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LUNA VALENTINA ANGULO ARIAS

DESENVOLVIMENTO DE UM PRODUTO ALIMENTÍCIO ENERGÉTICO FUNCIONAL A PARTIR DE SUBPRODUTOS AGROINDUSTRIAIS

DEVELOPMENT OF ENERGETIC FUNCTIONAL FOOD PRODUCT FROM AGRO-INDUSTRIAL BY-PRODUCTS

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Thesis presented to the School of Agricultural Engineering of the University of Campinas in partial fulfilment of the requirements for the degree of Doctor, in the area of Post-harvest Technology.

Tese apresentada à Faculdade de Engenharia Agrícola da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutora em Engenharia Agrícola, na área de Tecnologia Pós-colheita.

Supervisor: Prof. Dr. RAFAEL AUGUSTUS DE OLIVEIRA
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A Ata da defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do discente.

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RESUMO

A relevância e a necessidade do desenvolvimento de novas tecnologias para a produção de alimentos para atingir a demanda global e a qualidade nutricional de forma ecológica são uma tendência, objetivando fornecer segurança e proteção alimentar. Portanto, estão sendo realizadas pesquisas para reduzir os resíduos agroindustriais e plásticos, aproveitando os produtos não utilizados com potencial nutricional e com a capacidade de substituir materiais de difícil degradação utilizados na embalagem de alimentos e outros produtos. No processo de produção de alimentos, existem fatores limitantes, como altos custos tecnológicos e de fertilização, fundamentais para garantir alta produtividade e lucratividade e, mesmo atendendo essas necessidades, há perdas ao longo da cadeia. Além disso, o gerenciamento de resíduos ou subprodutos derivados de cadeias agroindustriais gera custos adicionais e favorece a poluição, quando mal planejado ou executado. Esses subprodutos podem ser ricos em nutrientes com potencial para serem utilizados na indústria de alimentos para consumidores normais, veganos e vegetarianos. Portanto, o correto gerenciamento e utilização desses subprodutos é vital para reduzir a poluição e obter benefícios econômicos, nutricionais e energéticos. Assim, o objetivo desta pesquisa foi desenvolver um produto alimentício em forma de gel aproveitando polpa e casca de café, casca de maracujá, casca de laranja e okara de soja, com embalagens reduzidas, usando filmes de amido. Esses subprodutos resultam do processamento de alguns dos produtos mais produzidos no Brasil, portanto, altamente disponíveis. Os subprodutos foram transformados em farinhas e caracterizados por sua composição centesimal, parâmetros físico-químicos e macro e micronutrientes. As farinhas apresentaram alto teor de proteínas, fibras, lipídios, carboidratos, Ca, K, Fe, Mg, Mn, Zn, concluindo que podem ser fonte desses nutrientes na alimentação diária. Foi feita uma mistura das farinhas para o preparo de um produto alimentar em forma de gel com teor de cafeína. Também foram desenvolvidos filmes a partir de amidos de batata e mandioca com características físico-químicas estáveis, estruturas homogêneas e resistentes e propriedades térmicas representativas de materiais capazes de substituir ou reduzir o uso de plástico nas embalagens de alimentos. Após avaliação da vida útil durante 13 dias a 10 °C do gel embalado usando tampas de amido de mandioca e batata, assim como de material plástico, concluiu-se que filmes

à base de amido de batata e mandioca podem ser usados como parte de embalagens de alimentos, reduzindo o uso do plástico.
Palavras chave: biopolímero; embalagem; café; laranja; resíduos.

ABSTRACT

The relevance and need of new technologies development for food production to reach the global demand and nutritional quality in a green friendly way are trends, as part of the objective of supply food safety and security. Therefore, research is being carried out in order to reduce agro-industrial and plastic waste, taking advantage of unused products with nutritional potential and with the ability to replace materials of difficult degradation that are used for packaging of food and other products. In food production process, there are limiting factors, as high technological and fertilization costs, fundamental to ensure high productivity and profitability and, even covering those needs, there are losses along the chain. In addition, managing wastes or by-products derived from agro-industrial chains creates additional costs and favors pollution, when poorly planned or executed. These by-products could be rich in nutrients with potential to be use at food industry for regular, vegan and vegetarian diners. So, the correct management and utilization of these by-products is vital to reduce pollution, as well as obtaining economic, nutritional and energetic benefits. The objective of this research was to develop a gel-shape food product exploiting pulp and coffee husk, passion fruit peel, orange peel and soy okara, with reduced plastic packaging using starches films. Those by-products are results from the processing of some of the most highly produced products in Brazil, so, highly available. The by-products were transformed into flours and characterized by its centesimal composition, physico-chemical parameters and macro and micronutrients. The flours showed high content of protein, fiber, lipids, carbohydrates, Ca, K, Fe, Mg, Mn, Zn, concluding that these flours could be source of those nutrients in a daily diet. A mix of the flours was made for the preparation of a gel-shape food product with caffeine content. Films were developed from potato and cassava starches, with stable physico-chemical characteristics, homogeneous and strong structure and thermal properties representative of materials able to replace or reduce plastic use in food packaging. After shelf life evaluation for 13 days at 10 °C of the packaged gel using cassava and potato starch lids, as well as plastic lids, it was concluding that films based on potato and cassava starches can be used as part of food packaging, reducing plastic use.
Keywords: biopolymer; packing; coffee; orange; waste.

