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Apple Industry: Wastes and Possibilities

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Author Details

*Anny Manrich**

Embrapa Instrumentation-National Nanotechnology Lab for Agribusiness, Brazil

*Corresponding author

Anny Manrich, Embrapa Instrumentation- National Nanotechnology Lab for Agribusiness, Brazil

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Abstract

Among the more than 7,500 varieties of edible apples, of which 40 are sold, three are those grown in Brazil: Gala (56%), Fuji (39%) and Eva (5%). Brazil, which at the beginning of the 1970s imported all the apples it consumed, today has an import volume equivalent to its export volume (70 thousand tons), reaching the 10th position among the countries that produce the most fruit, with a production of 1.1 million tons / year. As the production of apples increases annually, the production chain must, in the same way, pay attention to the residues generated by it, mainly apple pomace, originating from the production of apple juice, as it is a highly polluting waste and not suitable for cattle feed. Apple pomace, composed of pulp, peel, seeds and stalks, has been explored by several researchers around the world with a view to developing products with high added value. Due to its excellent nutritional quality, bagasse, after being dried and ground, can be added to bread and meat products, increasing its fiber and antioxidant values. Phenolic extracts obtained from bagasse or fiber extracts also serve as food ingredients. In the materials area, apple pomace can serve as a component of the manufacture of active packaging for edible food and films and also for the production of activated carbon.

In addition, obtained from apple peel, two hydrophobic compounds, ursolic acid and cutin, can be used in the pharmaceutical area and in the development of materials and films, respectively. Apple seed is also a source of oils that reach the cosmetics market. The various alternatives for the use of apple residues, mainly apple pomace, if put into practice, can contribute to the apple production chain in Brazil. The purpose of this review is, therefore, to present and discuss these alternatives.

Introduction

Among the more than 7.500 varieties of edible apples, of which 40 are commercialized, three are those grown in Brazil: Gala (56%), Fuji (39%) and Eva (5%). At the beginning of the 1970s, all the apples being consumed in Brazil were imported. Today, the imported volume of apples are equivalent to its exported volume (70 thousand tons), what brings the country to the 10th position among the countries that produce this fruit, with a production of 1.1 million tons per year. As the production of apples increases annually, the apple production chain should, in the same way, pay attention to the related residues, mainly apple pomace. This waste, which outcomes from the production of apple juice, as it is highly polluting and is not suitable for cattle feed. Apple pomace, composed of pulp, peel, seeds and stalks, has been explored by several researchers around the world with a view to developing products with high added value. Due to its excellent nutritional quality, apple pomace, after being dried and ground, can be added to bread and meat products, increasing its fiber and antioxidant values. Phenolic extracts obtained from apple pomace or fiber extracts also serve as food ingredients. In the materials science field, apple pomace can serve as a component of the manufacture of active packaging for edible food and films and also for the production of activated carbon.

In addition, obtained from apple peel, two hydrophobic compounds, ursolic acid and cutin, can be used in the pharmaceutical area and in the development of materials and films, respectively. Apple seed is also a source of oils that reach the cosmetics market. The various alternatives for the use of apple residues, mainly apple pomace, if put into practice, can contribute to the apple production chain in Brazil. The purpose of this review is, therefore, to present and discuss these alternatives.

Origin of the Apple

Apples (Malus domestica) are among the most important fruit crops in temperate regions of the world in terms of production levels [1,2]. Based on combined archaeological and molecular data, it is estimated that the species now considered the cultivated apple was initially domesticated from the wild apple, around 10,000BC and 4,000BC, in the region where Kazakhstan and Kyrgyzstan. Travelers on the major trade routes from central China to the Danube took wild apple seeds westward, along the major trade routes known as the Silk Road, in saddlebags or horse guts. The domesticated apple came into contact with other wild apples, such as *Malus baccata* in Siberia, *Malus orientalis* in the Caucasus, and *Malus sylvestris* in Europe, giving rise to *Malus domestica* [1,2].

Nutritional Aspects

Apples, which contain a large amount and variety of phenolic acids and flavonoids, are also sources of fiber (2.21g / 100g) [3], such as cellulose, hemicellulose and pectin [4,5]. Combined, these compounds have beneficial effects on vascular function and blood pressure, lipid metabolism, inflammation and hyperglycemia [3]. The main flavonoids present in the apple are flavanols, flavones, flavanones, anthocyanin and dihydrochalcones. Among phenolic acids, hydroxycinnamic acids and hydroxybenzoic acids are considered to be remarkable [3,5].

In addition, the apple contains vitamin C (4.6mg / 100g) and potassium (107.0mg / 100g) [3]. The apple is the second most consumed fruit in the world and the third most consumed fruit in Brazil, after banana and papaya [6]. Apple pomace has a greater amount of fiber and carbohydrates, since, due to the elimination of water, acids and soluble carbohydrates, apple pomace has its solid compounds concentrated. The apple nutritional table is shown in Table 1.

Table 1: Nutritional aspects of dried apple pomace [7,8].

