Chapter 7

Chemistry and Biotransformation of Coffee By-Products to Biofuels

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Additional information is available at the end of the chapter

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Abstract

Coffee is one of the most consumed infusion drinks in the world and contains a large variety of chemical compounds responsible for their sensory qualities and their effects on the body. The beneficial effects of coffee have been attributed only to its most important and researched ingredient, caffeine, but now it is known that other components have also contributed to its properties. Due to a huge demand for this product, large amounts of waste are generated in the coffee industry, which are toxic and represent serious environmental problems. During the process of mechanical extraction of the coffee seed, residues generated are: pulp, mucilage and parchment, mainly. Coffee cherry consists of soluble carbohydrates, insoluble polysaccharides, lipids, nitrogenous components, caffeine and minerals. More than 50% is considered a waste; it no longer has any commercial application, knowing that its components could be exploited for the production of inputs and energy. This chapter presents the chemistry and biotransformation of by-products and coffee residues into second-generation biofuels, which can be bioethanol, biogas and biodiesel by fermentation, anaerobic digestion and trans-esterification, respectively. Biofuels offer greater energy security, lower emissions of greenhouse gases and particulate matter, rural development, reduced demand for oil, among others.

Keywords: coffee cherry components, green coffee, roasted coffee, caffeine, biotransformation

1. Introduction

1.1. Coffee cherry

The coffee is the fruit and dried seed of the coffee plant regardless of whether it has been toasted or ground of the plant of the genus *Coffea* (**Figure 1**), generally of the cultivated species, and the products of these in their different stages of the process and use intended for human consumption. The fruits of coffee are often called cherries, since their appearance is like these and each one contains two hemispherical seeds. Coffee cherry is the set of non-dried fruits of *Coffea* plants after harvest [1].

According to the International Coffee Organization (ICO), in the period 2015–2016, countries around the world produced 147,997 in thousands of bags of 60 kg of coffee, of which two main varieties are produced: arabica and robusta. On the other hand, the consumption of coffee was 151,303 in thousands of bags of 60 kg of coffee. Data of global coffee production and consumption are summarized in **Table 1**.

Mexico contributed more than 2800 in thousands of bags of 60 kg, the most of the production is distributed in 13 states, including Chiapas, Veracruz, Puebla and Oaxaca, where more than 80% of production is concentrated. Approximately 402,099 tons of coffee cherry was grown in Chiapas, giving it the first place in national production; due to this, Mexico is the ninth largest coffee producer in the world [2].

In the historic part, coffee arrived in Mexico more than 200 years ago, entering Veracruz from Cuba. During the time of 1876–1911 (the Government of Porfirio Díaz), coffee plantation grew importantly in large specialized farms and later became an activity of small producers, mostly of indigenous origin.

A total of 97% of the coffee produced in Mexico is under the shade of trees, which respects the balance of the environment and protects many varieties of plants and animals. The strong harvest season covers the months from October to March.

Due to the characteristics of Mexican soils where coffee grows, mostly of volcanic type, its flavour is very characteristic, and its aroma is intense and with notes of chocolate, spices and flowers. This has served the Mexican coffee to receive two appellations of origin: Veracruz coffee and Chiapas coffee.

1.2. Biofuels—characteristics and advantages

Most economic scenarios are based on growth in global energy demand over the next 20 years. In this sense, nuclear and renewable energy as biomass, wind, hydropower, solar, photovoltaic, geothermal, etc., although do expansion, will remain secondary compared to fossil fuels, rising from 23.7 to 30% by 2040, concentrated in transportation sector and the oil industry mainly [3, 4].

In this context, the use of biofuels (fuels of biological origin) has huge potential and has a stronger expansion compared to other renewable alternatives. Biofuels are produced from biomass, a renewable resource provided that the crop cycle is respected [5].

Figure 1. Coffee cherry fruit (source: Authors).

Crop year (2015–2016)	Production	%total	Consumption	%total
Africa	16,831	11.37	10,815	7.15
Asia & Oceania	47,428	32.05	31,609	20.89
Mexico & Central America	16,739	11.31	5257	3.47
South America	66,997	45.27	24,717	16.34
Europe			50,870	33.62
North America			28,035	18.53

Table 1. Data of global coffee production and consumption.