SUMARY

INTRODUCTION

Food production has been manipulated to achieve high production peaks, and yet world hunger remains an issue to be resolved. In recent FAO statistics, world's population is increasing faster; it doubled since the early 1960s, approaching 7.5 billion people, confirming rising world hunger in recent years, after a prolonged decline. In 2017, estimated 821 million people (approximately one in every nine people) in the world still lack sufficient food to lead an active and healthy life. In addition, statistics based on the Food Insecurity Experience Scale (FIES) show that close to 10 percent of the world population was exposed to severe food insecurity (FAO, 2018). Throughout this development process, mankind has used engineering to achieve low-cost production goals, making cheaper food available to more people to supply basic needs of man's survival. However, these production processes generate waste and are far from being optimized processes, since the availability of food besides relying on production costs also depends on its proper storage and distribution.

Usually, by-products of agricultural activities are catalogued as "waste" as they are not primary products. Agricultural waste is widely available, renewable, with low cost and can be transformed into heat, steam, charcoal, methanol, ethanol, biodiesel and can also be transformed into other resources (animal feed, compost, energy, biogas and so on) (SABIITI, 2011). If agro-industrial by-products are not recycled or processed properly, they generate environmental problems. Some of them are burned or thrown into landfills, producing a large release of carbon dioxide, contamination of streams, stinks, proliferation of rats, flies and other insects. Agricultural by-products can be important resources for improving food security. However, if not properly treated, stored or disposed, these by-products may cause pollution or may affect human health. Despite these setbacks, agricultural by-products could be considered a great bio-resource for improving food security in small farming communities that would not be able to afford expensive inorganic fertilizers (SABIITI, 2011). Agro-industrial by-products are especially attractive because of their chemical compounds content (sugars, pigments, dietary fiber, protein, polyphenols, and lignin) and may have potential in the food industry after being subjected to chemical, thermal or microbiological treatments by turning products of earned value. According to the nutritional characteristics and the economic influence of agro-industrial by-products, it is possible to take advantage of their use in the preparation of various recipes by

identifying the nutritional composition. The full use of food provides a way to increase daily cooking, with the creation of new recipes such as jellies, pies, juices, sweets, and enriching the diet, providing more fibers, vitamins and minerals. However, the correct implantation of these foods in daily life depends on the knowledge about their centesimal composition (STORK, NUNES, OLIVEIRA & BASSO, 2013).

From a research and development point of view, functional foods represent an opportunity for innovative products that considerably satisfy existing demands. (BETORET, BETORET, VIDAL & FITO, 2011). Reducing costs and optimizing production processes are also important in order to recognize the nutritional potential of by-products and other possible uses at different areas of food and non-food consumption (bioenergy production, composting, pharmaceutical, among others). This could be seen as an innovation due to the functional components that can be obtained from of these by-products. Transforming raw materials in flour enables food availability, even in areas in which technology has no place, as it is processed food developed to maintain its quality without the need of further care in the storage and distribution phase, with an extended expiry date and that somehow complement human or animal nutrition and health. In this sense, it is possible to optimize agriculture production chains, also taking advantage of those deteriorated or rejected products and the by-products resulting from processing at any stage of the agro-industrial chain.

On the other hand, exploitation of plastic in food packaging is also a waste problem. Edible films and coatings are an innovation in active biodegradable packaging. They interact with foods to extend shelf-life, improve their sensory or functional properties, keeping food quality. These types of edible biopolymer-based packaging have been of great importance in the food industry thanks to representative factors such as biodegradability, which helps to reduce pollution and its ability to maintain food characteristics and the possibility of generating new markets for derived products from natural sources. These packages have been effective in preserving many foods, especially fruits and vegetables (DURANGO, SOARES & ARTEAGA, 2011). So, any type of material used for enrobing food to extend shelf life of the product that may be eaten together with food with or without further removal could be considered as edible film or coating (KUMAR, IRSHAD, RAGHUNATH & RAJARAJAN, 2016).

So, the aim of this work was to develop an energetic functional food from agro-industrial by-products, by the development and characterization of orange,

passion fruit, soybean and coffee by-products flours and to develop starch-based edible films to be used as part of food packaged.

In summary, this work was divided in four chapters. Chapter 1 shows the development of flours from orange and passion fruit peels by freeze drying, their nutritional characterization, their conservation and stability and their potential in food industry. Chapter 2 shows the development of okara flours by freezer drying and convection drying. At this chapter, the effects of the thermal treatments on their nutritional composition and their stability were compared. Chapter 3 shows the development of coffee by-products flours, in which the raw material were obtained from the wet and the dry process of coffee beans. The by-products from wet process were subjected to freeze and convective drying processes and the other material was dried just by convective method. The effects of the thermal treatments on their nutritional composition and their stability were also compared. An aqueous extraction of each flour was obtained in order to compare their caffeine content and organoleptic characteristics. Finally, Chapter 4 shows the application of the flours and the aqueous extract of coffee by-products using them to develop a nutritive gel. Along the chapter, the applied methodologies was showed to formulate edible films in order to use them as part of the packaging for the gel. The films were characterized by physico-chemical, mechanical properties, morphological and thermal analyses. Using starch from potato and cassava, films were developed and used as lids of a package. In order to compare the effects of the starch edible films and plastic lids at the packaged gel, an experiment of storage of the material was developed at refrigeration temperature (10°C) for two weeks, in which physico-chemical and microbiological changes along the time were analysed.

REVIEW

According to the Environment Protection Act of 1990 in United Kingdon, waste is any substance which constitutes scrap material, an effluent, unwanted surplus substance, article which requires disposing of as being broken, worn out, contaminated or otherwise spoiled (KUMAR, IRSHAD, RAGHUNATH, & RAJARAJAN, 2016).