Constituent		Amount	Unity
Cellulose		127.9	g/kg
Hemicellulose		7.2 – 43.6	
Lignin		15.3 – 23.5	
Pectin		3.5 – 14.3	% (m/m)
Total Carbohydrate		48.0 – 83.8	
Fibers		4.7 – 51.1	
Protein		2.9 – 5.1	
Lipids		1.2 – 3.9	
Reducing Sugars		10.8 – 15	
From which:	Glucose	22.7	
	Fructose	23.6	
	Sucrose	1.8	
	Arabinose	14-23	
	Galactose	6	
	Xylose	1.1	
Minerals			mg/100 g
From which:	Sodium	185.3	
	Potassium	398,4- 880,2	
	Calcium	55,6- 92,7	
	Phosphorus	64,9- 70.4	
	Magnesium	18,5- 333,5	
	Iron	2,9- 3,5	
	Zink	1.4	
	Copper	0.1	
	Manganese	0.4- 0.8	

Apples are grown commercially in more than 90 countries and are among the most cultivated fruits in the world [9]. According to FAO data (faostat.org), 86.14 million tons of apples were produced in 2018 [Table 2]. China holds between 40 and 50% of world production (more than 30 million tons), and is followed by the United States, Turkey, Iran, Italy, France, Poland, Russia and Argentina; in volume of production [6].

The beginning of apple cultivation in Brazil was in the early 1970s, in Santa Catarina with the initiative of the State Secretariat of Agriculture with collaboration of the Japanese Government [10]. Until then, Brazil was an importer of this fruit and sought self-sufficiency in supplying the domestic market. In 1989, pomiculture - commercial apple production - was consolidated in Brazil, with 1998 being a milestone in which the country became an exporting country. [11]. Currently, Brazil participates with 1.34% of the world production of apples, (1.1 million tons in the 2017/2018 harvest) and is among the 10 largest producers of fruit in the world.

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Table 2. Distribuition of the production of Apples in the World in 2018 (Continents).

Region	Tons	Million Tons
World	8,61,42,197	86.14
Africa	28,69,177	2.87
Americas	94,33,552	9.43
Asia	5,35,23,593	53.52
Europe	1,95,93,609	19.59
Oceania	7,22,266	0.72

Table 3: Distribuition of the production of Apples in the World in 2014 – Divided by Countries.

(http://www.fao.org/faostat/en/#data/QC).

Country	Production (2014)
China	4,09,23,200
United States of America	51,85,078
Poland	31,95,299
India	24,97,680
Turkey	24,80,444
Italy	24,73,608
Chile	17,57,225
Russia	16,24,000
Iran	15,72,844
France	15,31,625
Brazil	13,78,617

Brazil exports mainly to the Middle East - mainly Bangladesh - and European countries, Russia and India. The volume of fruit imports is equivalent to the volume of exports, around 70 thousand tons. 20 to 25% of the harvest is used for processing, mainly juice, which has grown in recent years. The production is located in the Southern States, mainly the cities of São Joaquim, Friburgo and Vacaria. The average participation of cultivars in the Brazilian apple production, in the last five years, was of 56% for Gala; 39% Fuji; and 6% for others, mainly Eva [6,12 ,13].

Products

There are more than 30,000 different apple varieties in the world, of which more than 7,500 are considered edible and about 40 cultivars represent the majority of commercial production. Among the economically important varieties are Golden Delicious, Elstar, Jonagold, Granny Smith, Braeburn, Fuji, McIntosh, Delicious, Pink Lady, Boskoop and Cox Orange [14,15]. Between 70 and 80% of the apple produced in the world are destined for its fresh consumption. Of the remaining volume, a large part is destined to the production of apple juice (approximately 70%) and other products, such as puree and dehydrated fruit [7, 16-18]. Figure 1 shows the images of the most consumed varieties in the world, highlighting also their region of origin and production.

Product derived from apples are diverse and numerous: apple juice, which is obtained through pressing, can be clarified, concentrated or whole; cider and cider vinegar, obtained by fermenting apple pomace, using yeast; apple sauce, which consists of a puree, cooked with or without sugar; apple butter, obtained by concentrating apple sauce, by slowly cooking apples with cider or water, until the sugars present in the apple are achieved and obtaining a deep brown color; and apple pectin, a mixture of polysaccharides, which is widely used in the pharmaceutical and food industries as a stabilizing and gelling agent. Other products are dehydrated apple slices, fruit ribbons, apple jam and apple essential oil. Direct animal feed and feed products are also cited as uses of the fruit [14,18,19].

Losses and Waste

Like most fruits produced worldwide, large volumes of apples are lost in the production chain due to poor storage and poor transportation conditions. These fruits are then considered unsuitable for consumption due to injuries or contaminations. These losses represent about 30% of the total fruit production [17].

The main destination of the apples produced worldwide is the fresh consumption (70 to 80%). From the remaining amount, between 65 and 70% are processed to generate concentrated apple juice. In 2019, around 5.5 billion liters of apple juice were consumed in the world (www.statista.com). Apple pomace (approximately 25 to 30% by weight of processed apple) is composed mainly of skin and pulp (95%), seeds (2% to 4%) and stems (1%) [20] and is generated after juice extraction [9,16-18]. This means that the total waste generated by the production of apple juice amounts to between 4 and 5 million tons. In Brazil, this value is around 50 thousand tons.

