the use of a technology such as UAE. **Figure 8.3** shows the experimental data and the adjustment of these to the corresponding mathematical models that presented the best adjustment. **Table 8.5** shows the parameters for each model as well as the correlation coefficient for each case.

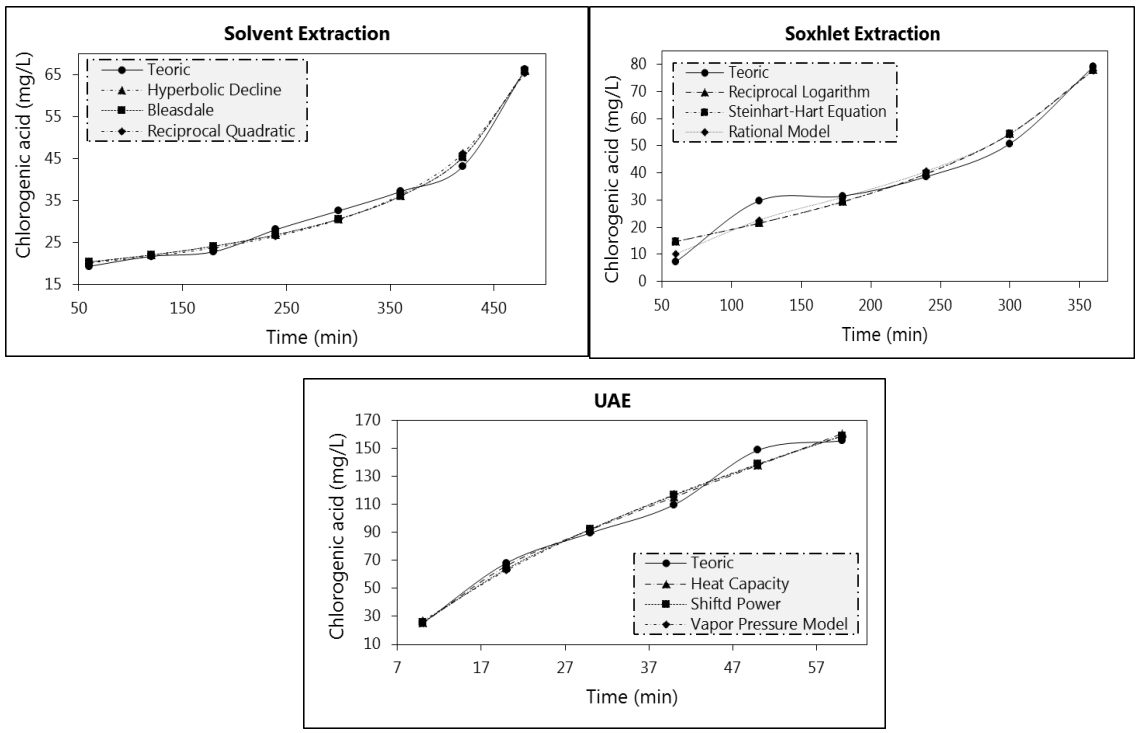


Figure 8.3. Adjustment of models for chlorogenic acid from naranjilla peel.

Table 8.5. Parameters of mathematics models of chlorogenic acid from naranjilla peel.

	Modelo	r^2	Parámetros			
			a	b	c	d
SE	Hyperbolic Decline	0.9913	9.14E+2	1.66		
	Bleasdale	0.9913	7.44e-3	-1.35E-5	1.66	
	Reciprocal Quadratic	0.9883	5.23E-2	-4.51E-5	-6.67E-8	
Sox-E	Reciprocal Logarithm	0.9506	1-93E-1	-3.06E-2		
	Steinhart-Hart Equation	0.9507	2.01E-1	3.28E-2	2.44E-5	
	Rational Model	0.9736	-1.48E+8	3.76E+6	1.46E+5	-2.87E+2
UAE	Heat Capacity	0.9854	2.82E+1	2.21	-2.51e+3	
	Shifted Power	0.9848	1.17E+1	6.66	6.56E-1	
	Vapor Pressure Model	0.9840	2.91	-9.13	5.65E-1	

9.2.3. Ferulic acid

Another component that can be found inside the naranjilla peel is ferulic acid. Compared to chlorogenic acid, this is found at lower concentrations. In contrast to chlorogenic acid, which is obtained by using non-conventional technologies such as UAE at high concentrations, this compound can be obtained at higher concentrations through Sox-E. Whereas with UAE a concentration of 27.5 mg/L at 60 min was obtained, with Sox-E the concentration at 360 min was 48.49 mg/L. However, when time is related to the concentration obtained, the UAE has greater advantages. Comparing the concentration of ferulic acid at the same operating time (60 min) for both technologies shows that with Sox-E the concentration is 4.62 mg/L, which is lower compared to that obtained with UAE. On the other hand, when comparing these results with SE, the advantages of using these two other technologies are evident. With SE the concentration of ferulic acid obtained at 480 min operation was 8.46 mg/L. **Figure 8.4** shows the behavior of the three technologies analysed as a function of time and the selected mathematical models that describe the evolution of experimental data. The parameters for each mathematical model and its correlation coefficients can be found in **Table 8.6**.

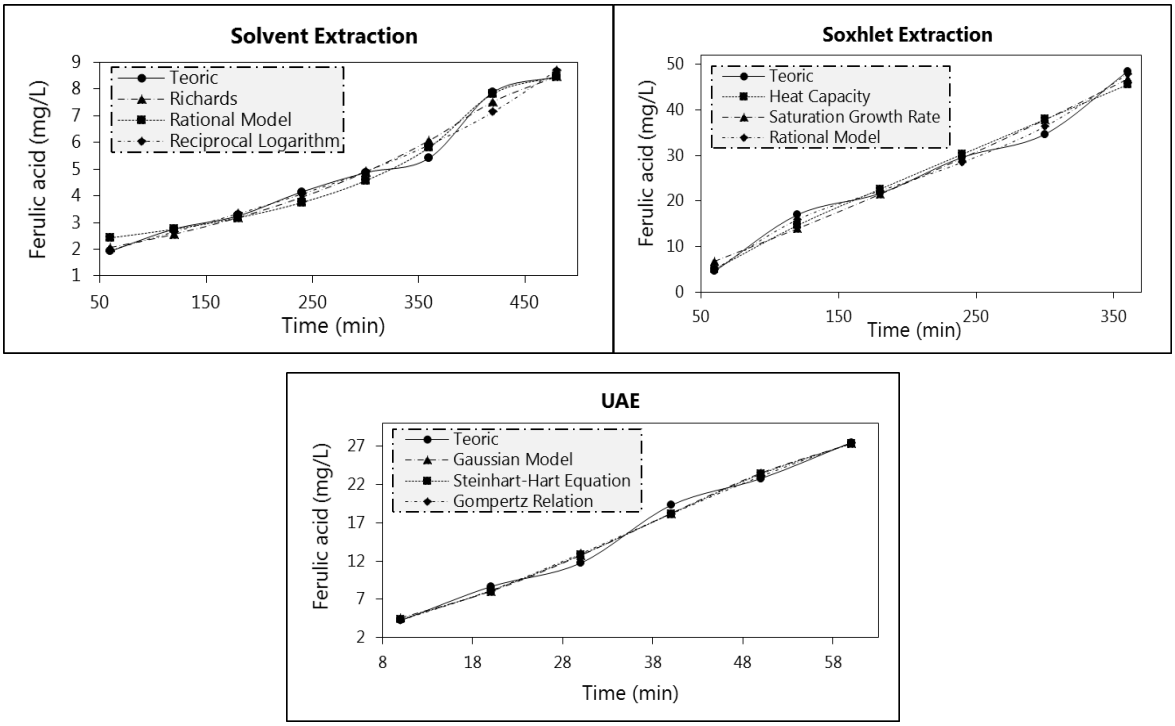


Figure 8.4. Adjustment of models for ferulic acid from naranjilla peel.

Table 8.6. Parameters of mathematics models of ferulic acid from naranjilla peel.

	Model	r^2	Parameters				
			q_0	a	b	c	d
SE	Richards	0.9831		8.46	2.59E+2	5.72E-1	1.60E+2
	Rational Model	0.9827		2.19	-4.43E-3	-3.77E-3	3.55E-6
	Reciprocal Logarithm	0.9772		1.28	-1.189E-1		
Sox-E	Heat Capacity	0.9774		1.98E-1	1.26E-1	-9.95E+3	
	Saturation Growt	0.9765		-2.58E+2	-2.35E+3		
	Rational Model	0.9947		-1.23E+8	2.61E+6	1.26E+5	-2.18E+2
UAE	Gaussian Model	0.9921		2.86E+1	6.94E+1	3.09E+1	
	Steinhart-Hart Equation	0.9923		7.50E-1	-2.50E-1	4.49E-3	
	Gompertz Relation	0.9921		4.25e+1	1.17	3.34E-2	

9.2.4. Quercetin

A behavior similar to that presented by ferulic acid is shown by quercetin, which presents lower concentrations than those presented by the other two polyphenolic compounds

analyzed. Whereas with SE a concentration of 2.38 mg/L was obtained in 480 min, with Sox-E and UAE the concentrations obtained were 19.63 and 22.51 mg/L, respectively. Although these values do not present a very significant difference, one factor that allows to decide which of the two technologies presents the best yield is time. While the concentration achieved with Sox-E took a time of 360 min, the time used with UAE was 60 min. The mathematical models that describe the behavior of each technology for the extraction of quercetin are presented in **Figure 8.5**, the parameters corresponding to each mathematical model are shown in **Table 8.7** as well as the corresponding correlation coefficients.

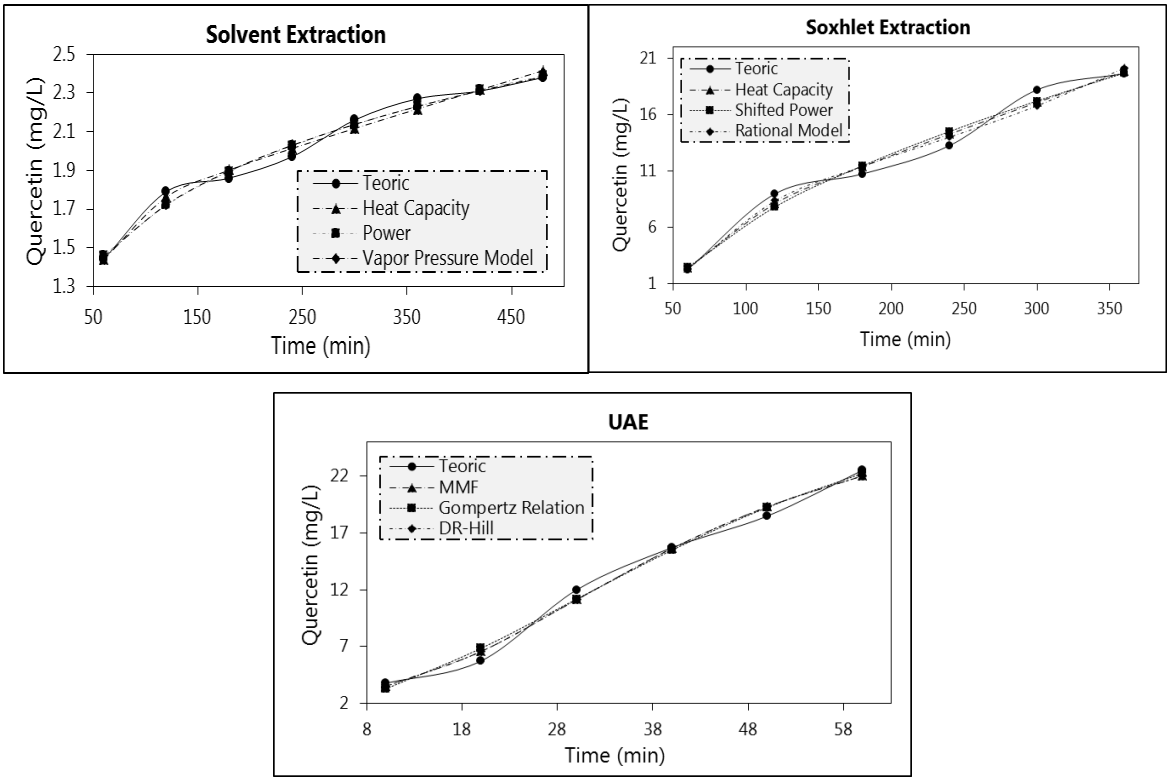


Figure 8.5. Adjustment of models for quercetin from naranjilla peel.

Table 8.7. Parameters of mathematics models of quercetin from naranjilla peel.

	Model	r^2	Parameters				
			q_0	a	b	c	d
SE	Heat Capacity	0.9857		1.65	1.61E-3	-1.08E+3	
	Power	0.9835		5.54E-1	2.37E-1		
	Vapor Pressure Model	0.9836		-5.54E-1	-1.34	-2.29E-1	

	Heat Capacity	0.9828	3.72	4.50E-2	-1.45e+4	
Sox-E	Shifted Power	0.9783	5.42E-1	4.87E+1	6.26E-1	
	Rational Model	0.9821	-4.17e+6	8.50E+4	7.17E+3	-9.79
	MMF	0.9908	2.70	9.22E+3	3.00E+1	2.45
UAE	Gompertz Relation	0.9893	2.97E+1	1.19	4.06E-2	
	DR-Hill	0.9908	2.70[a]	2.73E+1[b]	2.45[c]	4.17e+1[d]

[a]Alpha, [b]theta, [c]eta, [d]kapa

8.3. Biorefinery from Naranjilla Peel

The use of agro-industrial waste is presented as promising sources for obtaining of various value-added products. Between these residues can be found naranjilla peel which given its composition can be used to obtain various products under the biorefinery concept. The complexity of a process and more in the case of biorefineries is an important factor to be considered in the design stage. This study presents the exergy, economic and environmental evaluation of four scenarios from naranjilla peel, for the production of antioxidants, glucose, xylose, ethanol and xylitol under biorefinery concept (see **Table 8.8**). Which is an increase in the complexity in each scenario.