Agro-industrial waste or by-products are products derived from the processing of agro-industrial raw materials that initially do not play a major role in the production chain due to the lack of knowledge of their nutritional or functional characteristics for both the food and non-food industries. Some of these by-products are fruit peels, tailings, liquid waste resulting from processing and other organic matter that is discarded from the main product. The elimination of these by-products means management difficulties for production companies (BARRAGÁN, TÉLLEZ & LAGUNA, 2008). Due to the world population increase and people mobilization to urban areas, there is a growing demand for food, resulting in a high accumulation of agriculture residues at farm and urban levels. Agriculture food production at developing countries is transported to cities in its raw form, thus exacerbating the net effect on large waste deposits in urban markets, around homes and in slum metropolitan regions, as well as in various landfills (SABIITI, 2011). These by-products from agricultural production chains can be harnessed for extracting compost, nutrients or even developing new food products, helping to reduce excess waste contamination and gain economic benefit. Generating food products from these by-products is an option that can mitigate the need for increased food production and reach a percentage of the market's nutritional demand. In addition, generating a new food product also contributes to research in the area of harnessing agriculture by-products. Some agro-industrial by-product could be called as bio-materials (SUD, MAHAJAN & KAUR, 2008). In agro-industry, it is possible to identify waste at different points of the production chain and some of these wastes can be used as by-products for use in different industries such as food industry. Management of waste in food service, prevent spending money on raw materials that would otherwise go in the garbage. At the same time, money will be saved on labor costs associated with handling these materials (KUMAR, IRSHAD, RAGHUNATH & RAJARAJAN, 2016). The use of by-products in soil bio-remediation, wastewater treatment processes and biosorption process of toxic metal ions has also been of great interest and several processes have been reported (BARRAGÁN, TÉLLEZ & LAGUNA, 2008; SUD, MAHAJAN & KAUR, 2008). By-products must be

transformed in earned value products because of its low cost, high availability and for being a renewable source of resources (SABIITI, 2011; SUD, MAHAJAN & KAUR, 2008).

There is no single concept that defines functional foods, but generally it has the ability to benefit human health or supplement nutrition. Some authors have defined functional foods as those that provide additional benefits to food. Others say that a food may be functional if it contains a component (nutrient or not) that benefits one or a limited number of functions in the body to keep health or reduce disease risks, or if it has a physiological or adverse effect as well as the traditional nutritional effect. The US Food and Drug Administration (FDA) subdivides the term "functional food" into two subcategories: "Medical Foods" and "Foods for Special Dietary Use." Other organizations such as the American Dietetic Association (ADA), the International Food Information Council (IFIC) and the Institute of Food Technologists (IFT) have developed definitions based on providing additional health benefits, as disease risk reduction and/or promote optimal health. In Europe, for the European Commission Concerted Action on Functional Food Science, functional foods, in addition to reducing the risk of disease and/or promoting optimal health, must demonstrate their effects under conditions that would normally be expected to consume a diet. Japan is the only country that legally recognizes functional foods as a distinct category. This category legally provides effects for certain diets and use aimed at maintaining and regulating specific health conditions (BALDISSERA, BETTA, PENNA & LINDNER, 2011; ROBERFROID, 2000).

Brazilian law stipulates that functional property is that related to the metabolic or physiological role that the nutrient or non-nutrient has in the growth, development, maintenance and other normal functions of the human organism. Any kind of claim referring to cure or disease prevention is not allowed (ANVISA, 1999). The National Health Surveillance Agency (ANVISA) regulated functional foods by Resolution RDC n° 02 of January 7, 2002, which approves the technical regulation of isolated bioactive substances and probiotics with functional or health claims (ANVISA, 2002). However, in Brazil, a functional food is one that provides benefits for the proper functioning of the organism and for health. Innovative industries are increasingly trying to use co-products and by-products to add nutritional and functional value and avoid a greater environmental impact on their waste generation (BALDISSERA, BETTA, PENNA & LINDNER, 2011).

In this study, it will be possible to identify the nutritional potential of some agro-industrial by-products and their health benefit after being subjected to thermal treatments and used as raw material for food industry. Over the past two decades, the term functional has been related to a broad group of products and components, as well as to designate pharmaceutical, nutraceutical, or foods of some specific health utility that improve or enhance the body's functions (SIKORSKI, 2007).

Brazil is one of the largest producers of orange, passion fruit, soybeans and coffee. Thus, the by-products resulting from the production chain of those products were the focus of the analyses developed throughout this study, being possible to process orange peel, passion fruit peel, soy okara and coffee pulp and husk to obtain flours. The flours were properly characterized from their centesimal composition, their chemical-chemical composition and their macro and micronutrient content.

The flours resulting from the thermal treatments of the by-products turned out to be foods with nutritional potential, being sources of protein, fibers and minerals.

In order to take advantage of the resulting flours, a mixture of flours was prepared for the preparation of a food in gel-shaped, which was subjected to physico-chemical and microbiological analysis to evaluate its shelf life. The gel was packed in a reduced plastic packaging, using an edible film developed from starch as a lid.

Plastic waste is also an environmental problem. Plastic materials are widely used for food packaging. Plastic waste is a problem that, besides affecting the environment, it is affecting the marine trophic chain. JAMBECK *et al*. (2015) reported that 275 million metric tons (MT) of plastic waste was generated in 192 coastal countries in 2010, with 4.8 to 12.7 million MT entering the ocean, from those countries Brazil is on the top 20 countries ranked by mass of mismanaged plastic waste at 16th position. Source reduction, reuse and recycle are the most powerful and effective ways to manage waste (KUMAR, IRSHAD, RAGHUNATH & RAJARAJAN, 2016). Therefore, at this study, potato and cassava starches were tested in order to determine the formulations of plasticizer and starch that would best fit to the function of packaging when compared to a completely plastic package in order to demonstrate the possibility of developing new products with high nutritional value, low cost and environmentally friendly. FAKHOURI, MARTELLI, CAON, VELASCO & MEI (2015) reported that edibles films are potential substitutes for conventional plastics in food packaging.