In general, only a small fraction of the bagasse resulting from juice production has commercial uses [19]. In India, for example, where 2.32 million tons of apples are produced per year (APEDA Agri Exchange), only 1% of the apple pomace is used for the production of other products, especially bakery products [17] or in the production of apple cider vinegar [19]. The rest is burned or dumped in the fields or accumulated in the regions close to the juice producing units, what creates serious pollution problems, due to the highly fermentative nature of the manure, which has high humidity (70% to 75%) and high BOD values and COD [5,8,19]. Another practice is to use it as a natural fertilizer after composting, however, the high acidity of the compost produced makes it anti-germinative [5]. The use as feed for animals is very limited due to rapid deterioration, microbial growth and low nutritional value [21].

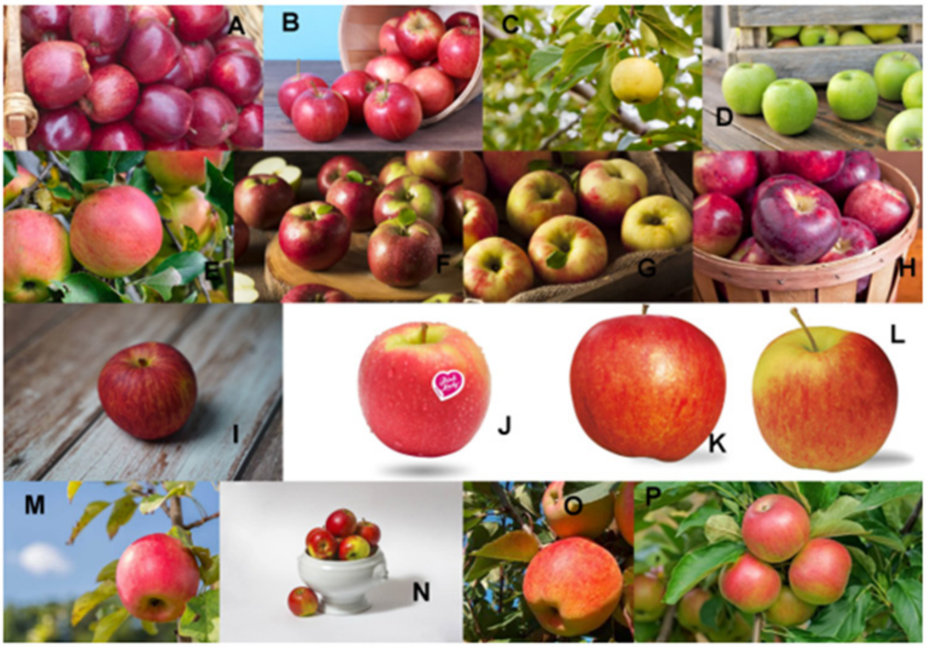

Figure 1: Apple varieties most produced and consumed in the world.

A. Red Delicious (United States, Italy)

B. Gala (New Zealand, Germany, Polen, Brazil)

C. Golden Delicious (United States, Italy, Spain, France)

D. Granny Smith (Australia)

E. Baldwin (United States)

F. Mc Intosh (Canada)

G. Honey Crisp (United States)

H. Cortland (United States)

I. Fuji (Japan, Brazil)

J. Pink Lady (France, New Zealand, Australia)

K. Braeburn (Holand)

L. Jonagold (Germany, Polen)

M. Orange Cox (England)

N. Elstar (Germany)

O. Champion (Polen, Czeck Republic)

P. Idared (Europe)

Sources: https://www.worldatlas.com/articles/the-world-s-most-common-types-of-apples.html

https://www.sevencooks.com/de/magazin/apfelsorten-2viAeKu1YE6MmugQmoIe2w

https://de.wikipedia.org/wiki/Liste_von_Apfelsorten/J

The high costs of waste treatments and the impossibility of simple disposing of the waste in the environment, due to environmental laws, leads to need for exploring new using alternatives for the apple pomace [19]. It took many decades for companies and society to understand the importance and need for waste management and pollution control. However, just the proper management of waste resulting from industrial consumption and production is not enough and today it is understood that it is essential that waste must be transformed into sources of resources, raw materials, thus enabling sustainable development [4,16,22]. For this reason, several application possibilities have been studied and developments are being proposed, with the objective of making apple pomace a product of high commercial value [4, 9,16-18,20,21-24]. Figure 2 presents a summary of the possible explorations for apple pomace, whose main objective is the economic valorization of this residue.

Pectin

Apple pomace has been used for pectin extraction for many years [17]. Pectin can be found in almost all plants as a constituent of the cell wall, pectin is a polysaccharide of complex composition, containing up to 17 different sugars in its branched structure, such as xylose, glucose and rhamnose, but mainly arabinose and galactose. [25,26]. Pectin in its native form differs greatly among species, however, in general it can consist of three main pectic chains that include homogalacturone, ramnogalacturone-I and rhamnogalacturone-II. Homogalacturone is a linear polymer composed of units of galacturonic acid randomly esterified with methoxy groups [27].