Table 8.8. Schemes from naranjilla peel.

Scenarios	Products
Scenario 1	Antioxidants
Scenario 2	Antioxidants + sugars
Scenario 3	Antioxidants + glucose + ethanol
Scenario 4	Antioxidants + ethanol + xylitol

Figure 8.6 shows the block diagram of the biorefinery, also this figure shows the connection between products such as sugars (glucose and Xylose) in obtaining other products of added value (ethanol and xylitol). In each scenario was considered as a basis for calculation a flow naranjilla of 1 tonne per hour. Below is presented a description of the process used to obtain the products listed in **Table 8.8**.

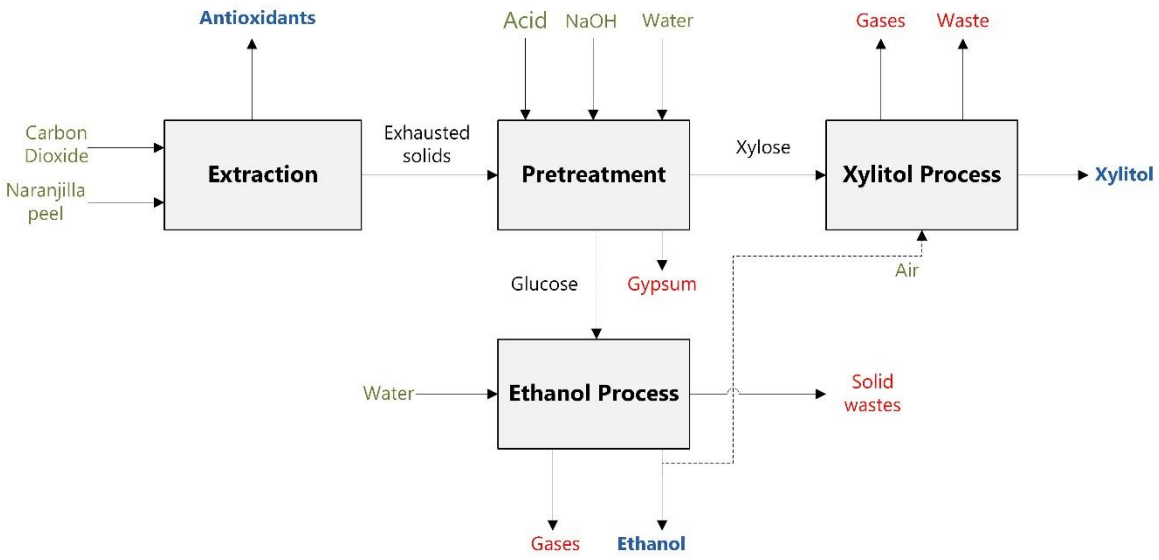


Figure 8.6. Flow diagram of biorefinery from naranjilla peel.

As result of the physicochemical characterization was obtained a percentage based dry 32.57% extractive, 29.57% cellulose, 17.41% hemicellulose, 16.94% lignin and 3.52% ash (see **Table 8.1**). Values used during the development of the simulation process. From the obtained characterization and under the conditions mentioned above was possible to achieve the performance presented in **Table 8.9**. Where was obtained yields glucose and xylose based on variety of solids from the process of extraction of 0.786 kg solids per kg of naranjilla. The potential presented by the naranjilla peel to be used in processes of extraction of antioxidants is evident in **Table 8.9**. Similarly, given the large amount of solid waste (lignocellulosic material) obtained as waste from this process presents a great potential for the production of sugars such as glucose and xylose. At the same time, it can see viability presenting obtaining ethanol and xylitol use these sugars. Obtaining as a result of the process group of a biorefinery presenting a high potential in terms of yields for employment of the naranjilla as raw material.

Table 8.9. Yields obtained in the obtaining of each product from naranjilla peel.

Product	Yield
Antioxidants	0.027*
Xylose	0.149*

Glucose	0.285*
Ethanol	0.152**
Xylitol	0.100*

* kg product per kg raw material, ** L product per kg raw material

Energetic analysis

Considering the scenarios analyzed in this work. It is possible to evidence the changes that occur due to the addition of steps to a complex process such as biorefineries. Thus, while higher is the biorefinery complexity, a high flow of exergy is presented, i. e., it is possible to obtain a greater use of the energy flows of the system to obtain work by the addition of other steps that allow to take advantage of this energy. The increase in exergy flow due to the addition of steps for the proposed biorefinery is presented in **Table 8.10**. With the addition of steps to the biorefinery in which precursors were obtained, which were used to obtain value-added products, it was possible to increase the flow of exergy of the process due to the increase in irreversibilities that each step involves.

Table 8.10. Exergy flow for each scenario.

Scenario	Exergy (kW)
Scenario 1	3.49
Scenario 2	1,565.85
Scenario 3	2,068.05
Scenario 4	3,147.19

Each processing step may have differences in the flow of exergy. These differences are caused by the changes involved in each stage, as well as the energy flow required by it. This is reflected in **Table 8.11**. This table shows that although ethanol and xylitol production is carried out through fermentation processes, the conditions and separation and purification employed plays an important role in the flow of exergy of each process. However, because the sugar production process involves higher mass flows compared to other processing steps, this step presents the highest exergy flow.

Table 8.11. Distribution of the exergy in each stage.

Stage	Exergy (kW)
SFE	3.49
Sugar production	1,562.36
Ethanol production	502.20
Xylitol production	1,079.14

Economic analysis

The influence of different economic parameters form an important part in the economic profitability of the products obtained from each of the scenarios using as raw material naranjilla peel and a raw material flow of 1 tonne/h. In addition, for each of the proposed scenarios, the total cost of production in USD per kilogram of product was obtained. **Table 8.12** presents the description of the economic behavior in obtaining antioxidants, ethanol and xylitol for each of the items taken into account. Among the parameters that had greater influence are the raw material costs with around 40.60 - 55.29% of their influence in each of the scenarios. Where scenario 2 presents a low cost compared to the other scenarios, inferring that in reagents such as sulfuric acid and sodium hydroxide used for acid hydrolysis and detoxification, do not have a great influence on the costs of the process. Another item with a large share in process costs was the utilities with the highest percentage in scenarios 3 and 4, due to the high energy requirement in the separation stage through the use of distillation towers required in the production of ethanol and xylitol. Additionally, the depreciation costs presented a significant influence for scenarios 1 and 3 with 27.13 and 25.18%, respectively.

Table 8.12. Production costs of the proposed scenarios from naranjilla peel.

Items	Scenario 1		Scenario 2		Scenario 3		Scenario 4	
	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)	USD/kg	Share (%)
Raw materials cost	0.82	55.29	0.47	47.06	0.86	40.60	0.68	42.71
Utilities cost	0.04	2.69	0.21	20.65	0.46	21.78	0.52	32.47
Operating labor cost	0.02	1.65	0.01	1.24	0.03	1.59	0.03	1.96
Maintenance cost	0.07	4.41	0.03	2.78	0.06	2.74	0.05	3.16
Operating charges	0.01	0.41	3.08E-3	0.31	0.01	0.40	0.01	0.49
Plant overhead	0.05	3.03	0.02	2.01	0.05	2.16	0.04	2.56
General and administrative cost	0.08	5.40	0.06	5.92	0.12	5.54	0.11	6.67
Depreciation expense	0.40	27.13	0.20	20.03	0.54	25.18	0.16	9.98
Total	**1.49**	**100.00**	**1.00**	**100.00**	**2.13**	**100.00**	**1.60**	**100.00**

From the economic evaluation, each of the production costs of the different products obtained was estimated as shown in **Table 8.13**. For the case of the cost of production of antioxidants, a value between 0.38 - 0.1.49 USD/kg was obtained, presenting the lowest cost in scenario 2 (0.38 USD/kg). In addition, this shows a production cost lower than the market price with an average value of 4 USD/kg and an eminent gain in its production. On the other hand, ethanol product with high applications as fuel for internal combustion engines, showed a cost of production of 0.64 and 0.38 USD/kg for scenarios 3 and 4, respectively. From this can be compete with the stipulated cost in the market (1.24 USD/kg). Finally, the xylitol obtained in scenario 4 showed a production price of 0.64 USD/kg, which is sold in the market with a price around 9 USD/kg, giving a high profit in its sale.

Table 8.13. Production cost of the products obtained from naranjilla peel.

Scenario 1	Scenario 2	Scenario 3	Scenario 4
Antioxidants: 1.49 USD/kg	Antioxidants: 0.38 USD/kg Glucose: 0.41 USD/kg Xilose: 0.21 USD/kg	Antioxidants: 1.48 USD/kg Ethanol: 0.64 USD/kg	Antioxidants: 0.88 USD/kg Ethanol: 0.38 USD/kg Xylitol: 0.34 USD/kg

Additionally, the Net Present Value (NPV) was obtained, with the objective of determining if the proposed scenarios are economically feasible, based on the calculation of the cash flows (income of the products). In **Figure 8.7** it can be seen that for scenarios 1 and 3, the income obtained is the same, requiring two years to recover the investment. Where scenario 3 presents its low recovery over the years of analysis, due to the low price of ethanol in the market. Scenario 2 presents the highest recovery and gain in the products of the naranjilla peel, demonstrating that parameters such as the use of sulfuric acid and sodium hydroxide do not show a strong effect in the NPV of this scenario. On the other hand, both in the case of scenario 2 and 4 there is a significant increase starting from the first year, with the most profitable scenarios for its realization. This is due to the case of scenarios 4 obtaining a product with high added value such as xylitol. As it was possible to observe the use of a raw material with low acquisition cost such as naranjilla peel, it presents its best applicability and profitability in obtaining value-added products such as antioxidants, ethanol and xylitol (scenario 4). However, these analyzes depend on more exhausting processes for industrial development.

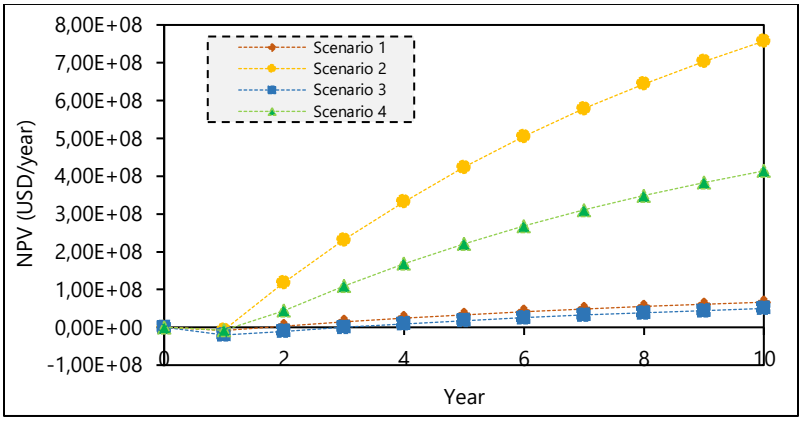


Figure 8.7. Net present value of the scenarios evaluated from naranjilla peel.

Additionally, an analysis of sensitivity to the costs of raw materials was carried out, with the objective of determining the influence that each of them provides for each of the proposed scenarios. As result was obtained the Net Present Value for each of the scenarios shown in **Figure 8.8**. It can be evidenced that in the raw materials the one that contributes and affects

the most is carbon dioxide (scenarios 1 and 2) and ethanol (scenarios 3 and 4). Ethanol showed greater influence when it was required to obtain xylitol. Additionally, it could be observed that the use of naranjilla peel provides a great advantage by presenting a low cost of acquisition and transport, even when its value increases by 100%. On the other hand, in scenarios 2, 3 and 4 it was observed that variables such as sulfuric acid, cellulase and calcium hydroxide do not have a strong effect on the NPV of the process. This, in addition to its low purchase cost, is due to the low flow required to obtain glucose and xylose.