Biopolymer-based edible packaging has a large number of benefits that influence food quality and environmental preservation. Some of these benefits occur

because they are biodegradable, have the ability to carry additives, effective barrier and mechanical characteristics and, in some cases, improve visual and protect properties during storage and handling (DURANGO, SOARES & ARTEAGA, 2011). The early Apollo astronauts ate foods coated with starch-based films to prevent the crumbs from becoming airborne and floating around the weightless environment of the cabin (KRAMER, 2009).

It has been reported that the greatest advantage of using this type of packaging is its ability to carry active ingredients as agents that inhibit microbial growth, colorants, flavours, nutrients, spices, reduce the growth of pathogens on the food surface and provide specific nutrients that positively affect one or more body functions (BETORET, BETORET, VIDAL & FITO, 2011).

CHAPTER 1

Freeze drying flours of orange and passion fruit waste

Freeze drying flours of orange and passion fruit waste

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Abstract

Food production has been forced to increase along with the growth of world population, allowing the increasing of food waste that could means a pollution problem and resources loss. In order to control this waste generation and to supply nutritional needs, new products has been developed. In this way, production of functional flours based on waste (by-products) has become a tendency on the food market, providing nutrients and others dietary benefits. In addition, it could be part of a solution for environmental problems, for generated waste and another source of economic income. Therefore, the aim of this research work was to characterize flours of orange and passion fruit peels (FOP and FPFP) produced by freeze drying. Both flours were submitted to centesimal, physico-chemical composition, colour, macro and micronutrients content analyses. By characterization, it was observed that both products are rich in nutrients like protein, calcium, potassium, iron and crude fiber in significant way to benefit animal and human nutrition. Orange and passion fruit peels flours resulting of freeze drying process presented values of 9.62 and 4.4 $g.100g^{-1}$ of calcium, 7.18 and 22.55 $g.100g^{-1}$ of potassium, 3.68 and 26.74 $mg.100g^{-1}$ of iron, 11.55 and 39.1 $g.100g^{-1}$ of crude fiber, respectively, higher than the same materials submitted to others thermal processes to produce flour. Regarding to stability of food, freeze dried flours showed low values of water content (6.21% and 2.7% for FOP and FPFP) and water activity (0.20 and 0.24 for FOP and FPFP), which are desired characteristics of a stable product from the microbiological point of view and helpful for a longer shelf life.

Keywords: food; nutrition; nutrients; sustainability

1. Introduction

According to FAO, population is quickly increasing. The world's population has doubled since the early 1960s, approaching to 7.5 billion people, confirming an intensification in world hunger in recent years, after a prolonged decline. In 2017, an estimated 821 million people (approximately one in every nine people) in the world still lack sufficient food to lead an active and healthy life. In addition, statistics based on the Food Insecurity Experience Scale (FIES) show that close to 10 percent of the world population was exposed to severe food insecurity (FAO, 2018). Therefore, looking for sources such as waste and technology to improve food production with nutritional value and extended shelf life is a necessity as a mitigation measure of those world difficulties.

The agro-industrial waste or by-products are products derived from the agro-industrial processing of raw materials that initially do not have a main function in productive chain, due to the lack of knowledge of their nutritional or functional characteristics for food and non-food industries. Some of this waste are fruit peels, tailings, liquid waste and other organic material resultant from the processing of the main product that are discarded.

Agricultural waste is widely available, renewable, technically free and can be transformed into heat, steam, charcoal, methanol, ethanol, biodiesel and can be transformed into other resources (animal feed, fertilizer, energy, biogas, among others) (SABIITI, 2011).

Waste (by-products) resultant from agro-industrial processes which are not recycled or processed properly, incurs loss of resources and environmental problems could be developed (TONINI, ALBIZZATI & ASTRUP, 2018). Some waste are burn or throw into landfills, producing a large release of carbon dioxide, contamination of water slopes, stinks, rats, flies and other insect proliferation etc. The disposal of waste implies management problems for the producing companies (BARRAGÁN, TÉLLEZ & LAGUNA, 2008).

Due to world population increase and the mobilization to urban areas, there is a growing demand for food and this has resulted in a high accumulation of agricultural residues, at farm, municipality and city levels. The burden of agricultural food in developing countries are transported to cities in its raw form, thereby, aggravating the net effect on large waste deposits in urban markets, around homes and in slums as well as in various dumping grounds (SABIITI, 2011).

However, several researches have been developed with the objective of taking advantage of waste generated at processing of raw materials from different agro-industrial chains, resulting at the transformation of waste into by-products that can be used in different areas since the fertilization of crops until production of additives for food products and energy production.

Attention has been diverted to bio-materials, which are waste of large-scale industrial operations and agricultural waste (SUD, MAHAJAN & KAUR, 2008). The use of waste in processes of soil bio-remediation and treatment of water effluents has also been of great interest (BARRAGÁN, TÉLLEZ & LAGUNA, 2008).

Waste could be an important resource for food safety improvement. However, if it is not properly handled stored or disposed, this waste can cause pollution or can affect human health. Despite these setbacks, agricultural waste can be considered a major bio-resource for improving food safety in small farming communities that would not have the resources to use expensive inorganic fertilizers (SABIITI, 2011). These wastes contain high levels of nitrogen, phosphorus, potassium and organic matter important for maintaining soil nutrient quality in urban agriculture.