In addition to these main sources, other raw materials such as banana peel, watermelon peel, mango peel, sisal residues, sunflower heads, green pistachio peel and tomato residues have already been studied as sources of pectin, varying in their yields and compositions [26,28]. Commercial pectin must contain a minimum of 65% galacturonic acid in its composition, what contributes for orange peel (about 85%) and apple pomace (about 14%) to be the main sources for its industrial production [25,26,28].

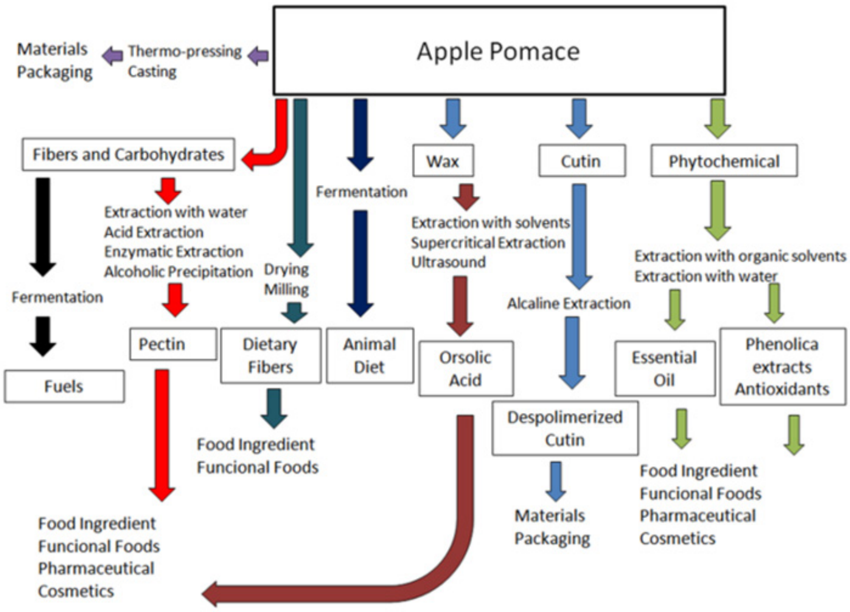

Figure 2: Searches for the economic value-adding to apple pomace.

The extraction of pectin from a raw material is a multi-stage physical-chemical process that includes a pre-treatment, an extraction operation and a post-extraction stage. In extraction, mineral acids at high temperature are used, such as hydrochloric acid, nitric acid and sulfuric acid. The extract containing pectin is then separated from the raw materials by filtration or centrifugation. Aluminum or copper salts are used to precipitate the pectin, and this mixture is then suspended in alcohol and treated with acid in a series of washing steps, then partially neutralized before drying. The final steps involve drying and grinding to produce pectin powder [25,26,28].

The main applications of pectin are found in the food industry, such as juices and bakery, and also in the pharmaceutical industry, as they are related to the formation of gel and water retention, which alter the rheological properties of products [25,26]. Pectin is related to several beneficial health effects, including blood lipid and cholesterol lowering effects, serum glucose and insulin lowering effects, delayed gastric emptying and anticancer activities [3,29].

Fuels, Enzymes and Other Biotechnological Products

The presence of a large amount of carbohydrates such as sucrose, glucose and fructose in apple pomace makes it a suitable substrate for solid state fermentation and production of enzymes and other substances [17,30]. The use of agricultural and food residues for the production of ethanol and other fuels is an alternative that gains strength in the debate on food security, since, with a growing population, there is concern about the ability of agriculture to supply the demand for food human consumption, animal feed and renewable energy generation. Using only non-edible residues, such as corn straw, sugarcane bagasse, apple bagasse, fruit skins and other foods for ethanol production, there is less pressure on the "food vs feed" dispute, added to the rational use of agricultural residues, preventing them from being handled improperly [21,31].

Apple pomace has been studied by several authors for fuel generation. In order to produce ethanol from apple pomace, Magyar et al. [21] tested industrial conditions in different scenarios, including whether or not pretreating the raw material with acid or base and converting apple pomace into fermentable sugars using enzymes commercial uses of biomass degradation. Ethanol yields were about 134g per kg of dried apple pomace, which is comparable to yields of obtaining second generation ethanol from sugar cane bagasse (average of 150g of ethanol per kg of pomace) in optimized process conditions, including pre-treatment and enzymatic fermentation [32].

Hijosa-Valsero and collaborators [33] compared five different pretreatments (self-hydrolysis, using acid or base, using organic solvents or surfactants) in a high-pressure reactor, for the production of butanol from apple pomace. In this work, after optimizing the process conditions to minimize the generation of inhibitors, the authors reached a maximum productivity of 9.11g/L of butanol, when polyethylene glycol (PEG 6000) was used in the pre-treatment; a low value, however, when compared to optimal conditions for obtaining butanol from sugar cane bagasse, above 20g/L [34].