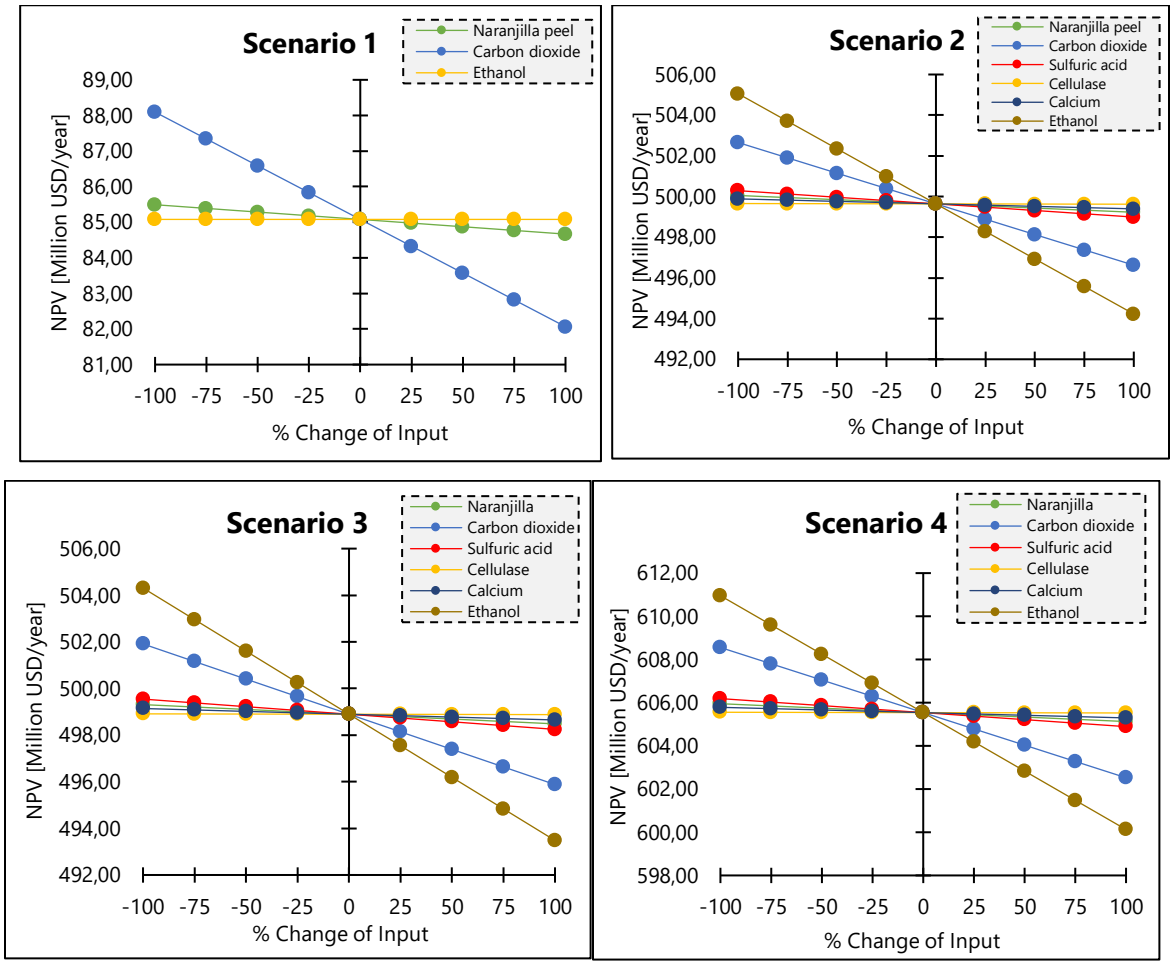


Figure 8.8. Influence of raw material costs in obtaining products from naranjilla peel.

When performing the variation of the sale prices of the products, the results shown in **Figure 8.9** were obtained. In scenario 1, it could be observed that the price of the antioxidant decreased less than 75%. This process was not feasible, since the only product obtained was

in this scenario. While in scenarios 2 and 4 the price of xylose and xylitol contributed the greatest influence in the system. On the other hand, the price of ethanol did not show a significant change like glucose. This is due to lower flows and lower prices compared to products such as antioxidants and xylitol. Scenario 3, showed the biggest solids with the variation in the price of the products (see **Figure 8.9**). Where even so, by varying the price of ethanol by 100%, the system remained in equilibrium. Through this sensitivity analysis, the risks that the four scenarios developed with the effect of the cost of raw materials and products could be exposed. Additionally, it was evident that all the proposed cases were feasible, with the exception of scenario 1 if the antioxidant cost 75% less.

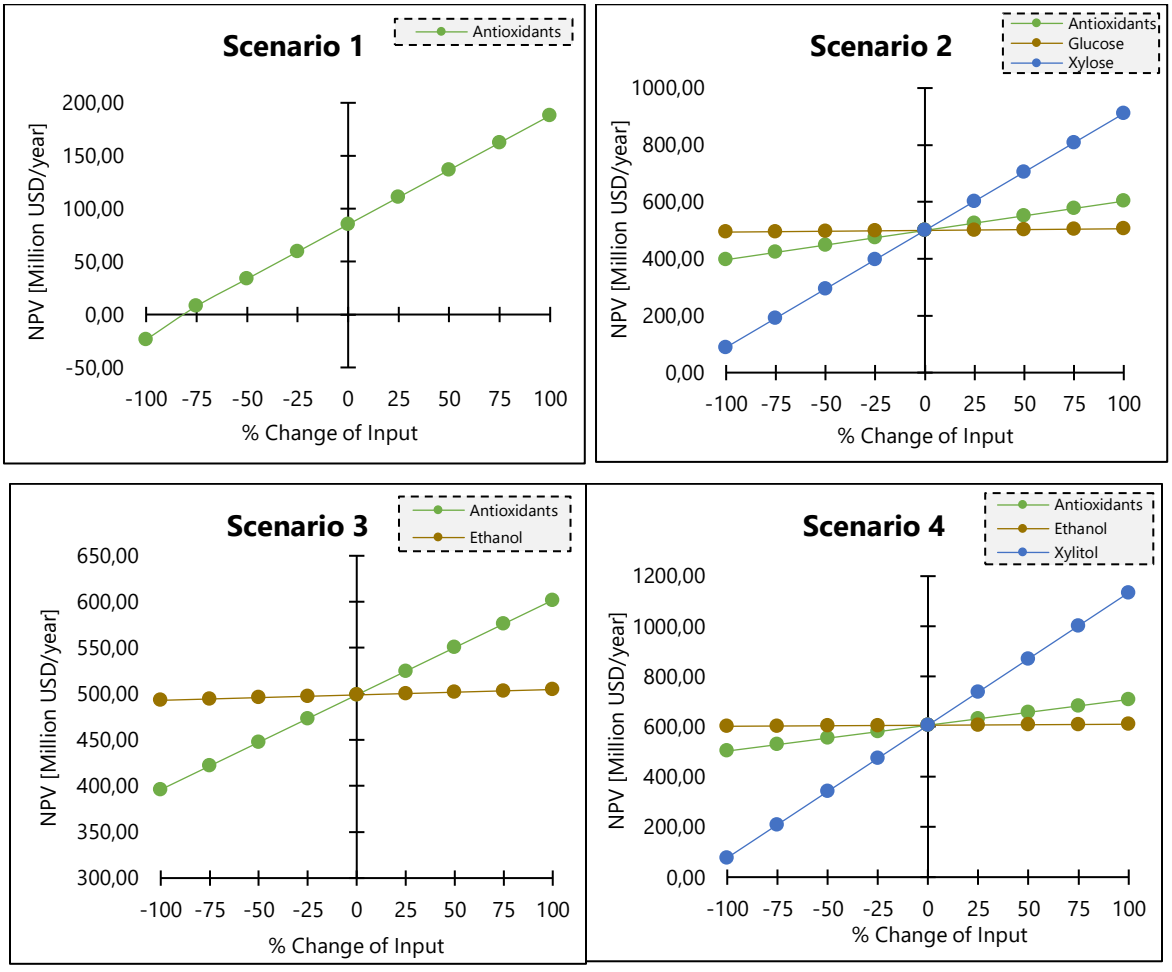


Figure 8.9. Influence of the cost of products from naranjilla peel.

Environmental analysis

Through environmental impact assessment, it is possible to obtain the viability of a process at environmental level, allowing identification of the damage that can cause the production of such products. The environmental analysis developed to obtain different value-added products from naranjilla peel (scenarios 1 - 4) are shown in **Figure 8.10**. Categories such as HTPI, TTP and PCOP showed a decrease in each of the scenarios as observe in **Figure 8.10-a**. On the other hand, the categories of AP, ODP and GWP (see **Figure 8.10-b, c** and **d**) for scenarios 1 and 3 presented approximately the same value of environmental impact potential. While scenarios 3 and 4 showed a significant increase in each of them, due to the high electricity consumption required in each of these schemes and the generation of waste such as stillage and gypsum.

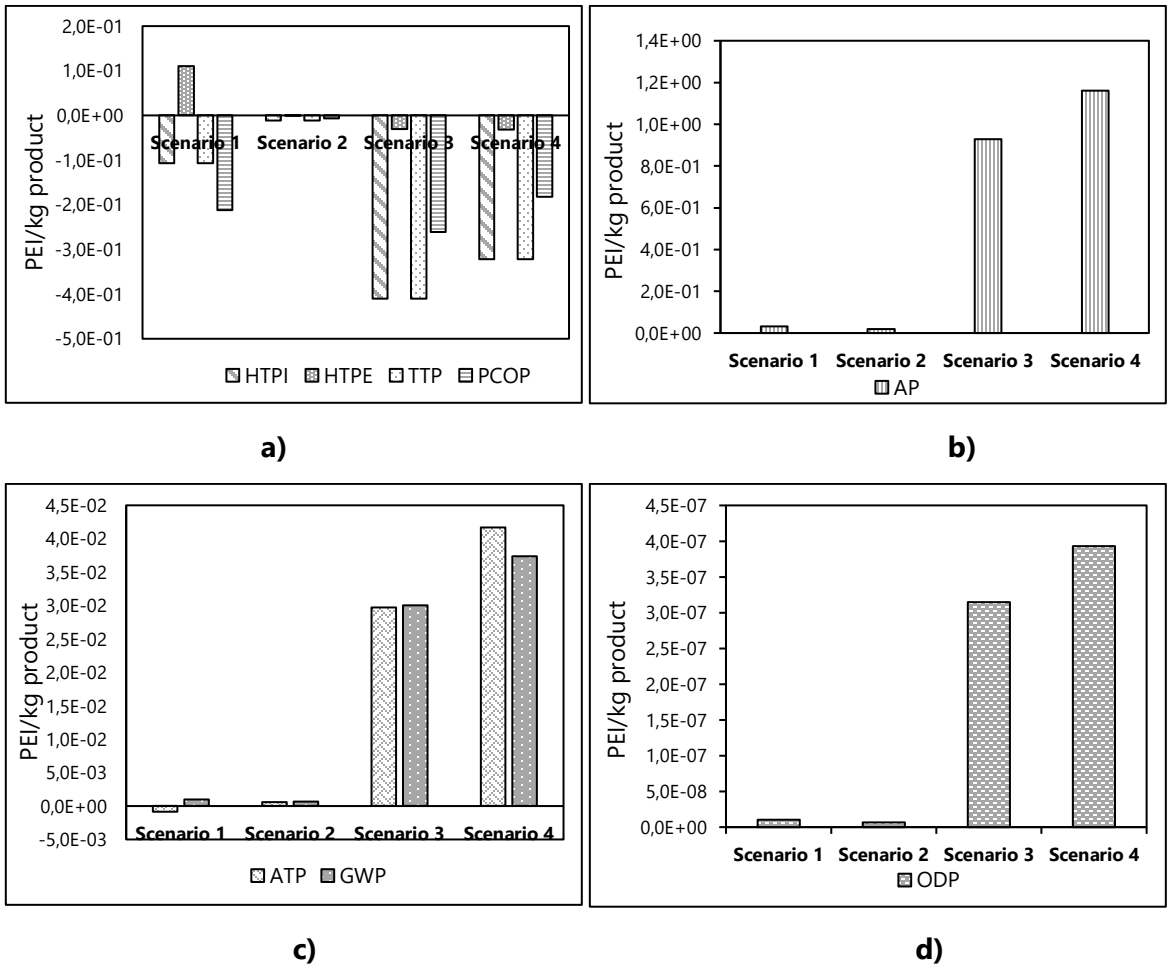


Figure 8.10. Potential environmental impact scenarios from naranjilla peel: a) HTPI, HTPE, TTP, PCOP; b) AP; c) ATP, GWP; d) ODP.

Figure 8.11 shows the potential for total environmental impact of the scenarios evaluated. Where scenario 4 presented the greatest environmental damage (0.38 PEI/kg product), due to its high acidification potential. While the other scenarios showed a decrease in their generation. From scenario 1 it can be inferred that when carrying out the recirculation of the solvents used (CO_2 and ethanol) there is a low environmental impact; as well as through scenario 2, it is shown that the adequacy of hydrolysis residues causes a low presence in the categories evaluated. Each one of the impacts caused by these proposed scenarios is caused by the presence of multiple toxic substances that cause damage to the environment, and must present a treatment for their reduction due to the chemical composition presented by each of them. This environmental analysis additionally requires another series of analyzes due to not taking into account the upstream impacts and only being a gate-to-gate analysis.

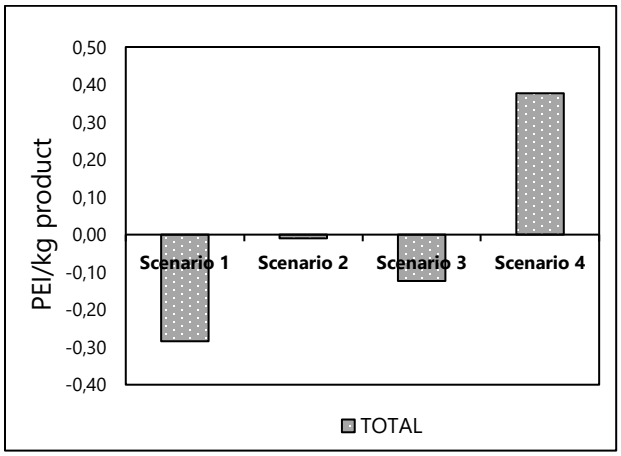


Figure 8.11. Potential environmental impact total of the scenarios from naranjilla peel.