Biofuels offer several advantages. It is considered that by reducing the demand for fossil fuels, biofuels could make the energy supply safer. Its use would also reduce import costs to countries with energy deficits and provide better trade balance and balance of payments. The emissions of greenhouse gas, carbon monoxide and particulate matter can be significantly reduced. Biofuels can also improve vehicle performance; in fact, the lubricity of biodiesel prolongs the life of conventional diesel engines [6].

Business will be generated and an increase in economic activity will be allowed with the transition to biofuels. Biofuels are renewable and both bioethanol and biodiesel are clean combustion. Another important aspect is that they can be marketed easier than other alternatives, because they can be stored and distributed using existing infrastructure. Biofuels should play a significant role in climate change policies and this will certainly open up opportunities for the development of biofuels in developing countries [7].

2. Main varieties of coffee

Robusta coffee (*Coffea canephora*) comes from Central Africa, which grows in dry areas and is a little digestive with a bitter taste. It has a lot of body with little fragrance and contains about twice as much caffeine as Arabica. The robusta plants usually have a size that can reach up to 6 m, and according to ICO, their cultivation represents 42% of the world production; it is more resistant to attacks of parasites, diseases and high temperatures (hence its name).

Robusta grains are smaller than those of arabica. Depending on the variety of plant, the seed shape is round, oval or elliptical with sharp tips. Robusta varieties include Comilon, Kouilloi, Niaouli and Uganda.

The other variety is arabica coffee (*Coffea arabica*), a native species of Ethiopia, which also grows in other countries that are between 500 and 2400 m above sea level. This variety represents 58% of world production and has a caffeine concentration of up to 1.7%. The result of this is that arabica coffee origin is considered to be of much higher quality, not because of its much lower caffeine content, but because of its intrinsic, more aromatic and aromatic organoleptic qualities; therefore, it has more aroma and softness. The arabica seed is flattened and elongated and its green colour is more intense. Some subspecies of arabica are Moka, Maragogype, Bourbon, Mundo Novo, Caturra, Icatu, Catuai, Catimor, Creole, among others.

3. Methods of characterization of coffee

Many authors that carry out investigations with coffee use different methodologies to characterize. Proximate composition, reducing and total sugar contents are evaluated on the basis of standard methodologies [8]. The contents of cellulose, hemicellulose and lignin are determined by crude fibre analysis [9].

Sugars, ethanol, glycerol and volatile fatty acids are determined by HPLC with a refractive index detector [10]. The concentration of glucose, xylose, arabinose, mannose and galactose also can be determined by HPLC using a refractive index detector. Furfural and hydroxymethylfurfural (HMF) are determined by HPLC using a UV detector [11]. Minor volatile components are analysed in a GC-MS with capillary-coated column [12].

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Important studies of gas chromatography coupled to mass spectrometry (GC-MS) have been performed to determine which and how many compounds are responsible for coffee aroma. Volatile compounds can be extracted by the simultaneous distillation and extraction (SDE) method and analysed in a GC-MS system. This tool allows determining the presence of compounds of the families of pyrazines, furan derivatives, ketones, pyrroles, acids, phenolic derivatives, pyridines, aldehydes and thiophenes [13] (Authors).

There are standards (ISO) for the quality of green coffee and its derivatives for domestic and international marketing; determination of the moisture content, routine method, olfactory and visual examination, determination of foreign matter and defects, analysis of grain size manual screening, determination of insect-damaged dams, sample preparation for sensory analysis, storage and transport, to name a few.

4. Coffee cherry components

The cherry coffee (*C. arabica*) structure consists of the outer skin (pericarp), pulp (exocarp), mucilage (mesocarp), parchment (endocarp), silverskin (perisperm) and coffee seed (endosperm) as shown in **Figure 2**.

4.1. Pericarp

The pericarp is composed of outer three layers of the fruit: the exocarp, mesocarp and endocarp (**Figure 3**).