Apple pomace has already been explored as a substrate for the production of various enzymes by filamentous fungi, including B-glucosidase, B-fructofuranosidase [17]; polygalacturonase, pectinase, xylanase [22]; cellulase [23] and inulinase [30]. The production of citric acid using apple pomace as a substrate was studied by Kumar et al. [35] in a solid-state fermentation process using Aspergillus Niger, with a maximum yield of 4.6g of citric acid / 100g of bagasse. Comparatively, Yadegary et al. [36] obtained, using the same fungus, about 9g of citric acid / 100g of sugarcane bagasse.

Food Ingredients

Oils

Only between 2 to 4% of the total apple bagasse from apple juice production corresponds to the seeds [8]. However, if separated, the amount of apple seed could reach 200 thousand and 2 thousand tons per year in the world and in Brazil, respectively. The apple seed, in addition to containing phenolic substances, contains about 80% fatty acids, the majority being linoleic acid and oleic acid [8].

Fruit seed oils, usually by-products of the fruit processing industry, have gained increasing importance in the cosmetics industry in Europe, given the concern for the use of natural ingredients. The main ones are: grape seed oil, mango seed butter, papaya seed oil, red fruits seed oils, such as raspberry and strawberry; apricot kernel oil and passion fruit kernel oil [37]. In view of this market, Kolanowski and Zakrzewska [9] explored apple seed for oil extraction and compared it to canola and grape seed oil. The oil fraction was extracted from the apple seed powder in a Soxhlet apparatus for 2h with boiling hexane, was then dried and then characterized. The oil extracted from apple pomace seeds contains a high level of unsaturated fatty acids and important nutritional aspects, so it can also be used in food applications. Several methodologies for separating seeds from the remainder of the bagasse have already been developed and patented, what could promote their practice.

The choice of solvent and processing methodology requires specific concern, especially when the application of the oil is for food purposes. It is important to mention, that together with fatty acids, other substances are extracted, such as cyanogenic glycosides, which, under certain conditions, can react and produce hydrogen cyanide, causing subacute cyanide poisoning in humans and animals. For this reason, supercritical extraction has been shown to be a promising alternative, as it does not result in the extraction of these glycosides [38].

Phenolics

Found in large quantities in the apple residue are phenolic substances, whose extraction and composition has already been studied by several authors, using organic solvents, such as ethanol and acetone and processes such as liquid-solid extraction, pressurized liquid extraction and subcritical extraction [8,39].

Rana et al. [40] used a solution of acetone in water (50%) for the extraction of phenolics from dried apple pomace by three drying methods: lyophilization, sun drying and oven drying. Best results were obtained through freeze drying, in which an amount of 5.78 ± 0.08 mg of gallic acid equivalent (GAE) / g of dry bagasse were obtained. Du et al., 2019 quantified the amount of phenolics extracted from apple pomace after extracting the juice by cold pressing and separate pomace fractions: (seed + peel) and pulp. Cold pressing is an optimized technology for processing apple juice, which has a considerable positive impact on product quality, as it prevents thermal and oxidative damage to antioxidant components.

They found that the fraction (seed + bark) contains 10 times more phenolic compounds (8.91 ± 0.66 mg GAE /g) than the fraction composed only by the pulp (0.83 ± 0.09 mg GAE /g). Çam and AAby [39] evaluated the variables temperature, extraction time and solvent / solid ratio for the extraction of phenolics from apple pomace with water, aiming at greater extraction of phenolics with minimal generation of 5-hydroxymethylfurfural. Under ideal conditions, the phenolic content of apple pomace was 8,341mg / kg of dry matter and twenty-nine different phenolic compounds could be identified by HPLC-MS. Fernandes et al., [4] studied the acidified aqueous extraction of phenolics from apple pulp to be, after drying, used as a yogurt fortifier, since extractions using other organic solvents may not be suitable for human consumption [4]. Water-soluble polyphenols, when incorporated into yogurt formulations, were not affected by fermentation and improved the antioxidant properties of the final product.

Fibers

Also very important for human health are dietary fibers, found in large quantities in apple pomace [5, 22,40] Apple pomace contains a significant amount of non-starch polysaccharides (35% to 60% dietary fiber), with a high amount of insoluble fiber (36.5%) and soluble fiber (14.6%) (Bhushan et al., 2008). For this reason, apple pomace can be an economically viable source of dietary fiber for use as a functional food ingredient [5,8,22,40,41].

The response surface methodology (RSM) was used by Liang et al., [41] to optimize the effects of the parameters used in the process of obtaining soluble fibers by vapor explosion. In this process, the destruction of the cell walls of biomass occurs, through its exposure to high temperature and high pressure for a certain (short) time, after which explosive decompression occurs in milliseconds. [41]. In optimal process conditions, the authors achieved a soluble dietary fiber yield of 29.85%, a significant increase compared to the extract not treated by vapor explosion (6.27%).

The acid-alkaline digestion was used by Issar et al., [42] to extract apple pomace fibers. The bagasse was subjected to sequential heat treatment with diluted acid and base and the extracted fiber was used to fortify yogurt. The addition of apple fiber contributed to the increase in acidity, total lipids and total fibers of the product, which, in posterior product sensory analysis, was positively evaluated.