Each one of the impacts caused by these proposed scenarios is caused by the presence of multiple toxic substances that cause damage to the environment, and must present a treatment for their reduction due to the chemical composition presented by each of them. This environmental analysis additionally requires another series of analyzes to take into account the upstream impacts and not to only being a gate-to-gate analysis.

8.4. Conclusions

From this study it was possible to demonstrate the high competitiveness of conventional technologies before non-conventional ones. Additionally, different solvents, temperatures and pressures could be analyzed, obtaining ethanol 60% as the best solvent. While in the case of UAE the best operating temperature was 50°C. On the other hand, the SFE showed the best performance at 300 bars. As for the raw material, the naranjilla peel has great advantages in the use of extraction processes. The latter due to being a waste and presenting a high content of extractives in its composition.

Prefeasibility analyzes showed that it is possible to produce antioxidants, ethanol and xylitol from naranjilla peel by means of product integration (biorefinery). In the selection of a production scheme for a raw material, it is necessary to carry out an analysis of the different alternatives that can be presented. To select the one that presents the best exergy, economic and environmental benefits. Taking into account the schemes analyzed, scenario 2 presented the greatest economic viability within the scenarios. However, in terms of exergy and environmental analysis, the scenario1 presented the best results.

9. OTHER RAW MATERIALS

Fruits with high harvest and agroindustrial residues are a potential source for the extraction of metabolites that present a high added value and use in the food industry, providing high availability and low cost. In this chapter an additional research work is carried out, studying the use of different raw materials, applying to each one of them a variation of extraction technologies in order to know the influence they have in obtaining polyphenolic compounds. In a first case, the tree tomato peel was studied using four extraction technologies (SE, Soxhlet, SFE, UAE) and the best operating conditions reported in literature for each of them. Additionally, with this raw material, an economic, energetic and environmental evaluation was carried out, based on the comparison of the technology with solvent extraction and SFE. In the second part the residues obtained from the olive tree (olive pomace, olive tree pruning and olive leaves) are used in obtaining polyphenolic compounds. Where it makes a focus on hydroxytyrosol which is considered as the second compound with the highest antioxidant potential after of galic acid. For this, the comparison of a conventional technology (solvent extraction) and a non-conventional one (SFE) was carried out. In the latter, variations in operating pressure were analyzed. Finally, three fruits of the family of *Passifloras* (yellow passion fruit, purple passion fruit and sweet granadilla) were used lyophilized in extraction processes, demonstrating an additional application for them and their nutritional value, having polyphenolic compounds with anti-carcinogenic properties, antioxidants, anti-diabetics, among others.

9.1 TREE TOMATO PEEL

9.1.1. Experimental results

The tree tomato, fruit with high harvest worldwide, therefore presents a large production having a high consumption in South America in juices and fresh fruit. However, this fruit produces industrial waste that is not used to obtain value-added products, which stands out the tomato tree peel. This peel has a high potential in obtaining polyphenolic compounds. For this reason, this study focuses on the application of different technologies (solvent extraction, Soxhlet extraction, SFE, and UAE) to obtain extracts using ethanol 60% (v/v) solvent as shown in **Figure 9.1**.

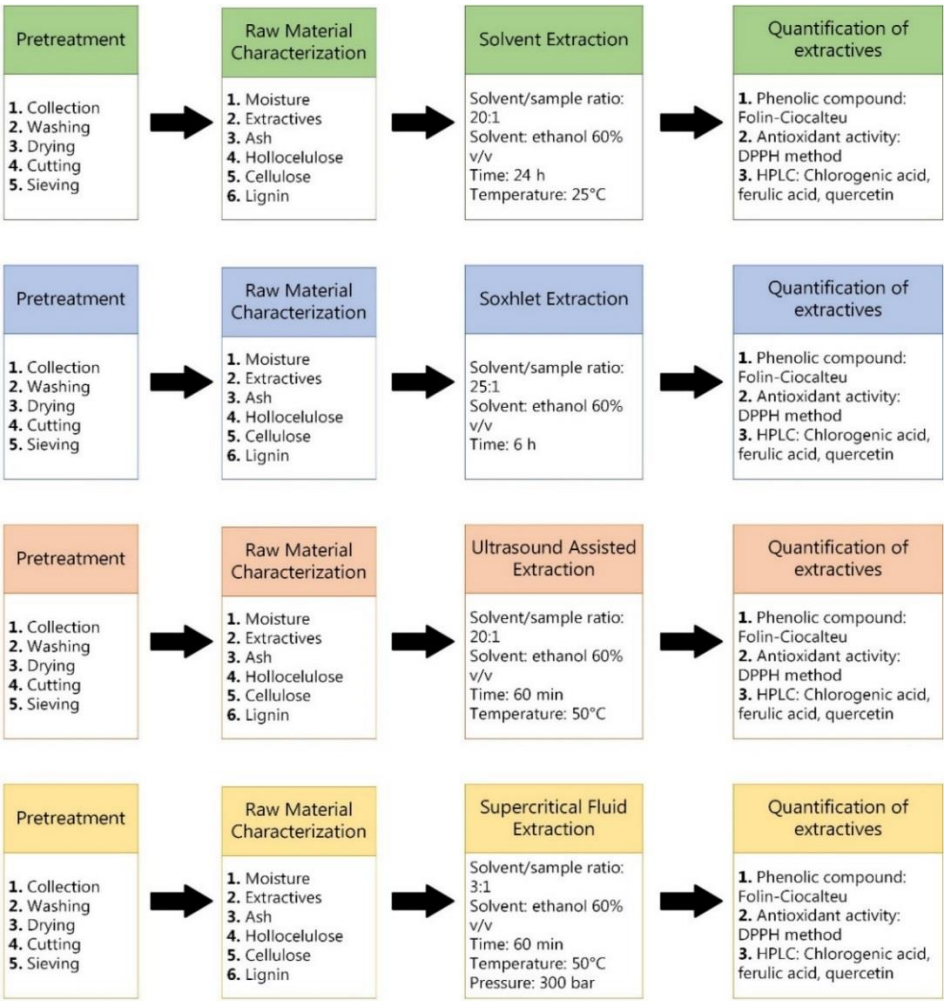


Figure 9.1. Experimental diagram from tree tomato peel.

The results of the characterization of tree tomato peel are presented in **Table 9.1**. This raw material presented a high content of extractives (38.21 ± 0.44% d.b), demonstrating that it is a raw material with high potential for extraction processes. These extractives mainly represent polyphenolic compounds. In addition, these results show that this raw material can have a high antioxidant activity and a large variety of compounds present, making it a raw material with high interest and use for its high nutritional value. On the other hand, the high content of polysaccharides make it raw material with high applicability for fermentation processes (Duque, Cardona, and Moncada 2015). While the lignin content can be exploited in power generation processes (Bahadur, Sujatha, and Carels 2013). These results obtained were similar to those reported by Gonzales et al (2016) in the lignin content (González Velandia et al. 2016). While in the case of physicochemical composition, Cerón (2013) reported similar values of holocellulose, and a high ash content (I. Cerón 2013). This variation may be due to the origin of the raw materials, and standardization of the same or the variety of tree tomato used.

Table 9.1. Physical-chemical composition of tree tomato peel.

Components	**This work**	**Reference** (I. Cerón 2013)*****	**Reference** (González Velandia et al. 2016)
Extractives (% DW)	38.24 ± 1.00	48.24 ± 0.44	50 - 59
Holocellulose (% DW)	38.85 ± 4.63	31.91 ± 1.04	---
Cellulose (% DW)	21.65 ± 1.03	---	44 - 45
Hemicellulose (% DW)	17.20 ± 4.61	---	---
Lignin (% DW)	18.57 ± 0.76	10.08 ± 0.41	20 - 25
Ash (% DW)	4.35 ± 0.11	9.77	---

All the percentages are expressed by weight.

*Normalized values

As a result of the Folin-Ciocalteu method, the yield of TPC shown in **Table 9.2** was obtained. From the conventional methods were obtained 15.35 ± 0.31 mg GA/g with Soxhlet extraction and 10.95 ± 0.03 mg GA/g with solvent extraction. While through SFE and UAE were obtained 7.38 ± 0.29 mg GA/g and 13.38 ± 0.14 mg GA/g, respectively. Although the highest yield

was obtained through the Soxhlet extraction. This technology requires a greater volume of solvent, temperature and time of operation, making the process more expensive, less friendly to the environment and with lower production per hour in the process.

On the other hand, the results obtained from TPC in this work were greater than those reported by Vasco et al (2009) with 6.20 mg GA/g from the purple-red variety and 3.87 mg GA/g with the Golden-yellow variety (Vasco et al. 2009). This difference may be due to the fact that Vasco et al (2009) uses a higher solid-liquid ratio (1:40 w/v) and another solvent (methanol 50%). Mutalib et al (2016) performed extractions from tree tomato pulp obtained concentrations of 2.53 mg GA/g (ethanol), 2.10 mg GA/g (n-butanol), 1.77 mg GA/g (ethyl acetate) and 1.49 mg GA/g (water), through a solid-liquid ratio 1:25 (w/v) and a temperature of 25°C for 24 hours (Mutalib et al. 2016). On the other hand, Ferreira et al (2015) reported yields of 1,335 mg GA/g and 0.682 mg GA/g for the tomato pulp and peel, respectively (Ferreira et al. 2015). While from the Mertz et al (2009) with tree tomato pulp reported between 3.08 - 5.70 mg GA/g, using acetone 70% (solid-liquid ratio 3:7 w/v) for 30 minutes (Mertz et al. 2009b). Meanwhile, Torres (2012) obtained 1.39 mg GA/g by means of 80% methanol acidified as solvent (Torres 2012). Other studies contributed by Mandal and Ghosal (2012) by Soxhlet extraction, in parts of the tree tomato fruit showed a TPC content of 2.75 mg GA/g in the peel, 3.80 mg GA/g in the seeds, 4.11 mg GA/g in the placenta, 3.95 mg GA/g in the endocarp and 1.50 mg GA/g in the pulp (Mandal and Ghosal 2012). Presenting a lower value that may be due to use of another operating extraction conditions (methanol 70%, for 8 hours).

The antioxidant activity of tree tomato peel extracts showed the best concentration by using SFE (592.21 ± 5.19 µg/mL), followed by Soxhlet extraction (542.58 ± 5.21 µg/mL) as observed in **Table 9.2**. These values were higher than those reported by Hassan and Bakar (2013) with 23.94 µg/mL and 21.76 µg/mL, using as solvent 80% methanol and water, respectively (Hassan and Bakar 2013). This large change may be due to the fact that Hawa uses a shorter process time in solvent extraction (2 hours) and a higher solids-liquid ratio (1:50 w/v). Similar

data to Atiqah, Maisarah and Asmah (2014) were reported by Atiqah from the pulp at 44.25 ± 0.82 µg/mL using 70% ethanol and 47.38 ± 1.11 µg/mL with water, performing the extraction at 50°C and a solid-liquid ratio 1:50 (w/v) for one hour (Atiqah, Maisarah, and Asmah 2014).

On the other hand, other authors obtained higher values of antioxidant activity to those of this work. Where Ferreira et al (2015) reported an EC_{50} of 1769 µg/mL and 3570 µg/mL for the tree tomato peel and the pulp, respectively (Ferreira et al. 2015). Likewise, Mutalib et al (2016) reported 800 µg/mL with ethanol and 700 µg/mL with ethyl acetate as solvent (Mutalib et al. 2016). This variation may be due to the use of the mesocarp as raw material, different solvents, a longer operating time (24 hours) and higher solid-liquid ratio (1:25 w/v).

Table 9.2. TPC and antioxidant activity from tree tomato peel.

Technology	TPC (mgGA/g)	DPPH (µg/mL)
SE	10.95 ± 0.03	413.52 ± 4.62
Sox-E	15.35 ± 0.31	542.58 ± 5.21
UAE	13.38 ± 0.14	487.44 ± 3.29
SFE	7.38 ± 0.29	592.21 ± 5.19

The quantification of polyphenolic compounds through HPLC resulted in the presence of the compounds shown in **Figure 9.2**. Chlorogenic acid was the compound with highest concentration using the Sox-E with 2.2 ± 0.03 mg/g and SFE 1.35 ± 0.02 mg/g. While the UAE and SE presented a concentration of chlorogenic acid of 0.63 ± 0.02 mg/g and 0.49 ± 0.04 mg/g, respectively. Comparing these results, Muñoz et al (2009) obtained 0.416 mg/g from tree tomato peel and performing the extraction through the use of methanol as solvent (A. M. Muñoz Jáuregui et al. 2009). Merzt et al (2009) reported the presence of chlorogenic acid isomers (0.21 ± 0.3 mg/g for Dicaffeoylquininc acid and 0.54 ± 0.4 mg/g caffeoylquinic acid) from the tree tomato pulp, using solvent extraction (acetone 70%) and a solid-liquid ratio 3:7 (w/v) during 30 minutes (Mertz et al. 2009b). In addition, Wrolstad and Heatherbell (1974) reported the presence of trace amounts of chlorogenic acid in the pulp of tree tomato

using maceration as extraction technology and adding acetone first, followed by chloroform and ethyl acetate (Wrolstad and Heatherbell 1974). Similarly Muñoz et al (2007) used tree tomato pulp obtaining 0.081 mg/g of chlorogenic acid from 60% ethanol as solvent (M. A. Muñoz Jáuregui et al. 2007). Ferulic acid, compound with antioxidant properties was also identified (see **Figure 9.2**), obtaining the best concentration through of UAE(0.17 ± 0.01 mg/g) and SE (0.14 ± 0.01 mg/g), followed of the Sox-E (0.10 ± 0.00 mg/g) and finally the SFE (0.05 ± 0.01 mg/g). However, although of SFE obtained the lowest yield, this was carried out with a lower volume of solvent and in some cases shorter operation time in comparison with the other extraction technologies used. In the same way studies contributed by Muñoz et al (2007) showed 0.003 mg/g of ferulic acid, low concentration to this process, in spite of being used the same solvent (ethanol 60% v/v) (M. A. Muñoz Jáuregui et al. 2007).