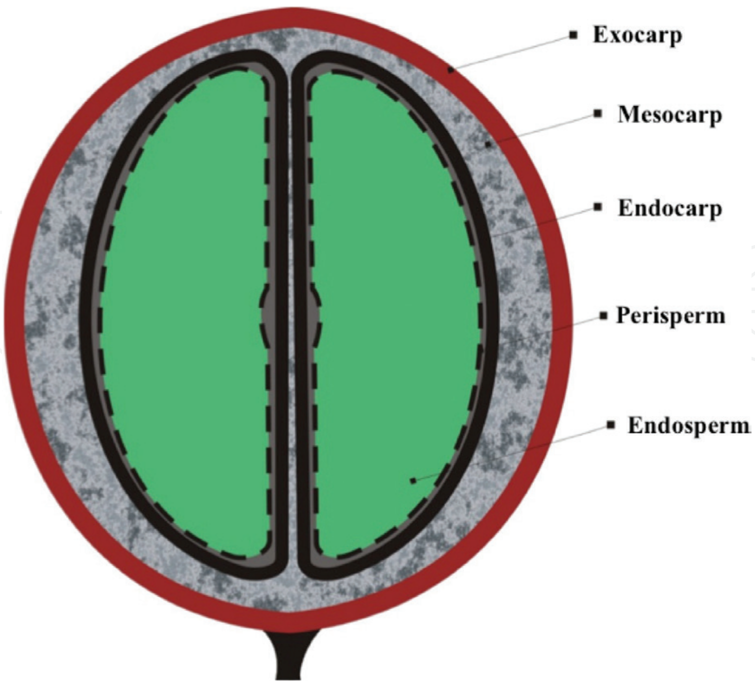

Figure 2. Coffee cherry structure (source: Authors).

Figure 3. Coffee cherry: exocarp, mesocarp bound endocarp (source: Authors).

4.1.1. Exocarp

The exocarp, also known as pulp, is the outer layer of cherry coffee. A single layer of cells of the compact parenchyma forms it. The colour of exocarp at the beginning of fruit growth is green due to the presence of chloroplasts that then disappear as the fruit matures. The colour of the ripening of the cherry depends on the variety of coffee that can be red or yellow. Red colour of the skin comes from anthocyanin pigments, whereas the yellow colour of the skin is due to luteins [14].

The coffee pulp when is discarded in the environment causes contamination. Due to this, many studies have been carried out to take advantage of it and reduce its toxic effect on the environmental process [15]. Among the ways of using it include silage for animal feed, coffee pulp cake, and juice treated with microorganisms for animal consumption [16]. The coffee pulp contains dry matter (92%), ethereal extract (2.6%), raw fibre (20.8%), crude protein (10.7%), ash (8.8%), nitrogen (49.2%), organic acids (12%), caffeine, trigonelline and tannins (1.8%) [17].

4.1.2. Mesocarp

The mesocarp or mucilage (a type of soluble and viscous fibre) is present in unripe coffee fruit. With maturation, pectolytic enzymes break down pectic chains, resulting in an insoluble hydrogel that is rich in sugars and pectins. Studies have shown that the mucilage/water ratio increases as altitude increases [14].

Coffee mucilage is a viscous liquid residue produced in the coffee industry that is disposed of without treatment directly into watercourses, causing serious contamination problems. The mucilage is composed of water (84.2%), protein (8.9%), reducing sugar (4.1%), pectates (0.91%) and ash (0.7%) [18].

Carbohydrates are the most important constituents in coffee mucilage. Also, syringaldehyde, which is produced by lignin hydrolysis, is found in low concentrations. Coffee mucilage (CM) contains several minerals; potassium is the most abundant element, followed by phosphorus, calcium, sulphur and magnesium (**Table 2**). Other compounds are also found, such as glycerol, caffeine, acetates, lactates, phenol, as well as 2,6 and 3,4-dimethoxyphenol.

Minerals	(mg/L)	Minerals	(mg/L)
Aluminium	0	Manganese	0.07
Arsenic	0.47	Molybdenum	0
Sulphur	30.19	Sodium	7.18
Boron	0.16	Nickel	0.01
Barium	0.02	Phosphorus	41.55
Beryllium	0	Lead	0
Calcium	37.08	Antimony	0
Cadmium	0	Selenium	0
Cobalt	0	Silicon	1.58
Chrome	0	Tin	0
Copper	2.45	Strontium	0.07
Iron	0.65	Thallium	0
Potassium	239.8	Vanadium	0
Lithium	0.01	Zinc	0.14
Magnesium	10.05		

Table 2. Minerals composition of coffee mucilage [10] (Authors).