Apple Pomace Flour

The dry and ground apple pomace (apple pomace flour) is also used in several food applications, due to its high fiber and phenolic content. Examples are applications in bakery, beverages, confectionery and cookies, meat products and dairy products [43]. The substitution of wheat flour for apple pomace flour in biscuits in quantities of 25, 50 and 75% was studied by Zlatanović et al., [44]. This substitution was responsible for the significant increase in the phenolic compounds and fibers of the cookies, that is, their functionality. Sensory analysis of the products carried out with consumers have shown that the substitution of wheat flour for apple pomace flour can be incorporated up to the level of 50% in cookie recipes, without significantly affecting sensory properties.

Impact drying, in which intensive hot air flows are applied to the product, allows for very rapid drying, and has proven to be an effective alternative in drying apple pomace to ensure the retention of large quantities of its bioactive (phenolic) compounds. This drying process was applied in a study conducted by Jung et al., [45] and after that, the apple pomace transformed into flour by grinding was added to biscuits and sausages based on chicken meat. As a result, there was an increase in the antioxidant activity and fiber content of the sausage and an increase in the softness of the biscuits.

Apple pomace transformed into flour was also used to replace wheat flour (in quantities of 10, 20 and 30% by mass) in the manufacture of cakes in a study carried out by Sudha et al. [46]. The addition of apple pomace flour affected the rheological properties of the dough and resulted in a lower final volume of the cake, however it significantly increased the content of dietary and phenolic fibers and had a positive contribution to the sensory properties of the product.

Masli et al., [47] added apple pomace in extruded foods based on corn starch in order to improve the nutritional value of snacks by adding fibers and at the same time preserving the quality of the product's texture. The introduction of fibers in processes involving extrusion of starch-rich formulations is a major challenge, since the fiber will compete with starch for water during its gelatinization [47]. The research was important for a better understanding of the process parameters that involve the extrusion of this type of food containing fibers.

Materials

Cleaner production of materials and goods is more than a modern concept well accepted in the Academic area. It is a necessity of today's society and a basis for sustainability. The valorization of agricultural industrial waste must become a priority, in order to obtain not only new foods, but also new materials capable of competing with conventional ones and to replace them [16]. Research focused on the exploitation of agricultural residues, often considered environmental problems, for the development of strategic materials is growing, and examples involving apple pomace are promising.

Gaikwad et al. [24] developed an active film from apple pomace and PVA, a water-soluble polymer, using the batch casting technique, for application in food packaging. The authors also determined the mechanical, thermal properties and gas permeability of the developed films, as well as their antioxidant activity. The results showed that there was a good interaction between the polymer and the bagasse, and the production of a compact film with good antioxidant capacity was possible. In a sequencial process, Yates et al. [16] applied the concept of biorefinery to apple pomace, with the purpose of, after extracting antioxidant substances and then pectin from the residue, producing a biocompatible material to be used as a scaffold for tissue engineering. Initially, apple pomace was treated in water under heating, from which a compound rich in carbohydrates and antioxidants was obtained. Then, it was treated with citric acid and the liquid fraction was used for pectin precipitation.

The material left after pectin production, which had a yield of 10% in relation to the initial bagasse mass, was transformed by heating at 500˚C into a material containing 30% potassium, 35% phosphorus and approximately 12% calcium, in addition to magnesium and silicon; being able to act as a cell growth scaffold. The authors demonstrated that it is possible to obtain products with high added value derived from apple pomace, without generating residues from this process.

The production of active porous carbon from apple pomace was proposed by Guardia et al. [19]. The objective was to explore a low-cost carbon source for the production of a material that can be used to remove pollutants from wastewater and to store electrical energy, for example. The authors used hydrothermal carbonization, and activation with CO_2 or KOH at 800 ˚C, obtaining a highly functionalized surface material and a specific surface area of 1000-2000 $m^2.g^{-1}$.

The ability that lignocellulosic materials have, subjected to pressure and heat, to undergo self-connection was explored by Gustafsson et al., [48], for the production of 3D thermo-pressed objects (plates) from apple pomace. After being washed, dried and ground, the apple pomace was mixed with glycerol and subjected to a pressing at 8 MPa and 100˚C for 20 minutes for the molding of small plates. In addition, from the same material, the authors produced thin films by the batch casting method, with the addition of citric acid and glycerol. Both materials developed can be used as packaging and edible film. Some materials developed with apple pomace are shown in Figure 3.

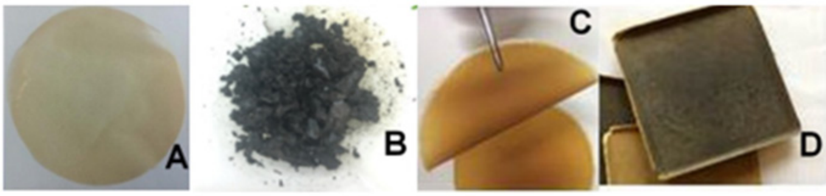

Figure 3: Materials developed from Apple pomace.