Waste are especially attractive because of their content of chemical compounds (sugars, pigments, dietary fibers, protein, polyphenols, lignin, etc.) and may have potential in the food industry after submitted to thermal, chemical or microbiological treatments.

Main use of agriculture waste is to turn them into resources that can be useful, not just discarded and can be exploited to enhance food safety by its application like bio-fertilizers, animal food and energy production (SABIITI, 2011).

Considering the nutritional characteristics and economic influence of agro-industrial waste, it is possible to exploit their use in the preparation of various recipes by the identification of the nutritional composition (STORK, NUNES, OLIVEIRA & BASSO, 2013). The authors also argue that the full use of food provides a way to increase daily cooking, creating new recipes such as jellies, pies, juices, sweets, and enriching the diet, providing more fibers, vitamins and minerals. However, the correct implantation of these foods in the daily life depends on the knowledge about its centesimal composition.

A chemical composition and bioactive compounds of the peels of some citrus fruits study reported the benefit potential of use these waste in food industry and in formulation of new products (RINCÓN, VASQUEZ & PADILLA, 2005).

Brazil is the largest producer of orange in the world and only in region of São Paulo was produced 74% of national production and 28% of world production for 2012, due to maintain a modern and advanced industrial complex for orange processing with international standard of competitiveness (INVESTE, 2013). According to the Brazilian Institute of Geography and Statistics, the estimated production of orange until august of 2019 was 16.507.309 of tons (IBGE, 2019). However, there is just a few technical scientific works about the disposal of resultant residues at this industrial level in Brazil. Orange peel is a waste resultant of production of pulp, juices, nectars and orange derivatives, with potential to be harnessed in food and non-food industry. Nowadays, there are women's accessories and some desserts that use orange peel as raw materials, but recent studies have shown how this waste can be used for other more cost-benefits purposes.

Orange peel is a waste that can be harnessed due to its functional characteristics (antioxidants) and fiber content. A study of addition of orange peel flour in the formulation of sausages obtained favourable results for yield, without affecting some texture and sensory parameters, and could be added to improve nutritional quality (GARCÍA & VERA, 2010). It is still possible to extract beneficial substances such as pectin or tannin from orange peels that can be used as coagulant in process of treating water for human consumption.

Brazil is also the world's largest producer and consumer of passion fruit, producing approximately 1 million tons per year, which production is mainly consumed in the internal market and exportation has occurred only on a small scale, in form of fresh fruit and concentrated juice (FALEIRO & JUNQUEIRA, 2016; MELETTI, 2011). Then, it is reasonable that with this great production of passion fruit, there is a great production of waste, making it essential to stablish strategies for its use.

According to specific technical standards of integrated production of passion fruit, only products harvested before falling of plant are allowed to be used when they are destined for consumption in raw form, while fruits on ground must be destined for industrialization (MAPA, 2005). This regulation restriction for using fruits creates difficulty for those producers who do not have market connections to destine their products to industrialization, inciting to the discard of fruits that become waste, including the peel and bagasse.

Passion fruit peels are 52% of the total fruit and the peels are mostly discarded, but some peels and pulp compounds can act as antioxidant, antihypertensive and can

decrease glucose and cholesterol rate in blood. In addition, it is rich in pectin, niacin (vitamin B3), iron, calcium and phosphorus (ZERAIK, PEREIRA, ZUIN & YARIWAKE, 2010).

However, it can be concluded that many nutrients are discarded jointly with the waste and a correct characterization of these materials will allow to correctly taking advantage of the agro-industrial waste, giving them a functional use and earned value, supporting the development of foods based on low cost raw materials. Thus, development of flours, which conformation is suitable to be included at any kind of food or pharmaceutics formulation, is an alternative to give earned value to orange and passion fruit peels at Brazil. Moreover, it is also important to apply technological treatments that keep nutritional and physico-chemical conditions of the products, extending shelf life. This extension of shelf life allows the distribution at places that need those low cost food, improving its benefits for customers and stimulating its consumption at unlike markets. According to FAO (2018), an adequate supply of food does not guarantee, by itself, household food security level. Food accessibility is influenced by incomes, food prices and the ability of households and individuals to obtain access to social support (FAO, 2018).

Hence, in this work, orange and passion fruit peels flours were produced by freeze drying treatment and characterized. The centesimal composition, physico-chemical analyses, macro and micronutrient contents were compared to flours based on orange and passion fruit waste as raw material, produced by other thermal treatment in order to state the influence of the treatment, maintaining favour condition of the final product.

2. Material and methods

Peels of orange and passion fruits were obtained from a local restaurant where they used just the orange and passion fruit pulps to produce juice. Peels and albedos were collected in sterilized black bags and carried to the laboratory, where the material was sanitized by 10 min immersion in peracetic acid (Pac200 Powder Disinfectant) solution with distilled water (0.0123g.L^{-1} of active compound in water). Then, the material was submitted to freeze drying (vacuum chamber stabilized at the minimum 0.75 Torr along the process, freezing temperature of -22 ºC, maximum defrosting temperature of 40 ºC and total process time of 26 h). The dry material were ground in hammer mill and sieved (60 mesh), in order to obtain the flours. The flours were stored in hermetically sealed glass jars at 25°C. Flours characterization was carried out to know its nutritional

potential according to its centesimal, physico-chemical composition, macro and micronutrients contents. These analyses were carried out on dry matter basis.