4.1.3. Endocarp

The endocarp, or parchment, is the hard layer that surrounds the coffee seed. It consists of three to seven layers of sclerenchyma cells. These cells harden during the ripening of the coffee fruit, delimiting the size of the coffee seed [14].

In processing of coffee, parchment or husks are the major solid residues and it is estimated that for every kilogram of coffee seeds produced, approximately 1 kg of husks is generated. It is mainly composed of cellulose (40–49%), hemicellulose (25–32%), lignin (33–35%) and ash (0.5–1%) [19].

4.2. Seed

The perisperm, the endosperm and the embryo compose the coffee seed. The size of seeds vary according to the variety of coffee, usually the average can be between 10 mm long and 6 mm wide.

Quality of the coffee seed has a high and direct influence on the success of the crop and is directly dependent on viability, identity, health and appearance.

The health of the seed influences its germination, appearance and vigour, related to the health of the plants, depending on its management and the environmental conditions. The appearance of the seed has to do with its colour, and it must be a homogeneous amber yellow colour, without spots, without blows, without signs and symptoms of diseases, and without the remains of coffee by-products. Viability is the ability of the seed to germinate properly, giving rise to healthy and vigorous plants. To the genetic correspondence of plants to variety [20].

4.2.1. Perisperm

The perisperm or silverskin is the outer layer that surrounds the seed. It is formed from the nucellus (the central cell mass of the ovule's body). Usually some remnants of the silver skin remain in the seed, but when being roasted they are detached. The silverskin can be polished off the grain; however, this decreases the coffee flavour. Some authors claim they have proposed that the presence of a large amount of silver skin in the ground coffee is a sign that the coffee was cut before its ideal maturity to be processed [14]. The main component is cellulose and others.

4.2.2. Endosperm

The endosperm is the tissue produced inside the seed. The chemical content of the endosperm is very important as it precedes the taste and aroma of roasted coffee. Water-soluble compounds are caffeine, trigonelline, nicotinic acid (niacin), chlorogenic acids, monosaccharides, disaccharides, oligosaccharides, proteins, minerals and carboxylic acids [14]. Components insoluble in water include cellulose, polysaccharides, lignin and hemicellulose, as well as some proteins, minerals, vitamins and lipids (triglycerides and esters of diterpene alcohols and fatty acids). The most abundant amino acids are 17, and glutamic acid, aspartic acid, leucine and valine stand out among them.

5. Chemical composition of green coffee and roasted coffee

The green coffee seed is the fruit obtained from the trees of the genus *Coffea*; peeled, decaffeinated and ready for roasting, it is called raw coffee or gold coffee. Roasted coffee is the product obtained from the roasting of green coffee. The green coffee is roasted with heat at 180–230°C for 15–20 min leading to increase in size due to the production of carbon dioxide inside, which acts as a preservative until released by grinding.

Generally, raw green coffee contains water, protein, caffeine, lipids, soluble carbohydrates, insoluble polysaccharides, acids (soluble and non-volatile), trigonelline, amino acids and minerals (**Table 3**). Roasted coffee contains reducing sugars, caramelized sugars, insoluble polysaccharides, fibre, proteins, minerals, non-volatile acids (caffeic, chlorogenic, citric, malic, oxalic, quinic, tartaric), caffeine, lipids, trigonelline and ash, in which the main constituent elements are potassium, phosphorus and magnesium (**Table 4**).

The protein volatiles obtained by pyrolysis have some relevance in relation to the coffee flavour. Amino acids containing sulphur, methionine and cysteine have been identified along

Component	Arabica*	Constituents
Soluble carbohydrates	**9–12.5**	
Monosaccharide	0.2–0.5	
Oligosaccharide	6–9	Fructose, glucose, galactose, and arabinose (traces)
Polysaccharides	3–4	Sucrose (>90%), raffinose (0–0.9%), stachyose (0–0.13%), and glucose (0–2%)
Insoluble polysaccharides	46.53	
Hemicellulose	5–10	Polymers of galactose (65–75%), arabinose (25–30%), and mannose (0–10%)
Cellulose	41–43	
Volatile acids	0.1	
Non-volatile aliphatic acids	2–2.9	Citric acid, malic acid, and quinic acid
Chlorogenic acid	6.7–9.2	Mono-, dicaffeoyl- and feruloylquinic acid
Lignin	1–3	
Lipids	15–18	
Wax	0.2–0.3	
Oil	7.7–17.7	Main fatty acids: 16:0 and 18:2 (9,12)
N compounds	11–15	
Free amino acids	0.2–0.8	Main amino acids: Glu, Asp and Asp-NH_2
Proteins	8.5–12	
Caffeine	0.8–1.4	Traces of theobromine and theophylline
Trigonelline	0.6–1.2	
Minerals	3–5.4	

* Values in percent dry-weight basis.