A. Apple pomace and PVA casted films [23]

B. Active Carbon [17]

C. Apple pomace casted film

D. Apple pomace thermo-pressed object [47]

Ursolic Acid

Among the various bioactive components found in the apple, one of them is found especially in the skin, ursolic acid, identified as (3β-hydroxy-urs-12-en-28-oic acid), a pentacyclic triterpenic acid. Terpenoids are the largest and broadest class of secondary metabolites produced by plants and are composed of different numbers of isoprene units (C_5H_8) [49]. The content of ursolic acid can reach up to 32% of the total wax, and is the main compound present in the cuticular wax of the apple [50,51].

Ursolic acid and its derivatives have attracted considerable interest in recent years. It has a wide spectrum of pharmacological activities and a high potential for pharmaceutical development, and its anti-inflammatory, antibacterial, antiprotozoal and anti-tumor activities have already been proven by many in vitro and in vivo studies [49]. Food supplementation with ursolic acid is also associated with increased skeletal muscle mass, increased energy expenditure, leading to reduced obesity and better glucose tolerance [52].

Although ursolic acid is found in the epidermis (cuticle) of several species of plants and leaves, apple peel has been identified as a commercially viable source, as it makes up a large part of apple pomace, the main residue of the apple concentrated apple juice industries [51]. The apple peel as a separate residue makes up a minimal portion of the waste generated by the processing of the apple, since they come from compote apple industries (Virk and Sogi). Kołodziejczyk et al. [53], when studying apple pomace, found that it is composed of 54% pulp, 34% of skin, 7% of seeds, 4% of seed core and 2% of stalk.

In spite of this, industrial methodologies for the separation of these parts and peel recovery are not yet known and most of the works carried out for the extraction and characterization of ursolic acid found in the literature used apple peels separated manually from whole apples or performed the extraction of the compound from dried (ground) apple pomace. Thus, solvents are used for the selective extraction of the lipid and waxy fraction present in the whole residue of apple pomace [49].

Ursolic acid from four apple varieties was isolated by Frighetto et al. [50]. Using the solvents 96% ethanol, ethyl acetate, $CHCl_3$ and CH_2Cl_2, they compared the extraction yield of ursilic acid from the apple peel after they were immersed in the solvents for 15 hours. The extracts were identified and quantified by high performance gas chromatography coupled with mass spectrometry and nuclear magnetic resonance 13C. The average amount of ursolic acid found in the Fuji and Smith varieties was 0.8mg/cm^2 while for Granny Smith and Gala it was 0.5mg/cm^2 and 0.2g/cm^2 respectively.

The extraction with hexane, chloroform and methanol was tested by Yamaguchi et al., [54] at room temperature for24 h and had an average yield of 0.71% in relation to the dry skin mass, analyzed by chromatography. After eliminating the solvents, the extracts were used to treat tumor cells from mice. Results show that ursolic acid at 10 μM proved to be very effective in suppressing the growth of tumor cells, affecting more than 82% of these cells, while the growth of normal cells was affected by only 7%.

There are several methodologies proposed to isolate ursolic acid from apple pomace for its commercial extraction for application in medicines and drugs, using mainly reflux in Soxhlet system and non-polar solvents, often alkalized, aiming at high extraction selectivity. This is because, as it is a very poorly soluble compound, the solvent must be suitable to penetrate tissues and reach cells to solubilize ursolic acid, which takes time and does not always achieve good extraction yields [49,51,55]. Fan et al., [56] proposed extracting ursolic acid directly from apple pomace by ultrasound (300 W) using methanol as the extraction solvent, at 50 ˚C. The extract was purified (filtered by membrane), obtaining a yield of 1.34% in relation to dry bagasse mass. With that, the authors demonstrated that the extraction using ultrasound energy is a fast and efficient extraction technique, in which there is economy in the extraction time, and the volume of solvent used.

Conventional methods for the extraction of bioactive compounds from raw materials, such as Soxhlet and heated reflux extraction, are characterized by the consumption of large volumes of solvent and energy, low yields and long extraction procedures, which can result in the loss or degradation of the compounds . In addition, other solvents have been sought, less harmful to health (green solvents) and methodologies aiming at a more economically and environmentally correct extraction [57,58].

The supercritical / subcritical extraction methodology was used by Ordoñez-Quintana et al. [57] for simultaneous extraction of ursolic acid and phenolic substances from apple pomace. The extractions took place in extraction equipment using a constant flow of CO2, following an experimental design of the Plackett-Burman type in which the effect of the variables temperature, pressure, static time, dynamic time, co-solvent, pre-treatment and size was evaluated. particle in ursolic and phenolic acid extraction yield. The yield was 0.611mg/g of ursolic acid in relation to dry bagasse.

Supercritical extraction is among the best environmentally friendly technologies, due to its high extraction efficiency and process time, good reproducibility and low solvent consumption [57]. This technique was also used by Woźniak et al. [59] to obtain ursolic acid and apple pomace phytosterols using CO_2 as a solvent. The experiments, which had the final objective of gathering the data necessary for the industrial implementation of the process, were able to verify the effect of the process parameters on the extraction yield of the compounds, and to obtain the kinetic modeling of the process.