The methods described by AOAC were used to determine water and ash contents. Protein content was determined by Kjedahl method (AOAC, 2005). Lipids and crude fiber content were determined by method described by IAL (IAL, 2008); while carbohydrates were determined by difference. The nitric-perchloric acid method was used to determine macro and micronutrients contents. To determine the titratable acidity was used the method described by (CEREDA *et al*., 2001) and for the determination of the colour, pH and water activity were used specific equipment for direct reading.

For colour analyses, orange peels flour (FOP) and passion fruit peels peels (FPFP) were also submitted to convective drying at forced air stove (S) as described for ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) using 65 °C for 72 hours. For this analyses, the materials treated by freeze drying were marked with F. The treatment S was conducted like described by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018).

The parameters collected for colour were: L*, that indicates the luminosity (ΔL*=L*treatment-L*WHITE), a*, related to red and green colours (Δa*=a*treatment-a*WHITE), b*, related to yellow and blue colours (Δb*=b*treatment-b*WHITE), total variation of colour ($\Delta E^* = ((\Delta L^{*2})+(\Delta a^{*2})+(\Delta b^{*2}))^{½}$), chroma, that represents saturation ($C = (a^{*2}+b^{*2})^{½}$) and hue angle, related to the tonality (hue= arctang (b*/a*)). The values of L*, a* and b* were obtained by digital colorimeter with light source D65 and 10mm aperture, observation angle 10°, calibrated by the reference system of the excluded specular reflectance module (RSEX) and operating by means of the three-parameter reading system, in the CIE (International Commission of L'Eclairage) space and the equations proposed for HUNTERLAB (1997) were used to calculated the complementar paramethers.

These analyses were carried out on dry matter basis. It was used a t-test for mean comparison at confidence level of 95%.

3. Results and discussion

3.1 Centesimal composition

Table 1 shows centesimal characterization of orange peel flour (FOP), in addition to other data reports. The centesimal composition values were expressed in $g.100g^{-1}$ of dry matter.

Source	FOP	(ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018)[1]	(FORMICA *et al*., 2017)[1]	(M'HIRI, IOANNOU, GHOUL & MIHOUBI BOUDHRIOUA, 2015)[2]	(ADEWOLE, ADEWUMI, JONATHAN & FADAKA., 2014)[ut]	(BUBLITZ *et al*., 2013)[3]	(AL-SAADI, AHMAD & SA´EED, 2009)[ut]
Water content	6.60±0.04	11.33±0.05	6.86±0.21	3.17±0.12	11.75±0.27	11.75±0.27	11.86
Ashes	3.37±0.01	3.35±0.21	2.79±0.06	3.17±0.04	5.51±0.02	2.45±0.04	5.34
Lipids	1.37±0.31	1.49±0.21	ns	0.80±0.03	2.78±0.01	0.42±0.27	ns
Protein	4.23	4.78	ns	8.12±0.12	16.51±0.40	5.89±0.41	4.00
Crude fiber	12.37±0.67	9.53±0.50	ns	ns	12.47±0.54	16.20±0.90	ns
Carbo-hydrates	78.66	69.53	ns	ns	40.47±0.37	63.39±0.50	ns

Centesimal composition expressed in g.100g^{-1}. Treatments: [1]convective drying; [2]storage at -20°C; [3]orange albedo dried at 70°C/10h; [ut]untreated; ns indicates that the information was not specified

Table 1. Centesimal composition of orange waste flour from different research sources.

The centesimal composition of FOP indicates its nutritional potential as food, mainly because of its fiber content. Regarding to the treatment (freeze drying), the flour achieved a low water content and conserve the fiber content of the fresh matter, that favour flour quality.

Table 2 shows centesimal characterization of passion fruit peel flour (FPFP), in addition to other data reports about this type of waste.

For powder products, a low water content is preferred. So, related to this characteristic, freeze drying process showed better results for producing lower water content flour. However, the values are below the maximum allowed by Brazilian legislation for flour 15% (ANVISA, 1996). Thereby, it can be said that the water content obtained in this work was within the parameters suitable for the product. These values favour the conservation of the product, in addition to avoiding growth of microorganisms and allowing an extended shelf life. In addition, analysing the results variability of different references, thermal treatment affects water contents of orange and passion fruit peel flours.

Source	FPFP	(ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018)[1]	(DOS REIS, FACCO, SALVADOR, FLÔRES & RIOS, 2018)[ut]	(CAZARIN, SILVA, COLOMEU, ZOLLNER & JUNIOR, 2014)[1]	(SOUZA, FERREIRA & VIEIRA, 2008)[cf]	(CARNEIRO, 2001)[4]
Water content	2.76±0.04	9.34±0.06	ns	9.48±0.26	ns	ns
Ashes	6.00±0.52	6.99±0.16	6.62±0.24	6.88±0.02	8.66	5.90
Lipids	0.48±0.12	1.00±0.10	4.20±0.03	0.31±0.01	1.75	3.09
Protein	5.44	5.95±0.31	3.40±0.06	3.94±0.18	12.52	7.53
Crude Fiber	39.10±3.40	26.61±0.93	ns	ns	41.67	56.59
Carbohydrates	48.98	50.11±0.56	85.78±0.00	79.39	77.38	ns

The units of the centesimal parameters were at $g.100g^{-1}$. [1]convective drying 65°C; [4] convective drying 70°C/0.28$m.s^{-1}$; [cf]comercial flour; [ut]untreated; ns indicates that the information was not specified

Table 2. Centesimal composition of passion fruit waste flour from different research sources

The ashes content of FPFP, showed that it is richer in mineral than FOP. Comparing the values of different thermal treatments, ashes content of FPFP were closer to the showed by the cited literature, just being lower than a commercial flour (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018;DOS REIS, FACCO, SALVADOR, FLÔRES & RIOS, 2018; CAZARIN, SILVA, COLOMEU, ZOLLNER & JUNIOR, 2014; CARNEIRO, 2001; SOUZA, FERREIRA & VIEIRA, 2008). These values indicated a low level of impurities, since the ashes obtained are not essentially of same composition as the mineral matter originally present in food, because there may be loss by volatilization and/or some interaction among constituents of the sample (IAL, 2008).