Table 3. Chemical composition of green coffee [13].

with indole and tryptophan. Volatile matter includes numerous compounds such as acids, alcohols, aldehydes, diacetyl, furfural, hydrogen sulphide, ketones, mercaptans and phenols [21].

On the other hand, because of caffeine, drinking coffee can significantly affect the nervous system, cardiovascular, respiratory, among others. However, caffeine does not accumulate in the body, so its effects become short-lived. The body can become accustomed to caffeine and

Component	Average*
Cellulose	8.6
Hemicellulose	36.7
Xylose	0
Arabinose	1.7
Galactose	13.8
Mannose	21.2
Protein	10
Lipids	11–16
Ashes	1.6
No volatile acids	0.4
Soluble	24
Insoluble	4
Organic matter	90.5
Nitrogen	2.3
Carbon/nitrogen	22/1
Caffeine	1.2–2.4
Trigonelline	0.4
Protein	9
Minerals	4

* Values in percent dry-weight basis.

Table 4. Chemical composition of roasted coffee ground (seed) [24, 25].

make regular users less sensitive to its stimulating effects than others. Among all the effects of coffee, the best known is to be a stimulant to the nervous system. Consuming coffee can make one feel more awake, alert and able to concentrate. Caffeine has been shown to counteract fatigue and wake up the mood, but it can also cause anxiety, nervousness and irritability. In some people caffeine can delay sleep, but it all depends on how much has been consumed [22, 23].

Tables 3 and **4** show the chemical composition of green coffee and roasted coffee.

In samples of catuai (variety of *Arabica coffee*) roasted coffee, 111 compounds were isolated and identified, among which 7 pyrazines and 10 furan derivatives were outstanding. The pyrazines are important contributors in the coffee aroma, 2-ethyl-3,5-dimethyl-pyrazine was the most abundant followed by 2-ethyl-5-methylpyrazine in this sample.

Many furanic compounds are common in samples of roasted coffee. In samples of roasted bitter coffee, 119 isolates and 16 compounds were obtained. Of which 8 are pyrazines and 15 are furan derivatives. Of the pyrazines, the 2-ethyl-3,5-dimethyl-pyrazine was found in greater abundance followed by 2-ethyl-6-methylpyrazines. Similarly, in roasted catuai coffee, furanic derivatives such as 2-furancarboxaldehyde, 2-furanmentol and 5-methyl-2-furancarboxyaldehyde were found [13] (Authors).

In robusta coffee, 122 compounds were found and 120 compounds were identified. Of which only 18 are pyrazines and 11 are furanic derivatives. Among pyrazines, 3,5-dimethyl-2-propylpyrazine is the most abundant derivative in this coffee and compared to the other varieties is the only sample that is presented and is followed by 2,5-methyl-pyrazine.

2-furancarboxyaldehyde is one of the most abundant compounds found in all the varieties and provides a sweet aroma to the coffee and is a very penetrating caramel in the coffee variety of Kilimanjaro [26].

The 5-methyl-2-furancarboxyaldehyde and 2-furanmentol compounds were found in different concentrations in the three analysed varieties, of which the specific contribution they have in the coffee aroma has not yet been reported. But it belongs to the group of furanic derivatives that provide the note of roasted coffee. It is known that phenolic compounds are products of the thermal degradation of carbohydrates, chlorogenic acids and lignin substances [27].

6. Biotransformation of the main coffee components for biofuels production

Since more than 50% of the coffee fruit is not used for the production of commercially available green coffee, it is therefore discarded during processing. So far, most of the advances have been made in its use for industrial purposes other than the food industry, such as energy production, adsorption of compounds and the manufacture of industrial products such as particle boards, ethanol, gibberellic acid and α-amylase [28].