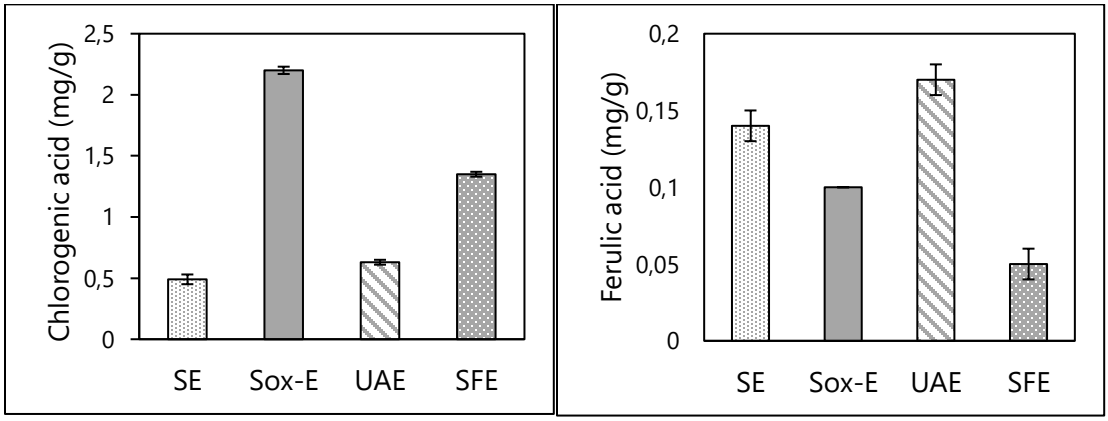


Figure 9.2. Chlorogenic, and ferulic acid content from tree tomato peel extract.

In **Figure 9.3**, the quantification of vanillic acid is also presented. These results shown concentrations of 0.39 ± 0.02 mg/g (SE), 0.38 ± 0.03 mg/g (Sox-E), 0.49 mg/g (UAE) and 0.53 mg/g (SFE) were obtained. Much higher results than those reported by Mutalib et al (2016) (0.001 mg/g) from the pulp and a solid-liquid ratio 1:20 (w/v) using ethanol 80% (Mutalib et al. 2016). Studies provided by Muñoz et al (2007) reported concentrations of 0.022 mg/g and 0.0025 mg/g of caffeic acid from peel and pulp, respectively (M. A. Muñoz Jáuregui et al. 2007; A. M. Muñoz Jáuregui et al. 2009). On the other hand, Mutalib et al (2016) reported the presence of caffeic acid in very low concentrations (0.001 mg/g) from pulp, ethanol 80%

and with the same solid-liquid ratio used in this work (1:10 w/v) (Mutalib et al. 2016). These values presented lower concentrations than those obtained in this study. The highest concentrations were presented with 0.31 ± 0.03 mg/g and 0.27 ± 0.02 mg/g through of SFE and UAE, respectively. While with SE and Soxhlet a concentration of 0.22 ± 0.02 mg/g and 0.21 ± 0.01 mg/g was achieved for each of these.

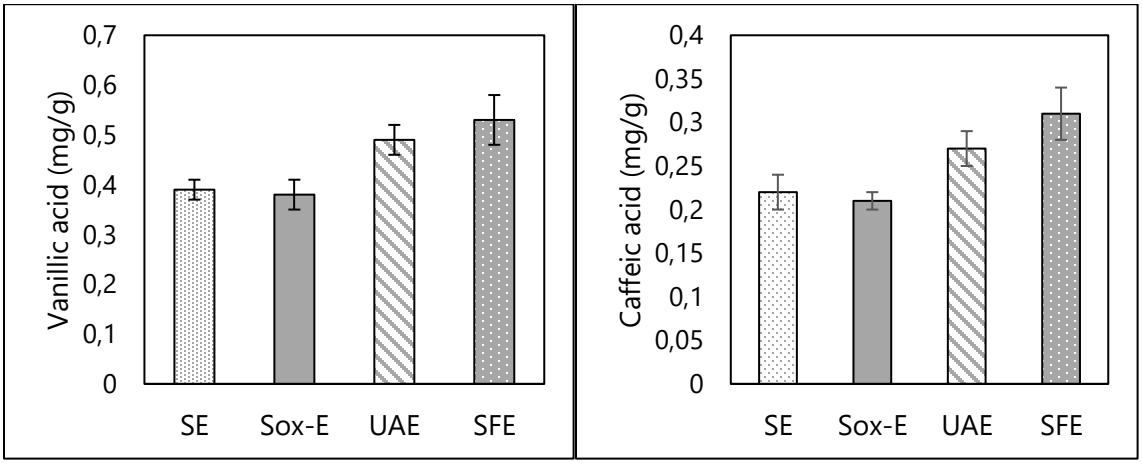


Figure 9.3. Vanillic and caffeic acid content from tomato tree peel extract.

Vasco et al (2009) also reported the presence of hydroxycinnamic acids (0.39 - 0.61 mg/g) in tree tomato peel extracts, which included ferulic acid, vanillic acid, caffeic acid and 4-hydroxybenzoic acid (Vasco et al. 2009). From these were obtained values in the range of quantified in this work in the sum of the concentrations obtained for ferulic acid (0.05 - 0.17 mg/g), vanillic acid (0.38 - 0.53 mg/g) and caffeic acid (0.21 - 0.31 mg/g), despite different conditions from those of this study. However, Vasco et al (2009) uses a greater volume of solvent and methanol as a solvent (Vasco et al. 2009).

Quercetin, the compound used as a dye, was identified in tree tomato peel extracts, presenting the behavior shown in **Figure 9.4** for each of the used technologies. This compound did not present a significant change in its concentrations through of conventional technologies, obtaining in them 0.02 mg/g. While through non-conventional technologies it showed an increase of 0.04 mg/g for UAE and 0.04 mg/g for SFE. From UAE and SFE values similar to those reported by Vasco et al (2009) were obtained with 0.04 - 0.06 mg/g, from

purple-red variety, using methanol 50%, solid-liquid ratio of 1:40 (w/v) for 1 hour (Vasco et al. 2009). While Muñoz et al (2007) reported 0.003 mg/g from tree tomato pulp using ethanol 60% for the preparation of the extracts (M. A. Muñoz Jáuregui et al. 2007). Similarly studies conducted by Gomes et al (2016) indicated low presence of quercetin and ferulic acid from tree tomato pulp (Gomes et al. 2016).

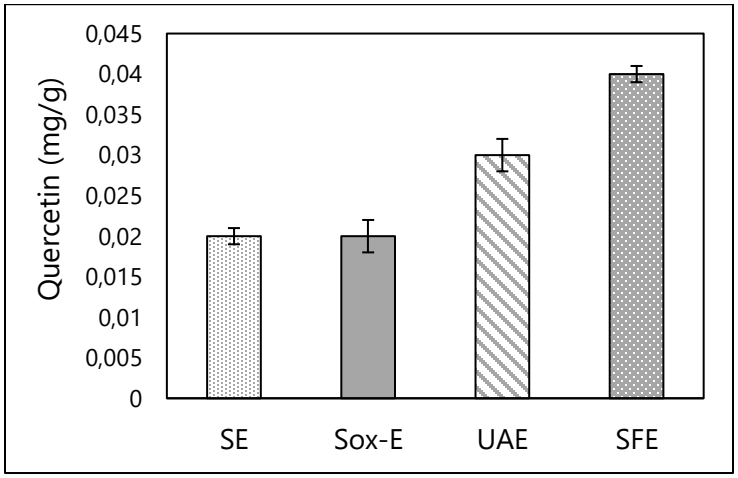


Figure 9.4. Quercetin content from tomato tree peel extract.

9.1.2. Simulation of antioxidants obtained from tree tomato peel

This study consisted of the determination of the prefeasibility of two technologies of extraction, solvent extraction and SFE. Additionally, it use of agroindustrial waste (tree tomato peel). For this, the yield obtained in the experimental procedure of polyphenolic compounds for each of the technologies was used. From these, the simulation of the extraction processes was carried out to carry out the energy, economic and environmental evaluation of the two proposed scenarios.

Energetic assessment

The obtaining of polyphenolic compounds from lignocellulosic materials as the tomato tree peel are present two technologies of greatest interest. On the one hand, the SE mentioned above is carried out to moderate conditions. However, long operation times are needed to

obtain high yields. Additionally, it is possible to find supercritical fluids extraction. This technology uses high pressure and temperatures moderate during short periods of operation. **Table 9.3** presents the energy and exergy as well as the percentage distribution in the different stages of the process. In this result, it was possible appreciated a high difference between both technologies in terms of energy values. The SE and SFE presented a consumption of 17,457.50 kW and 376.28 kW. In the case of SE, the high energy consumption was presented on the stage of purification due the low concentration presenting the polyphenolic compounds. This factor was caused by the high amount of solvent that was used in this process. While for the SFE, stages which presented higher energy consumption were sustaining temperature operation (heater) for the change in the temperature of -19°C to 50°C by the CO_2 and the step of purification of these. Where the last was employed in order to reduce the amount of CO_2 that should be fed to the system. In both cases the energy was distributed between energy in the form of heat (enthalpy) and potency. In this sense, the case of SE and SFE power represents 1.10 and 2.47% of the total energy consumed, respectively. However, given that in the case of SFE operating time was much lower in comparison with SE, the amount of power required for the process is lower.

Table 9.3. Results of exergy and energy analysis from tree tomato peel extract.

	Exergy (kW)		**Energy (kW)**	
	SE	SFE	SE	SFE
Total process	120,811.10	1,898.40	17,457.50	376.28
		Stage (%)		
Increased pressure	0.16	1.33	1.10	2.47
Heater	0.01	16.66	1.06	53.33
Extractor	0.04	26.12	0.61	0.13
Purification	99.75	13.81	94.73	0.06
Recovered ethanol	0.04	5.21	2.49	0.35
Recovered CO_2	-	36.87	-	43.65

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 CO_2 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.

Economic analysis

The economic evaluation of the extraction processes are of great importance for the determination of the prefeasibility of the processes. As can be seen in **Table 9.4**, the main item that provides the most influence in the production costs of these scenarios are the costs of raw materials. These costs also include the purchase and transportation of the raw material (tree tomato peel), the costs of the supplies required for the process, such as ethanol, carbon dioxide and water. These costs had a greater impact on the SE due to the high volume of solvent required in the extraction stage. Utilities costs presented their highest requirement in high pressure steam and cooling water, followed by electricity. On the other hand, the depreciation costs were highly influenced in the SFE, which correspond to the equipment costs or also called fixed costs. The total production costs were 1800% higher for solvent extraction than for supercritical fluid extraction. In the market, the sale price of antioxidants is around 9 USD/kg, competing SFE and presenting profit in the process.

Table 9.4. Productions cost of the proposed scenarios from tomato tree peel.

Item	SE (USD/kg)		SFE	
	(USD/kg)	Share (%)	(USD/kg)	Share (%)
Raw material cost	15.22	89.90	0.52	55.32
Utilities cost	0.13	0.77	0.01	1.06
Depreciation expense	0.28	1.65	0.28	29.79
General and administrative cost	1.23	7.27	0.05	5.32
Plant overhead	0.02	0.12	0.03	3.19
Maintenence cost	0.02	0.12	0.02	2.13
Operating labor cost	0.02	0.12	0.03	3.19
Operating charges	0.01	0.06	0.01	1.06
TOTAL	**16.93**	**100**	**0.94**	**100**

The SFE presents a great opportunity in the market due to its low production cost compared to SE. The analysis of the Net Present Value (NPV) showed a positive behavior for the SFE, which after two years, the investment in the process was recovered, as shown in **Figure 9.5**. While in the case of solvent extraction, there was no recovery of the investment. This is mainly due to the high costs of raw materials (ethanol 60%).