According to Tables 1 and 2, FOP and FPFP showed a low lipids content; this is a desired and expected requirement by consumer within a low caloric diet.

Comparing the protein content of FPFP, it was higher than the content at FOP. According to the cited literature, it was possible to say that the protein content could vary depending on different factors besides the thermal treatment. The protein content of carioca beans after cooking is similar to the obtained for FOP and FPFP (4.8 $g.100g^{-1}$) (TACO, 2011). So, using FOP and FPFP for novel products or direct consumption could be an alternatives as nutrient for people who practice vegetarian food consumption. COLOMEU, ZOLLNER & JUNIOR (2014) affirm that passion fruit peels can be used as a source of fiber. Since fiber-rich passion fruit peels are available in

large quantities as a waste of juice production, it could be used as an intermediate ingredient in the development of functional food.

In other words, according to centesimal composition, there must be other factors, such as the variety of the fruit, which affect the final composition of the flour, besides of the type of thermal treatment to produce it. Comparing FOP and FPFP, FPFP showed better nutritional characteristics and low water content that improved it shell life, allowing it consumption as a functional flour because of its protein and crude fiber contents.

3.2 Macro and micronutrients of orange and passion fruit peel flours

In human nutrition, macronutrients have the function of help in the health care and micronutrients are used to produce energy. So, it is important to supply those nutrients every day in order to keep good health and enough energy to fulfil human daily tasks. Table 3 shows that FPFP flour is richer in most of the macro and micronutrients when compared with FOP, which presents higher values for Ca, B and Cu. A similar relation was found by (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018), who concluded that, studying macro and micronutrients content of flours of orange and passion fruit peels produced by convective drying, the flour of passion fruit peels was also richer for macro and micronutrients.

		Flour	
Nutrients	**Unit***	**FOP**	**FPFP**
N	**g**	0.632	0.846
P	**g**	0.098	0.115
K	**g**	0.718	2.255
Ca	**g**	0.962	0.440
Mg	**g**	0.089	0.111
S	**g**	0.042	0.071
B	**mg**	1.416	0.929
Cu	**mg**	0.258	0.184
Fe	**mg**	0.368	2.674
Mn	**mg**	0.797	1.958
Zn	**mg**	0.886	6.357

*** for 100g**

Table 3. Macro and Micronutrients of orange and passion fruit peel flour

FOP showed higher values of Ca, Mg and Mn (0.962 $g.100g^{-1}$, 0.089 $g.100g^{-1}$ and 0.797 $mg.100g^{-1}$), when compared to the flour of orange peel produce by convective drying, as found by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) (0.496 $g.100g^{-1}$,

0.069 g.100g^{-1} and 0.245 mg.100g^{-1}), who showed higher values for the others macro and micronutrients. In this way, the same work found higher values for flour of passion fruit peels. In addition, FPFP presented higher values for Mn and Zn (1.958 mg.100g^{-1} and 6.357 mg.100g^{-1}) when compared with the found by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) (0.985 mg.100g^{-1} and 1.031 mg.100g^{-1}). According to CÓRDOVA, GAMA, WINTER, NETO & FREITAS (2005), passion fruit peels had calcium content of 28.4 mg.100g^{-1}, value that exceed calcium content of the pulp. Whereas, for the sodium and iron contents, the peels also presented the highest values, concluding that passion fruit peels can be a source for obtaining these minerals and support development of new products based on passion fruit peel.

FPFP showed higher content of Fe (2.674 mg. 100g^{-1}) when compared to other vegetables sources considered rich in this nutrient (TACO, 2011), such as: spinach (0.4 mg.100g^{-1}), broccolis (0.5 mg.100g^{-1}), *carioca* beans (1.3 mg.100g^{-1}). In addition, FPFP showed higher content of Zn, Mn and N when compared to yellow passion fruit peel without thermal treatment, in which were 1 mg.100g^{-1} of Zn, 0.5 mg.100g^{-1} of Mn and 6.2 mg.100g^{-1} of N (DOS REIS, FACCO, SALVADOR, FLÔRES & RIOS, 2018). Furthermore, FPFP is good alternative for fortification of iron as it can be handled in solid form to manufacture a fortified flour-based food, such as cookies, breads, among other products.

3.3 Physico-chemical analyses of orange and passion fruit peel flours

Table 4 shows the results obtained for physico-chemical analyses of the flours. FOP samples presented higher value of titratable acidity, indicating higher presence of citric acid equivalent in the flour when compared with FPFP. This compound has multiple benefits, not only for food preservation, but also for human health, in part, due to its antioxidant capacity. Citric acid is an acidulant, preservative, emulsifier, flavorant, sequestrant and buffering agent widely used, especially in food, beverage, pharmaceutical, nutraceutical and cosmetic products (VERHOFF, 2005). According to CIRIMINNA, MENEGUZZO, DELISI & PAGLIARO (2017), citric acid was the main biotechnology product of chemical industry and a chemical key of emerging bio-economy. Titratable acidity of FOP was similar to the 5.38 found by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) for the same raw material flour. However, ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) found a value of 5.96 for passion fruit peels flour, which is higher than the titratable acidity of FPFP.