Cutin

The epidermis of the upper plants is lined with an epidermal cell wall in the form of a hydrophobic skin, to limit the loss of water through perspiration, called the cuticle [60]. The cuticle is formed by cutin, waxes, aliphatic constituents of wax mainly with up to about thirty chains of carbon atoms; cutin, and carbohydrates that make up its inner layer [61]. Cutin is a cross-linked, amorphous and viscoelastic polymer made up of hydrocarbons of long chain interesterified fatty acids joined by ester bonds and represents between 40 and 80% of the dry weight of the cuticle. The main components of cutin are derived from monomers C16 and C18 with hydroxyl or epoxide groups located in the middle or at the end of the chain [62,63]. Other monomers may also be present, to a lesser extent, such as unsubstituted fatty acids, fatty aldehydes, dicarboxylic acids and primary alcohols, ferulic acid and cumaric acid [60].

Also composing the cutin are other compounds with emulsifying properties, such as fatty acids, free alcohols and triterpenes, which enable the connection with hydrophilic polymers, that is, with a layer rich in pectins at the wall interface between the cuticle and the polysaccharides [51]. This is because pectin has, in its chain of galacturonic acid units, free carboxyl groups capable of binding to esthers [60]. Despite being found in several plants, such as grapes, olives, raspberries, cherries and apples, tomatoes appear as the main source and for this reason it has been explored and characterized by several authors, by Infrared Spectroscopy, Scanning Electron Microscopy, Microscopy of Atomic Force, Thermogravimetry and Solid State Nuclear Magnetic Resonance [63- 65].

In addition, tomato cutin has been the focus of several studies for the development of materials, such as waterproofing varnish (bio-resin) for metal packaging [66] and for the production of hydrophobic films [65]. Cifarelli et al. [66] carried out the extraction of tomato cutin by three methods aiming at a better material for the production of bio-resins: alkaline hydrolysis, hydrolysis assisted by hydrogen peroxide (using NaOH / H_2O_2) and alkaline hydrolysis followed by selective precipitation, resulting in extracts with different characteristics, melting points, solubility and visual appearance. The cutin obtained by alkaline hydrolysis resulted in the best raw material for the preparation of the resin. Hydrolysis in an alkaline medium using NaOH or KOH solutions, or alkaline alcoholic solutions, are commonly used for the extraction of cutin, in a process in which its depolymerization occurs [51]. Severe chemical extractions with ammonium oxalate / oxalic acid or ZnCl2 / HCl are also possible [67].

Apple cutin was isolated from apple peel by DeVries (1970) by reflux using KOH in methanol and characterized. The free fatty acids were determined colorimetrically and identified by gas chromatography. However, the apple as a source of cutin has not being well studied or explored. In order to extract ursolic acid efficiently and cheaply, Tostes et al. [52] used apple peels manually removed from Brazilian Fuji and Gala varieties. Initially, they immersed the dry and ground residue (25g) in a solution (250mL) of 95% ethanol containing 5g of NaOH. The extraction took place for 6h while stirring at room temperature. Comparatively, they performed extraction by Soxhlet with 200mL of ethanol (99.9%) or methanol (ultrapure) in 5g of dry ground residue in three cycles of 2h.

The extraction yields obtained were similar, however in the case of the extract obtained by alkalized ethanol, the cutin, as it was hydrolyzed, was precipitated and separated by filtration, which was not possible in the case of the extract obtained by Soxhlet, where the cutin remained whole. This allowed, in the first case, the recovery of two different products, depolymerized cutin and ursolic acid [68].

Other Practices

Animal feed is the destination of many agricultural residues, such as soybeans, peanut skin and apple pomace. In the case of apple pomace, there are two disadvantages: first, related to its low protein content. The second disadvantage is that, when destined to animal feed without biological treatment, fermentation of apple pomace can occur in the animal's rumen, leading to the production of alcohol, and with this it can cause intoxication. This phenomenon is known as blood alcohol [22]. However, there are several studies on the use of apple pomace for animal feeding. Bae et al., [69] observed that the addition of 39% of apple pomace to the cow's diet resulted in an increase in the protein content of the milk produced, but there was a decrease in the lactose content, compared to conventional feeding.

The fermentation of apple pomace proved to be an effective strategy in increasing the protein content of the residue, thus enabling its use in pig diets. Ajila et al. [7, 70-76] improved the protein content of bagasse by solid state fermentation using the fungus Phanerochaete chrysosporium. There was a 36% increase in protein content in the experimental diet using 5% fermented apple pomace. The fermented apple pomace generated nutritious product and improved the animals' performance.

Similarly, Vendrusculo et al. [22] used the fungus Gongronella butleri in order to increase the protein content of apple pomace, through cultivation in solid state, to be added to the fish feed (Tilapia). Under ideal conditions, obtained through experimental factorial design, a 3.3-fold increase in the soluble protein content of the diet was obtained, compared to the control. As a result, there was an increase of 13% in length, 11.5% in height and 44% in body weight of fish fed a protein-enriched diet.

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