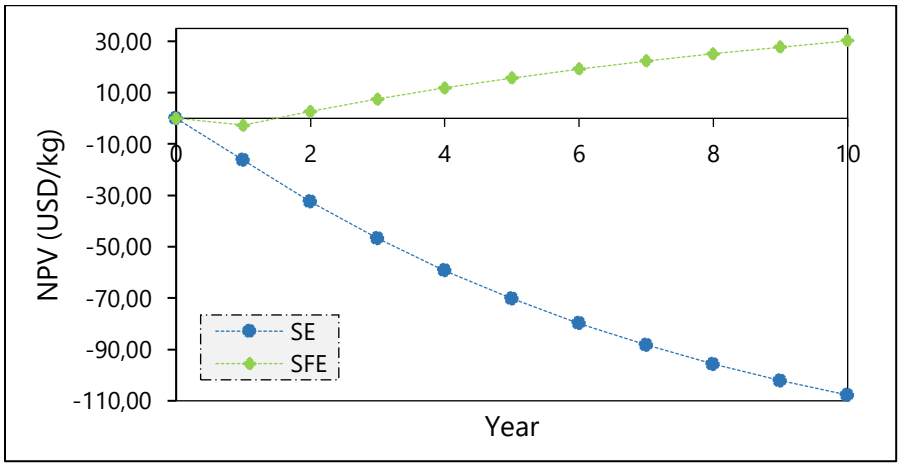


Figure 9.5. NPV of polyphenolic compounds extraction from tree tomato peel.

Environmental analysis

Two different technologies are presented to obtain a value-added product such as the antioxidants extraction. One way of comparing both technologies is an environmental analysis. **Figure 9.6** shows the result of the environmental analysis for SE and SFE. The negative values in each case indicate the decrease in the impact that can be obtained when the raw material was used for the extraction processes. Both SE and SFE show no significant differences in the indicators analyzed except in the AP (see **Figure 9.6-a**). Where the SE presented a PEI of 1.13. While the SE presented 2.61E-2 per kg of product. This indicator has presented a higher value compared to the value obtained for SFE, due to the fact that in the consumption of energy, combustion gases (NO_x, SO_2, CO_2, others amount) were generated that contribute to the generation of acid rain. The main reason why SE presented a higher energy consumption compared to SFE was the longer operating time used for the SE. Another factor that contributed to the high value of AP for SE was the large amount of solvent required in this process that was higher than the amount used in SFE; which could not be recovered in its entirety leaving traces that affect the process of environmental analysis.

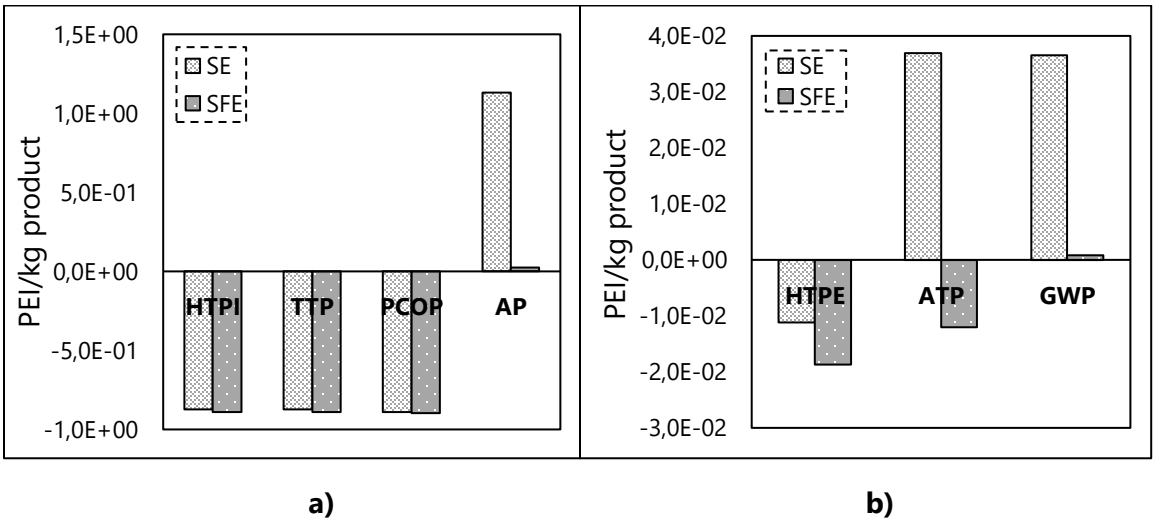


Figure 9.6. Potential environmental impact of obtaining antioxidants: a) HTPI, TTP, PCOP and AP; b) HTPE, ATP and GWP.

The determination of the environmental impact of each of the scenarios was a criterion for selecting the appropriate scenario to generate a lower impact on the environment. The SE and SFE processes gave a total environmental impact potential of -1.14 and -2.68 per kg of product, respectively. These demonstrated that they are not processes that impact the environment. Even so, the most friendly configuration was the one that used the 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 antioxidants using the tomato tree peel as raw material.

10.1.3. Conclusions

From these results it was possible to demonstrate that through of the use of unconventional technologies such as the UAE and SFE, which use less volume of solvent, time and environmental impact, it is possible to obtain a great variety of polyphenolic compounds as in the case of quercetin, vanillic acid and caffeic acid with equal or higher yield than conventional technologies. In addition, previous studies showed that tree tomato peel, a waste that is not used to obtain value-added compounds, has more total phenolic compounds and antioxidant capacity than pulp, making it a promising raw material for pharmaceutical applications and the food industry.

It was demonstrated that it is possible to obtain high quality polyphenolic compounds through the SFE technology. In addition, interesting yields were obtained to study the potential for obtaining metabolites through of the supercritical fluid extraction technology and solvent extraction that produced the tomato residues.

Exergy analysis is a powerful tool for 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, thus enabling maximization of operational

efficiency. In this sense the exergy analysis is presented as a tool for the formulation of solutions for the thermo - economic problems presented in industrial processes.

9.2. PASSIFLORAS

9.2.1. Experimental results

The use of *Passiflora* pulps (yellow passion fruit, purple passion fruit and sweet granadilla) in obtaining polyphenolic compounds, has a high potential as raw materials with constant annual harvest. This study consisted of obtaining extracts present in freeze-dried passiflora pulps by means of the application of three technologies: solvent extraction, UAE and SFE. For this, the experimental scheme shown in **Figure 9.7** was used. The extracts was analyzed through of Folin-Ciocalteu, DPPH and HPLC.

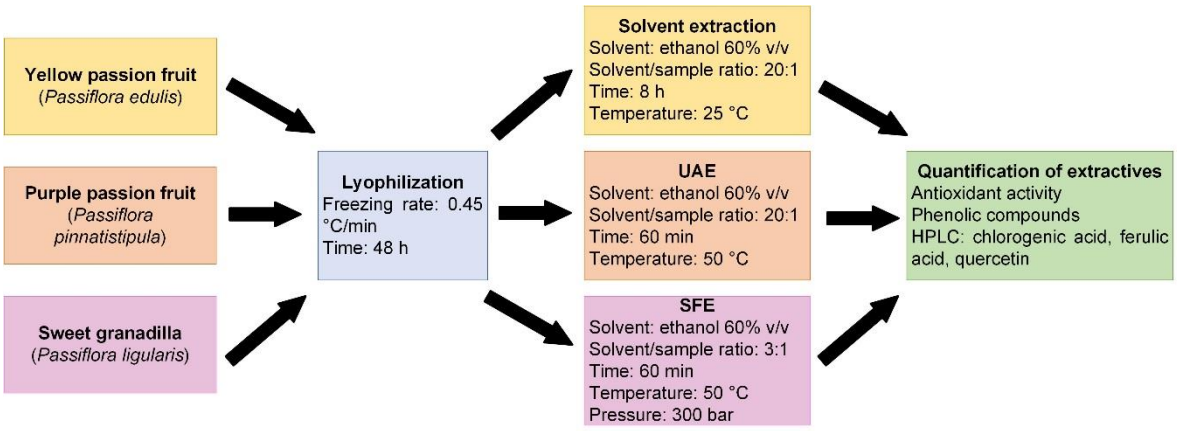


Figure 9.7. Experimental diagram for obtaining extracts from *Passifloras* pulps.

The lyophilization step was carried out in the Virtis Pilot Lyophilizer kit (Genesis SQ XL-70). The freezing rate of the process was 0.45°C/min for 32 hours, with the pressure chamber operating in a range of 300 - 500 mTorr. During this time the starting temperature was -38°C for one hour, followed by -45 C for 31 hours. The maximum surface temperature 43.3°C, presenting a final drying temperature of 37°C. It performed the lyophilization step was

obtained granulated raw materials manner shown in **Figure 9.8**, which was used for the extraction processes.

Figure 9.8. Lyophilized Passifloras pulps. A) yellow passion fruit, b) purple passion fruit, c) sweet granadilla.

Performed the extraction stage were quantified polyphenolic compounds present in each extract. The results of the analysis of TPC are presented in **Table 9.5**. In the case of yellow passion fruit as a raw material, better performance was presented by SFE (517.35 ± 0.69 mg GA/g) and UAE (432.04 ± 3.07 mg GA/g), which used a lower volume of solvent in the case of SFE and shorter operating time compared to solvent extraction. Comparing these results with data shown in literature, a higher yield was obtained than that reported by Wong et al (2014) with 1.58 mg GA/g which uses passion fruit peel, solvent extraction, ethanol 40% and an operating time of 60 min (Wong et al. 2014). On the other hand da Silva et al (2013) analyzed the leaves of the passion fruit obtaining 8.3 mg/g with a 1:25 solid-liquid ratio and at 100°C. This has a low content to that found in this work in the yellow passion fruit extract (da Silva et al. 2013). Oliviera et al (2016) reported a TPC of 336 ± 22 mg GA/g when using UAE, ethanol/water as a solvent and as a raw material yellow passion fruit cake (Oliveira et al. 2016). For SFE technology with CO_2 Oliviera et al (2016) reported the best yields at 150 bars with 31 ± 2 mg GA/g and 26.4 ± 0.8 mg GA/g using cake and granadilla seeds, respectively (Oliveira et al. 2016). In addition, research provided by Ramaiya, Bujang and Zakaria (2014) with solvent extraction reported values of 2.37 ± 0.11 mg GA/g, with methanol as solvent, values lower than those reported in this work (Ramaiya, Bujang, and Zakaria 2014).

On the other hand, the extract of purple passion fruit pulp showed a high content of TPC as shown in **Table 9.5**. The analysis of Folin-Ciocalteu for this extract resulted in lower yields of

TPC when using conventional solvent extraction technology (345.15 ± 0.02 mg GA/g). While UAE and SFE showed yields of up to 479.62 ± 0.03 mg GA/g and 620.68 ± 0.01 mg GA/g, respectively. These values were higher than those reported in literature by Ramaiya et al (2014) using raw materials from the same family, with 3.32 ± 0.06 mg GA/g and 2.17 ± 0.43 mg GA/g for *Passiflora Maliformis* and *Passiflora quadrangularis* leaves using solvent extraction (methanol), in a solid-liquid ratio 1:10 (w/v) for 48 hours (Ramaiya, Bujang, and Zakaria 2014).

Additionally, the TPC for sweet granadilla extract (see **Table 9.5**) gave the best result using SFE with CO_2 and ethanol 60% (636.742 ± 0.92 mg GA/g). While UAE and SE reached a value of 554,394 ± 0.72 mg GA/g and 376,592 ± 0.98 mg GA/g, respectively. From solvent extraction of *Passiflora ligularis* pulp, Saravanan and Parimelazhagan (2014) reported with methanol 137.90 ± 1.52 mg GA/g, petroleum ether 102.40 ± 1.89 mg GA/g and chloroform 125.70 ± 2.60 mg GA/g lower values than those determined in this study (Saravanan and Parimelazhagan 2014). Moreover Saravanan also used acetone (640.70 ± 2.95 mg GA/g) which presented a similar value to the extract obtained from SFE in this work. Research provided by Chirinos et al (2013) obtained a TPC of 6.4 mg GA/g using lyophilized sweet granadilla pulp as a raw material and methanol/water mixture as a solvent (Chirinos et al. 2013). From the three raw materials used, a higher content of total polyphenol compounds was obtained from sweet granadilla extract (376.59 - 636.74 mg GA/g), followed by purple passion fruit extract (345.15 - 520.68 mg GA/g). In the case of sweet granadilla this result is favorable, being a crop with high annual production, to bear fruit throughout the year.

Table 9.5. TPC (Folin-Ciocalteu) from *Passifloras*.

Technology	Yellow passion fruit (mg GA/g)	Purple passion fruit (mg GA/g)	Sweet granadilla (mg GA/g)
SE	300.68 ± 0.68	345.15 ± 0.02	376.59 ± 0.98
UAE	432.04 ± 3.07	479.62 ± 0.03	554.39 ±0.72
SFE	517.35 ± 0.69	620.68 ± 0.01	636.74 ± 0.92

The antioxidant activity for yellow passion fruit extract showed a higher value with SFE followed by SE with 65.33% and 62.67%, respectively. Analyzing the results obtained with the literature studies were found. Where through solvent extraction and from the yellow passion fruit peel reported by Wong et al (2014), it showed a percentage of inhibition around 57%, a value higher than that obtained in this work (45.21%) shown in **Table 9.6**. However, the study carried out by Wong et al (2014) uses a solid-liquid 1:10 ratio, using less solvent than the one used in this work (Wong et al. 2014). This value may be due to the variation in the operating conditions or origin of the raw material used. Likewise, da Silva et al (2013) reported a value of 1100 µg/mL for the extract from yellow passion fruit leaves with solvent extraction (da Silva et al. 2013). These presented a greater antioxidant activity than that reported in this work, which may be due to the raw material, use of water as a solvent and extraction temperature of 100°C. Other authors reported values of EC_{50} with SE 653.5 ± 6.1 µg/mL with yellow passion fruit pulp and methanol as solvent (Ramaiya, Bujang, and Zakaria 2014), UAE 241 µg/mL and with SFE 8565 µg/mL using passion cake and ethanol/water as solvent (Oliveira et al. 2016).