With 14% of a total of 18%, bioenergy is the largest source of renewable energy. In contrast to other sources of renewable energy, biomass can be transformed into solid, liquid and gaseous fuels. This is shifting from an unusual source of energy to an increasingly globalized market [29].

Bioethanol and biogas production by fermentation has received great importance in the last years due to its increase of the demand of fuels. Fermentation is one of the most important processes for agro-waste reuse producing yeast and clean fuels. This process does not require the use of toxic substances; this makes it an environmentally friendly process.

The outer layers of coffee cherry (pulp, skin, mucilage, etc.) are removed by various processes, including washing, drying and fermentation. Useless waste products, grains and coffee are classified. During these processes are generated different residues that being rich in sugar and compounds with functional properties do not receive adequate treatment and become sources of contamination of rivers and streams, mainly [30].

In order to carry out the extraction of the coffee components to be used as substrate to produce biofuels, among the different methods of extraction, the mechanical extraction of the coffee seeds reduces the amount of water used, and consequently allows the recovery of the fraction of mucilage, pulp and seed of coffee [10, 31].

Some applications of cherry coffee residues such as pulp, mucilage, parchment and coffee seed are processed through fermentation, anaerobic digestion and trans-esterification to produce chemicals (**Figure 4**).

6.1. Fermentation

Fermentation is a biological process in which complex molecules are degraded to transform them into simpler molecules, generating liquid products. Bioethanol is produced by alcoholic fermentation of sugars; this biofuel is considered as a good candidate to replace conventional fossil fuels. The advantages of biofuel over fossil fuels are that it is clean, renewable and fully combustible and generates less waste. However, the implementation of biofuel technology is intended to solve the energy problem that is presented, in order to reduce the current dependence on fossil fuels [32].

In the investigation of Pérez-Sariñana et al., a response surface design was performed to obtain the optimal operating conditions of fermentation system using coffee mucilage as a substrate and *Saccharomyces cerevisiae*, the aim being to obtain a maximum bioethanol production. The conditions were pH of 5.1, temperature of 32°C and initial sugar concentration of 61.8 g/L. With this, the estimated production of bioethanol was 15.02 g/L and the experimental production was 16.29 g/L ± 0.39 g/L. It was demonstrated that carbohydrates are the most important constituents in coffee mucilage; for samples analysed here, the sugar composition

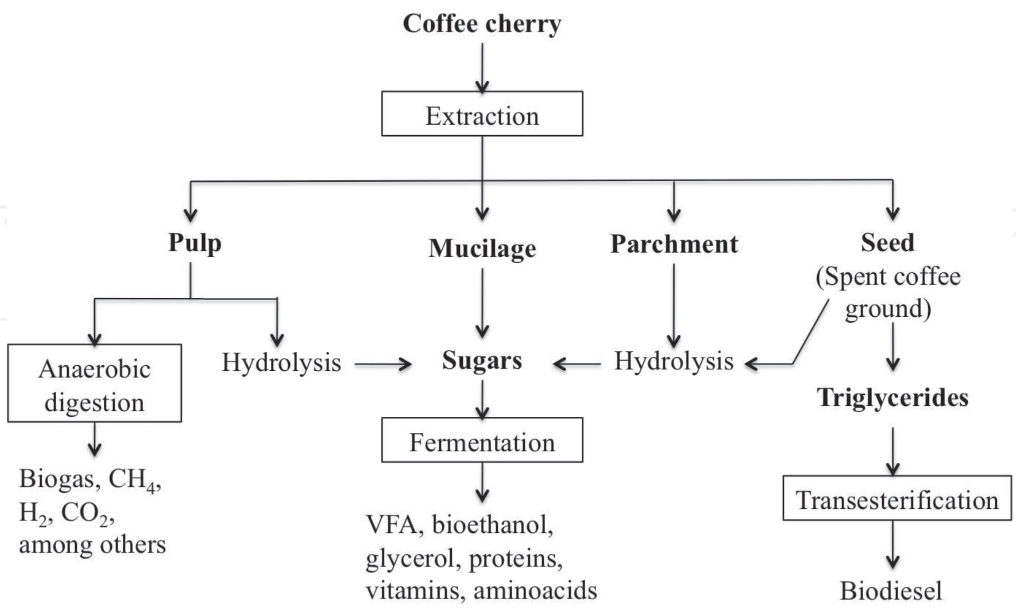

Figure 4. Applications for pulp, mucilage, parchment and seed of coffee using three processes—fermentation, anaerobic digestion and transesterification (Source: Authors).