The purple passion fruit extract showed up to 70.87% inhibition as observed in the **Table 9.6**. Where the EC_{50} resulted in an antioxidant activity of up to 31.95 µg/mL, lower than that reported by Ramaiya, Bujang and Zakaria (2014) with 456.9 ± 13.1 µg/mL with *Passiflora Maliformis* and 785.2 ± 1.8 µg/mL (Ramaiya, Bujang, and Zakaria 2014). However, that studies used methanol as a solvent, a solid-liquid ratio of 1:10 (w/v) and 48 hours of processing. On the other hand, sweet granadilla extracts obtained a 73.04% inhibition with SFE (see **Table 9.6**). Where the EC_{50} obtained a maximum content of 69.37 µg/mL, which is higher than that reported by Saravanan and Parimelazhagan (2014) with 23.71 µg/mL using methanol (Saravanan and Parimelazhagan 2014).

Table 9.6. Antioxidant activity from *Passifloras*.

	Yellow passion fruit		Purple passion fruit		Sweet granadilla	
	% Inhibition	EC_{50} (µg TE/mL)	% Inhibition	EC_{50} (µg TE/mL)	% Inhibition	EC_{50} (µg TE/mL)
SE	45.21	62.67	70.87	29.19	42.75	68.37
UAE	56.37	37.12	64.75	31.95	48.46	48.30
SFE	42.61	65.33	60.00	13.76	73.04	25.71

In the quantification of the polyphenolic compounds by HPLC showed as a result that yellow passion fruit extracts had the highest presence of chlorogenic acid with respect to the other raw materials used with 6.70 ± 0.11 mg/g with SE, 9.73 ± 0.03 mg/g with UAE and 9.82 ± 0.08 mg/g of SFE as observed in the **Table 9.7**. Where the technology with SFE and UAE presented similar performances. While the purple passion fruit and sweet granadilla showed a concentration of to 2.19 ± 0.14 mg/g and 3.25 ± 0.06 mg/g, respectively. This concentration of chlorogenic acid shows values close to the grains of *Coffea canephora* and Artichoke Leaves reported a value of 9.25 mg/g and 8.40 mg/g, respectively (Marín and Puerta 2008; Saleh et al. 2016). Additionally, the analysis in the extracts showed the presence of ferulic acid as shown in **Table 9.7**. Where the yellow passion fruit extract reported values between 1.97 - 15.42 mg/g, purple passion fruit extract 2.81 - 13.37 mg/g and sweet granadilla extract from 0.64 - 6.27 mg/g. The determination of ferulic acid showed that the use of non-conventional technologies is an alternative with high potential due to the improvement in yields, since through this a greater income is achieved in the matrix of the raw material increasing the selectivity in the extraction process.

Quercetin was another compound determined in the extracts by HPLC. This compound did not show a trend in technology as shown in the **Table 9.7**; in which values of to 7.60 ± 0.06 mg/g (SFE), 5.55 ± 0.19 mg/g (UAE) and 15.76 ± 0.13 mg/g (SE) were obtained with yellow passion fruit, purple passion fruit and sweet granadilla, respectively. These extracts of pulp obtained from each of the *Passifloras* can compete with raw materials reported in literature such as onion (4.83 mg/g), carrot (1.50 mg/g) and fruits such as strawberry (0.50 mg/g) and

blackberry (0.16 mg/g) when presenting higher concentrations (Paganga, Miller, and Rice-Evans 1999; HERRMANN 1976; Hakkinen and Torronen 2000). On the other hand, vanillic acid and caffeic acid showed low concentrations from yellow passion fruit and sweet granadilla as shown in **Table 9.7**. While from the purple passion fruit concentrations of to 0.70 mg/g and 0.33 mg/g were obtained for vanillic acid and caffeic acid, respectively. This through of the technology of ultrasound assisted extraction.

Table 9.7. Polyphenolic compounds content in *Passifloras*.

Raw material	Technology	Chlorogenic acid (mg/g)	Ferulic acid (mg/g)	Quercetin (mg/g)	Vanillic acid (mg/g)	Caffeic acid (mg/g)
Yellow passion fruit	SE	6.70±0.11	1.97±0.08	1.43±0.09	0.06±0.01	0.03±0.00
	UAE	9.73±0.03	13.0±0.05	7.06±0.02	0.03±0.00	0.01±0.00
	SFE	9.82±0.08	15.42±0.10	7.60±0.06	0.03±0.00	0.02±0.00
Purple passion fruit	SE	0.91±0.07	2.81±0.19	4.13±0.11	0.42±0.04	0.24±0.03
	UAE	1.33±0.06	3.79±0.18	5.55±0.19	0.70±0.04	0.33±0.03
	SFE	2.19±0.14	13.37±0.32	4.13±0.15	0.19±0.02	0.10±0.01
Sweet granadilla	SE	0.54±0.03	0.64±0.04	15.76±0.13	0.04±0.00	0.02±0.00
	UAE	2.25±0.09	1.51±0.07	0.66±0.01	0.03±0.00	0.02±0.00
	SFE	3.25±0.06	6.27±0.10	11.46±0.11	0.01±0.00	0.01±0.00

9.2.2. Conclusions

The extracts from *Passiflora* are a great source of various polyphenolic compounds. Where conventional technologies such as UAE and AFE are alternatives for obtaining improved performance, selectivity and reducing operating time. Additionally, the presence of chlorogenic acid, ferulic acid and quercetin with high concentrations could be identified. While, the vanillic and caffeic acid presented lower concentrations.

9.3. OLIVE RESIDUES

Olive waste such as olive pomace produced in large quantities during the process of obtaining olive oil. Given their compositions are raw materials that can be used in obtaining antioxidants. In this work the use of tree raw materials is carried out through of the development of extraction processes, in which the effect in the use of supercritical fluid extraction is demonstrated before the conventional technology of solvent extraction. The olive residues (olive pomace, olive tree pruning and olive leaf) were conditioned, obtaining the raw material shown in

Figure 9.9.

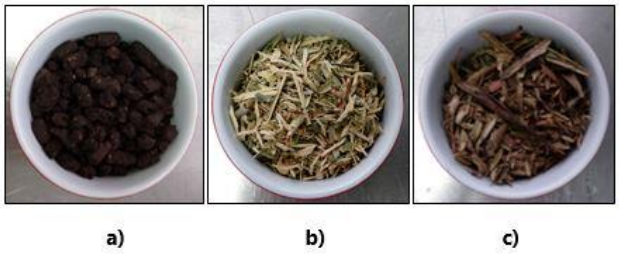


Figure 9.9. Olive residues: a) olive pomace, b) olive tree pruning, c) olive leaves.

The characterization of the different olive biomasses used was carried out following the scheme of **Figure 9.10**.

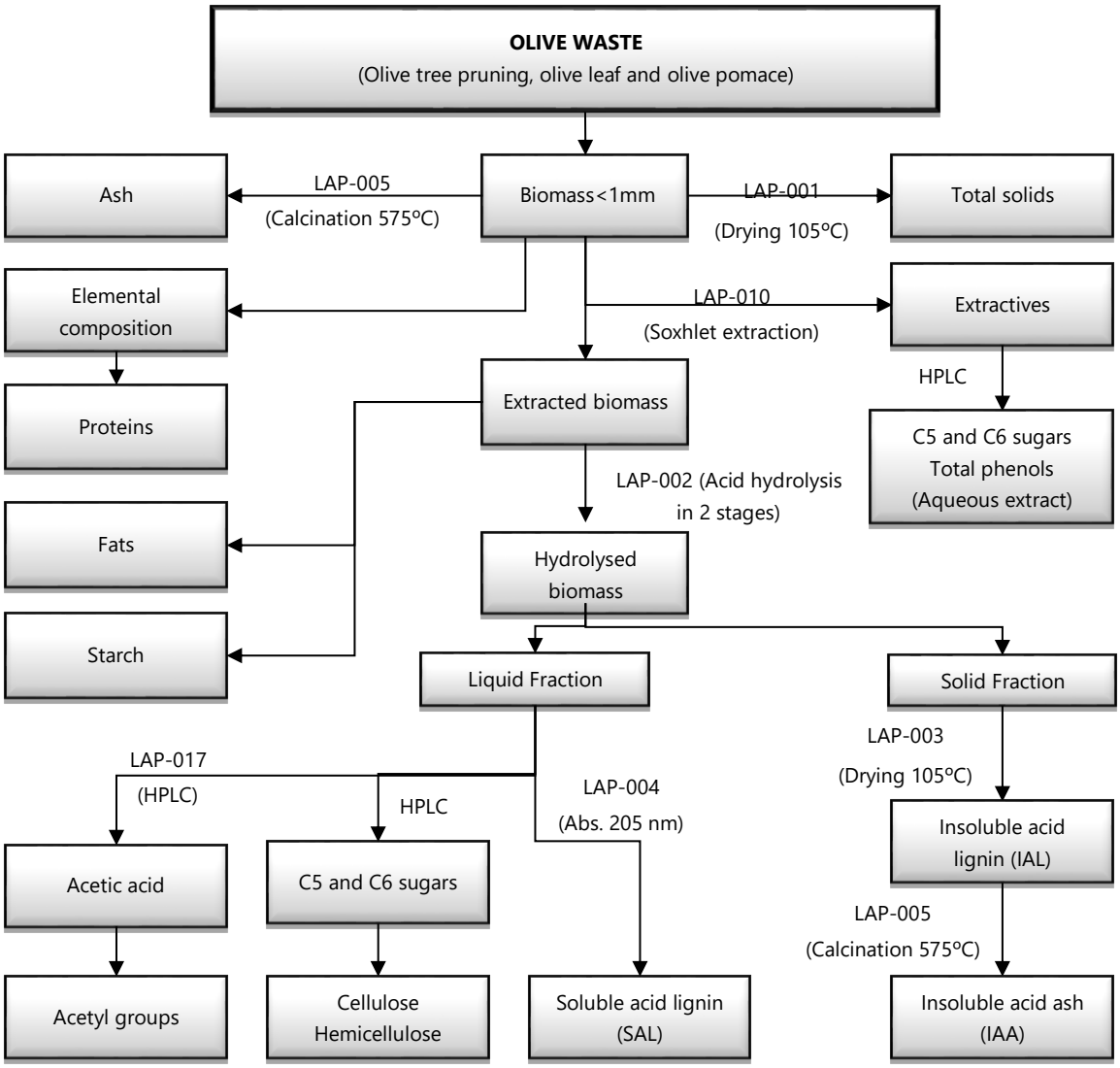


Figure 9.10. Scheme of the procedure for the characterization of olive residues.

9.3.1. Experimental results

Table 9.8 shows the composition of the three biomasses used in this work. It should be noted that in the three the largest fraction are the extractives with values between 28.6 and 49.7% (OTP<OL<OP) in agreement with the values reported by other authors (Cara et al. 2008). These values are much higher than other biomass in the olive grove, such as olive stone, which shows values of 5.5-8.9% (Lama-Muñoz et al. 2014; García Martín et al. 2010) and superior to other biomass such as rapeseed Straw 13.1-14.6% (López-Linares et al. 2014; Díaz et al. 2010), sunflower stalks 15.9-21.6% (Díaz et al. 2011), sugar-cane bagasse 5.6-

5.75% (Mesa et al. 2010), eucalyptus chips 5.5-18.6% (Lima et al. 2017), wheat straw 4.9-5.2% (Smit and Huijgen 2017; Vargas et al. 2012) or corn stover 13.4-16.7% (Adjalle et al. 2017; Katahira et al. 2013).

Regarding the fraction of structural carbohydrates (cellulose + hemicellulose) is between 20.5 and 36.1% (EOP <OL <OTP) in the order of values reported in literature for these biomasses (Romero-García et al. 2014). In order to valorize this carbohydrate fraction, the previous removal of the extractives has shown a very substantial improvement in the overall recovery of sugars (cellulosic + hemicellulosic). This improvement may be due to the avoidance of "lignin-like" formation during pretreatment, which improves the subsequent stage of enzymatic hydrolysis (I. Ballesteros et al. 2011). In addition, these extracts show an important content of phenols between 2.92 and 6.14% (OTP <OL <OTP) which are toxic for the microorganisms responsible for the produced sugars fermentation (Jönsson, Alriksson, and Nilvebrant 2013). Remove part of the extractives (phenolics) can have a double benefit on the one hand reduce the toxicity of liquor improving biotransformation thereof and other recovering bioactive compounds with antioxidant capacity and high added value that can make more viable a potential biorefinery. Bioactive compounds with antioxidant capacity and a high added value such as oleuropein, hydroxytyrosol, tyrosol, among others, are present in the different biomasses of the olive grove (Romero-García et al. 2014; Ruiz et al. 2017).

Finally, as regards the lignin content, the great difference between OL and, EOP and OTP should be highlighted, 35.7% at 20.9% and 17.7% respectively. The value found of lignin in OL is quite similar to that reported by García-Maraver (39.6%) (Garcia-Maraver et al. 2013). The transformation of this lignin in bioproducts with high added value would also allow the advancement of biorefinery from the biomasses studied (Fernández-Rodríguez et al. 2017). In summary the composition of these olive grove raw materials with a large fraction of extractives makes them different from the rest and therefore the processes of valorization will also be. An initial stage of extraction is essential in order to remove the phenolic

compounds, improving later stages of the process, in addition to obtaining compounds with high added value.

Table 9.8. Composition of olive residues.

	OP			OTP			OL		
Total solid (%)	91.43	±	0.15	93.41	±	0.01	94.16	±	0.09
Composition (% dry matter)									
Extractives	49.71	±	0.61	28.62		1.33	37.93		0.97
Water-extract	45.78	±	0.45	23.49	±	1.39	25.29	±	0.92
Glucose	7.63	±	0.26	7.27	±	0.11	4.19	±	0.18
Xylose	0.45	±	0.09	nd	±	0.00	nd	±	0.05
Galactose	1.37	±	0.04	0.73	±	0.06	0.67	±	0.05
Arabinose	1.67	±	0.06	0.28	±	0.25	1.38	±	0.16
Mannose	0.89	±	0.01	1.13	±	0.05	0.00	±	0.00
Mannitol	5.03	±	0.15	3.00	±	0.05	0.22	±	0.10
Total phenols*	6.14	±	0.14	2.92	±	0.01	4.25	±	0.08
Ethanol-extract	3.93	±	0.22	5.13	±	0.24	12.64	±	0.23
Cellulose	9.78	±	0.34	21.58	±	0.18	13.89	±	0.26
Hemicellulose	10.71	±	0.20	14.47	±	0.20	7.88	±	0.20
Xylose	9.90	±	0.27	10.18	±	0.02	5.05	±	0.15
Galactose	0.98	±	0.03	2.23	±	0.04	1.31	±	0.04
Arabinose	0.95	±	0.01	3.22	±	0.15	2.55	±	0.08
Mannose	0.25	±	0.04	0.64	±	0.09	0.00	±	0.06
Lignin	20.90	±	0.08	17.72	±	0.39	35.72	±	0.24
Acid-soluble lignin	1.91	±	0.01	2.33	±	0.07	2.67	±	0.04
Acid-insoluble lignin	18.99	±	0.07	15.39	±	0.39	33.05	±	0.23
Acetyl groups	1.15	±	0.06	0.90	±	0.06	1.84	±	0.06
Ash	8.70	±	0.19	3.85	±	0.55	8.22	±	0.05

*expressed as gallic acid (GA), Results are expressed as g/100 g raw material oven dry weight.

The analysis in obtaining extracts of olive residues could show a higher content of total phenolic compounds from the olive pomace as seen in **Table 9.9**. However, their difference was not as significant compared to the olive leaf. On the other hand, from the use of olive pomace, the best concentration of TPC could be obtained through SFE at 300 bars (14.01 ±

0.03 mg GA/g). While from the conventional technology a concentration of up to 12.89 ± 0.22 mg GA/g was obtained. Additionally, by using a pelletized olive pomace, higher TPC values could be found in this work than those found in literature. Where Cepo et al (2017) reported concentrations between 2.2 - 3 mg GA/g through of solvent extraction (Čepo et al. 2017). While Goldsmith et al (2018) obtained higher values (22.01 mg GA/g) (Goldsmith et al. 2018). Chanioti and Tzia (2017) from the use of olive pomace oil reported a TPC between 0.165 - 0.262 mg GA/g (Chanioti and Tzia 2017). Meanwhile, Alburquerque (2004) determined concentrations between 6.2 - 23.9 mg GA/g for the alperujo residue of the olive tree coming from the second phase of decantation (Alburquerque 2004). While the olive pomace is obtained in the third phase through of hot water.

On the other hand, olive tree pruning obtained the best values with SE followed by the SFE at 300 bar with 11.54 ± 0.20 mg GA/g and 10.39 ± 0.18 mg GA/g, respectively. This value was higher than that determined by Conde et al (2009), which obtained a TPC of up to 1.89 mg GA/g (Conde et al. 2009). For the olive leaf, a similar behavior was observed as the other two raw materials, through the use of a pressure of 300 bars, the highest concentration was presented with SFE (13.12 ± 0.26 mg GA/g). The TPC value obtained in this study from of the olive leaf extract was lower than that reported by some studies, which may be due to the use of other technologies, longer extraction time and origin of the raw material. Al-Rimawi et al (2014) through maceration with water at 40°C obtained a TPC between 18.63 - 48.30 mg GA/g, in which determined the influence of the culture conditions and the time of year (Al-Rimawi et al. 2014). Hassam et al (2013) obtained up to 66 mg GA/g with solvent extraction (Margarita Hussam Ahmad-Qasem et al. 2013). While Ahmad et al (2014) reported values of 25-67 mg GA/g and Ibbay et al (2014) from 21.56 - 47.58 mg GA/g (Margarita H. Ahmad-Qasem et al. 2014; İlbay, Şahin, and Büyükkabasakal 2014). Through the use of olive cake were found values of up to 42.26 mg GA/g using methanol during 24 hours (Uribe et al. 2014).

Table 9.9. TPC of olive waste extract.

Technology	Olive pomace (mg GA/g)	Olive tree prunning (mg GA/g)	Olive leaf (mg GA/g)
SE	12.89 ± 0.22	11.54 ± 0.20	11.28 ± 0.14
SFE-200 bar	9.18 ± 0.17	7.94 ± 0.13	5.83 ± 0.10
SFE-250 bar	12.35 ± 0.25	8.66 ± 0.19	9.76 ± 0.16
SFE-300 bar	14.01 ± 0.31	10.39 ± 0.18	13.12 ± 0.26

The analysis of the antioxidant activity presented the highest EC_{50} with the olive leaf (274.91 - 382.43 µg/mL). While OTP had the lowest value (8.38 - 13.77 µg/mL) as shown **Table 9.10**. The use of OP for the extraction of its compounds, presented the highest antioxidant activity by SFE-300 bar (85.33 ± 7.04 µg/mL). With this raw material SFE obtained 23.33% of antioxidant activity greater than through SE. This EC_{50} value obtained was lower than that reported by Cepo (2017), which determined values of antioxidant activity of up to 750 µg/mL (Čepo et al. 2017) and Goldsmith et al (2018) up to 263 µg/mL for the OP (Goldsmith et al. 2018). On the other hand, results similar to those found by Pereira et al (2016) by using alperujo an EC_{50} between 28.79 - 41.56 µg/mL (Alexandra and Gameiro 2016).

In the case of OTP, the best values were obtained with SFE-200 and SFE 250 bars with 13.77 ± 0.72 µg/mL and 12.8 ± 0.42 µg/mL, respectively. These antioxidant activity values were higher than those reported by Zbid et al (2009), which obtained an EC_{50} of 6.8 µg/mL when using solvent extraction (Zbidi et al. 2009). For the olive leaves, Taamalli et al (2012) determined an antioxidant activity of 550.5 - 796.1 µg/mL and 284.9-633.5 µg/mL with SE and SFE, respectively (Taamalli et al. 2012). While in this work the best values were obtained with SE with 382.43 ± 10.47 µg/mL and SFE-300 bar with 365.18 ± 8.99 µg/mL, which presents the range of that reported by Taamalli et al (2012).

Table 9.10. Antioxidant activity of olive waste extract.

Technology	Olive pomace EC_{50} (µg/mL)	Olive tree prunning EC_{50} (µg/mL)	Olive leaf EC_{50} (µg/mL)
SE	69.19 ± 5.20	11.68 ± 0.83	382.43 ± 10.47
SFE-200 bar	46.20 ± 3.58	13.77 ± 0.72	274.91 ± 9.18
SFE-250 bar	64.72 ± 6.41	12.84 ± 0.42	321.25 ± 11.35
SFE-300 bar	85.33 ± 7.04	8.38 ± 0.54	365.18 ± 8.99

The results of the quantification of polyphenolic compounds present in the OP, OTP and OL extracts are shown in **Table 9.11**. Among the compounds identified in these extracts were hydroxytyrosol, chlorogenic acid, quercetin, vanillinic acid, ferulic acid, caffeic acid and vanillin (only present in olive tree pruning extracts). In the case of hydroxytyrosol showed the highest concentration through SFE-300 bar from the OL (1.35 ± 0.05 mg/g) and OP (1.25 ± 0.01 mg/g). While the chlorogenic acid obtained the highest concentration with solvent extraction through of the use of OP (0.31 ± 0.02 mg/g) and OL (0.09 ± 0.004 mg/g). But in the case of the use of OTP as a raw material, it obtained up to 0.24 ± 0.04 mg/g with SFE-300 bar. The quantification of vanillin obtained concentrations of up to 0.79 ± 0.04 mg/g with SE from OTP. Quercetin and caffeic acid showed the highest concentrations in the extracts of OP with up to 0.09 mg/g. Where for the quercetin the SE contributed the best results, and for the caffeic acid the SFE. On the other hand, ferulic acid was the second compound followed by hydroxytyrosol with greater presence in the extracts analyzed. This compound presented the greatest presence from the use of OP as raw material (0.52 - 0.99 mg/g), and the best results with SFE-200 bar (0.99 ± 0.01 mg/g).

These concentrations of polyphenolic compounds obtained showed values in the range of that reported in other investigations. Where Pereira et al (2016) reported content of hydroxytyrosol (0.1 - 0.9 mg/g), as well as tyrosol and oleuropein from alperujo (Alexandra and Gameiro 2016). While other studies determined in the OP a hydroxytyrosol concentration of 0.08 mg/g (Čepo et al. 2017). In OTP Conde et al (2009) obtained concentrations of 1.2 - 1.9 mg/g for vanillin, 1.3 - 1.9 mg/g for vanillic acid and 25.4 - 49.3

mg/g for hydroxytyrosol (Conde et al. 2009). For the OL, Jemai et al (2008) reported the presence of hydroxytyrosol (Jemai et al. 2008). While Hussam et al (2013) and Taamalli et al (2012) determined the presence of luteolin, caffeoyl and oleuropein, quinic acid and apigenin (Margarita Hussam Ahmad-Qasem et al. 2013; Taamalli et al. 2012).

Table 9.11. Polyphenolic compounds present in olive waste extracts.

Raw material	Technology	Hydroxytyrosol (mg/g)	Chlorogenic acid (mg/g)	Ferulic acid (mg/g)	Vanillin (mg/g)	Quercetin (mg/g)	Vanillic acid (mg/g)	Caffeic acid (mg/g)
Olive pomace	SE	1.02 ± 0.008	0.31 ± 0.02	0.76 ± 0.008	NR	0.06 ± 0.002	0.16 ± 0.01	0.09 ± 0.001
	SFE-200 bar	0.91 ± 0.005	0.13 ± 0.005	0.99 ± 0.01	NR	0.09 ± 0.005	0.07 ± 0.004	0.02 ± 0.001
	SFE-250 bar	0.95 ± 0.007	0.11 ± 0.008	0.71 ± 0.003	NR	0.05 ± 0.003	0.11 ± 0.01	0.04± 0.002
	SFE-300 bar	1.25 ± 0.01	0.08 ± 0.003	0.52 ± 0.005	NR	0.04 ± 0.02	0.13 ± 0.008	0.05 ± 0.002
Olive tree pruning	SE	0.12 ± 0.02	0.06 ± 0.005	0.11 ± 0.01	0.79 ± 0.04	0.01 ± 0.002	0.04 ± 0.004	0.02 ± 0.003
	SFE-200 bar	0.03 ± 0.00	NR	0.19 ± 0.03	0.40 ± 0.04	0.02 ± 0.001	0.03 ± 0.002	0.02 ± 0.002
	SFE-250 bar	0.07 ± 0.01	0.09 ± 0.002	0.15 ± 0.01	0.45 0.03	0.03 ± 0.002	0.01 ± 0.001	NR
	SFE-300 bar	0.18 ± 0.01	0.24 ± 0.04	0.04 ± 0.01	0.60 0.07	0.03 ± 0.002	0.01 ± 0.002	NR
Olive leaves	SE	0.97 ± 0.04	0.09 ± 0.004	0.22 ± 0.02	NR	0.01 ± 0.001	0.05 ± 0.002	0.03 ± 0.001
	SFE-200 bar	0.42 ± 0.02	NR	0.10 ± 0.2	NR	0.02 ± 0.002	0.02 ± 0.003	0.01 ± 0.02
	SFE-250 bar	0.73 ± 0.00	0.01 ± 0.002	0.11 ± 0.02	NR	0.04 ± 0.003	0.02 ± 0.001	0.01 ± 0.01
	SFE-300 bar	1.35 ± 0.05	NR	0.13 0.02	NR	0.07 ± 0.005	0.01±0.002	NR

9.3.2. Conclusions

The use of olive residues presents high economic and environmental benefits to be raw materials with high potential for obtaining antioxidants and which are not used in its entirety. From the extraction of these residues, it was possible to identify the presence of a great variety of polyphenolic compounds such as hydroxytyrosol, chlorogenic acid and caffeic acid that have a high antioxidant, anticancer and antidiabetic capacity, among others. Additionally, the effect of the supercritical fluid extraction was observed against conventional extraction (solvent extraction). Where in the SFE there was a higher concentration of total polyphenolic compounds and higher antioxidant activity. On the other hand, a higher performance at high pressures (300 bar) was observed, demonstrating that the implementation of non-conventional technologies such as the SFE are promising alternatives for the application at the industrial level since it is a technology that requires less time and quantity of solvent for its development.

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