in coffee mucilage was 37.67 g/L galactose, 35.65 g/L glucose, 1.06 g/L lactose and 0.1193 g/L proteins. The fermentation medium used to propagate the yeast was YPD (yeast extract, peptone and dextrose) agar, 1% yeast extract, 2% peptone, 2% glucose and 2% agar. The medium was pasteurized at 65°C for 30 and 20 min on ice and was supplemented with 0.5 g/L ammonium sulphate as a nitrogen source. Subsequently, the required volume was transferred to each serological bottle previously sterile. The strain was cultured in serological flasks, stirred at 200 rpm and 28°C [10] (Authors).

The use of the mucilage of coffee as a substrate by its chemical composition in sugars such as glucose and galactose allows or favours an adequate management of agro-industrial residues in the coffee-growing.

Harsono et al., carried out research on how to use coffee residues to produce value-added products and reduce the impacts of pollution on the environment, as well as to evaluate the bioethanol production potential (estimated optimum conditions) using *S. cerevisiae* yeast. They obtained a yield of 77.29% of bioethanol, which they consider may be a viable alternative for obtaining second generation bioethanol specifically in rural areas and for plantations of small coffee producers. They also assessed the cost of producing bioethanol that was evaluated from the processing of residual coffee [33].

Thnari et al. have used coffee residues for the potential they manifest with a dual-purpose in the production of ethanol and the preparation of activated carbon. A direct method of hydrolysis and direct fermentation is considered as the main option used in this study for the generation of ethanol fuel from biomass residues. Factors such as *S. cerevisiae* fillers, temperatures and substrate content were investigated to maximize ethanol yield. Coffee extract residue was also used to prepare activated carbons using chemical and physical activation methods. The effects of process parameters such as temperatures and acid concentrations were varied and determined in terms of yield, BET surface areas and porosity of the final product [34].

Other research points to the analysis of the carbohydrate content of coffee residues waste for fermentable sugars such as glucose, galactose and mannose, which can be fermented by *S. cerevisiae*. The rate of enzymatic conversion of coffee residues waste into fermentable sugars was 85.6%. The concentration of ethanol and yield (based on sugar content) after enzymatic hydrolysis, by simultaneous saccharification and by fermentation were 15.3 g/L and 87.2%, respectively [35].

6.2. Anaerobic digestion

Anaerobic digestion is a biological process in which organic matter is decomposed into different gaseous products by the action of a consortium of microorganisms.

In this context, biogas from waste will play a vital role in the future, as biogas is a versatile source of renewable energy that can be used to replace fossil fuels in energy and heat production, and can also be used as a gaseous fuel for vehicles. Biogas rich in methane (biomethane) can also replace natural gas and can also be used as raw material to produce chemicals and materials. The production of biogas through anaerobic digestion through the use of locally available resources offers significant advantages over other forms of bioenergy production. It has been evaluated as one of the most energy efficient and environmentally beneficial technologies [36]. It can drastically reduce GHG emissions compared to fossil fuels. Another advantage is that it is produced as digestate residue that is an improved fertilizer for crops that can substitute mineral fertilizer.

In the work of Pérez-Sariñana et al., pulper with desmucilating was used, a litre of water was added to a kilogram of coffee cherry and the coffee mucilage extracted was stored in bottles at −20°C to prevent degradation due to the sugar content it has. The concentrations of sugars in the experimental design were (72, 65, 50, 35 and 27 g/L). Optimal conditions for the methane production from coffee mucilage using methanogenic sludge as an inoculum and buffer solution (minerals) were estimated by the software as pH 8.2, temperature 37°C and sugar concentration of 27 g/L. The experimental optimum conditions for the production of methane from coffee mucilage were identified, which were pH 8.2, temperature 37°C, sugar concentration of 25.5 g/L and 313 mL methane .

On the other hand, Corro et al. mentioned that biogas could be produced by co-digestion of coffee pulp and cow manure under solar radiation. They reported that the methane content in the biogas reached 50% of the yield. This content increased to 60% and remained almost constant for at least 8 months of additional digestion. By means of gas spectroscopy analysis, more than 70 chemical compounds were found in the biogas generated after 4 months of co-digestion [37].

Hernández et al. used the coffee mucilage as a substrate for the production of hydrogen. The study evaluated three proportions of mucilage manure by performing a co-digestion and also increased the organic load to improve hydrogen production. The average rate of hydrogen production reached 7.6 NLH_2/Ld of coffee mucilage (parameters as the hydrogen production rate), indicating a high potential for hydrogen compared to substrates such as palm oil and wheat starch [38].

Luongo et al. (2015) indicated that methane-specific production reached 0.15 $NLCH_4$/g TVS using glucose as the most readily biodegradable carbon source, and a material rich in lignocelluloses (coffee seed skin). The application of multiple anaerobic digestion extracts more energy from organic waste [39].

A continuous flow stirred tank reactor was started for the treatment of coffee residues at thermophilic temperatures and long-term operation. In this experiment, the reactor was fed a substrate mixture (total solids of about 70 g/L) of ground coffee, coffee wastewater, milk waste and municipal sludge and was run at 55°C for 225 days. They show that the effectiveness of the complete parameters (total volatile fatty acids, propionic acid, intermediate alkalinity/partial alkalinity, intermediate alkalinity/total alkalinity and CH_4 content) controlled the thermophilic system [40].

6.3. Trans-esterification

Trans-esterification is a chemical reaction in which there is an exchange of the alkoxy group of an alcohol; the glycerol contained in the oils is replaced by an alcohol in the presence of a catalyst.

Biodiesel from vegetable oils, animal fats or other materials is an alternative to petroleum diesel for use in compression ignition engines. The composition and quality of biodiesel depends greatly on the composition of the raw material used. In the trans-esterification process for biodiesel, monoalkyl esters are produced from a glycerol-containing vegetable oil of long chain fatty acids with a low molecular weight alcohol (methanol) [41].

Used or spent coffee seeds are currently being used to turn them into biodiesel. This process produces 10–15% oil depending on the species of coffee (Arabica or Robusta). Kondamudi et al. carried out research on coffee-derived biodiesel where it projects that 340 million gallons of biodiesel can be produced from coffee residues around the world [42].

Rocha et al. presented a study of ultrasonic-assisted extraction; they used solid residues from the coffee process as a substrate for the production of oils in order to produce biodiesel and ethanol. The process for producing biodiesel showed a yield of 97% in methyl esters of fatty acids. And the highest glucose yield (192 mg $gSCG^{-1}$) was obtained by hydrolysis with 0.4 mol/L sulphuric acid at 121°C for 15 min [43].

7. Conclusions

In this chapter, the characteristics of coffee from the production, main varieties, characterization methods, components of cherry coffee and residues that were discarded after the extraction of the coffee bean were presented. These residues are used to produce energy as it is raw material in the form of biomass; the products that can be obtained after being transformed into energy with fermentation processes and anaerobic digestion are liquid and gaseous biofuels (bioethanol, biodiesel and biogas).

The agro-industrial residues are generated by the fruit and vegetable sector primary activity that shows the need to propose alternatives to use of the residues with a very important potential to be used as a source of chemical components that can be used for the production of biofuels. Their energy potential allows it to know their usefulness in the production of bioethanol, biogas and biodiesel, as well as the alternatives of using the by-products of the processes elaborated in order to avoid the generation of residues that contaminate the soil, water or the air.

Most of the research work has been done at laboratory scale and pilot scale; the next step would be to assess the technical feasibility and energy efficiency of these processes to carry out scaling at the industrial level.

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Appendices and nomenclatures

GC-MS	gas chromatography-mass spectrometry
HPLC	high performance liquid chromatography
ISO	International Organization for Standardization
CM	coffee mucilage
VFA	volatile fatty acids
CH_4	methane
H_2	hydrogen
CO_2	carbon dioxide
GHG	greenhouse gas
g	gram
L	litre
d	day
SCG	spent coffee grounds
H_2	hydrogen
CH_4	methane
NL H_2	parameters as the hydrogen production rate
NL CH_4	parameters as the methane production rate
TVS	total volatile solids
BET	Brunauer-Emmett-Teller
SDE	simultaneous distillation and extraction

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