Flour	**Titratable Acidity** (% citric acid)	**pH**	**Aw** (decimal)
FOP	5.54±0.13	4.18±0.24	0.42±0.02
FPFP	2.16±0.14	4.29±0.08	0.22±0.02

Table 4. Physico-chemical composition of orange and passion fruit peel flours

The pH values obtained for orange and passion fruit peels flours were similar to the values found by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018) (4.43 and 4.18), exceeding the characteristic pH range for citrus fruits (3.4-4) described by CORRÊA-NETO & FARIA (1999). These values can be considered low for FOP and FPFP, being a safety feature, since low pH values inhibit the development of pathogenic microorganisms in the product.

Water activity demonstrates how much water the food has available to favour microbial growth. When below 0.3, there is no water available for development of microorganisms (SILVA, BORGES & FERREIRA, 1999). Thus, FPFP samples are considered stable (Table 4) from a microbiological and degradation chemical reactions point of view and the shelf life is prolonged as long as product is stored in order to maintain constant low water activity, lower than 0.43 found for CAZARIN, SILVA, COLOMEU, ZOLLNER & JUNIOR (2014).

Table 5 shows the colour analyses of orange peels flour (FOP) obtained by forced air stove (S) and by freeze drying (F). The treatment S was conducted like described by ARIAS, SILVA, OLIVEIRA & FAKHOURI (2018). The colour of a product is an important characteristic that could determinates its consumption, and is commonly related to its quality. For FOP, thermal treatment did not influence the final result of yellow coloration (b; Δb*), while the saturation of the flours colour (Chroma) was not statistically different for the treatments. As yellow is a desired characteristic colour for an orange peels flour, both treatment could be implemented to produce FOP. The results for ΔL* and Δa* show that both FOP are clear, but S treatment produce a darker product and F presents a higher yellow tonality (hue angle). The flour photos at Figure1 supported the previous results.

	Treatment						
	S		F				
Parameters	**Mean**	**Std. Dv**	**Mean**	**Std. Dv**	**t**	**df**	**P**
L*	75.79	0.22	82.33	1.01	-12.38	2	0.006
a*	5.18	0.09	3.29	0.22	15.08	2	0.004
b*	34.39	0.23	33.86	0.26	2.18	2	0.161
ΔL*	21.76	0.22	15.22	1.01	12.38	2	0.006
Δa*	-5.00	0.09	-3.11	0.22	-15.08	2	0.004
Δb*	-34.60	0.23	-34.07	0.26	-2.18	2	0.161
ΔE*	41.18	0.31	37.45	0.49	13.55	2	0.005
Chroma	34.78	0.24	34.02	0.28	3.01	2	0.095
°hue	81.43	0.09	84.46	0,33	-16.55	2	0.004
WHITE	L*=97.55	a*=0.18	b*=-0.21				

"Mean differences are statistically significant at p < .0500"

Table 5. Colour parameters of orange peels flour produced by different thermal treatments

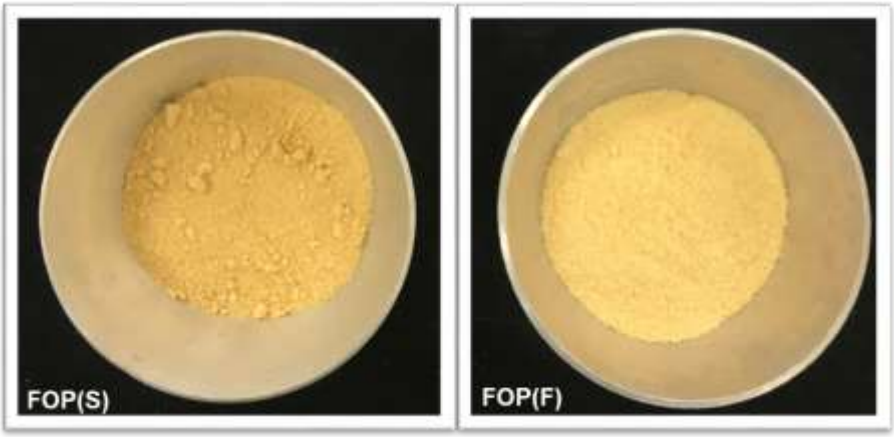

Figure 1. Orange peel flour (FOP) dried by forced air stove (S) and by freeze drying (F)

For FPFP, both treatments result in clear flours with significant difference on all the colour parameters, in which S treatment produced the darkness flour and F results in luminous, pale, yellow flour. A clear, bright and light yellow is a desired colour for ripe fruits of orange and passion fruit (PEREIRA, MACHADO & COSTA, 2014) (REOLON, 2008). Therefore, good colours characteristics were obtained for both treatment, but S produced a burned yellow, due to the reaction of carbohydrates and nitrogen compounds at high temperature exposure or Maillard reactions, concluding that FPFP components of colour are more sensitive to thermal treatment. The flour photos at Figure 2 supported the previous results.

	Treatment						
	S		F				
Parameters	**Mean**	**Std. Dv**	**Mean**	**Std. Dv**	**t**	**df**	**p**
L*	77.45	1.38	87.74	0.63	-9.84	2	0.010
a*	4.02	0.38	0.72	0.20	10.77	2	0.009
a*	30.89	0.59	21.95	0.70	16.12	2	0.004
ΔL*	20.10	1.38	9.81	0.63	9.84	2	0.010
Δa*	-3.84	0.38	-0.54	0.20	-10.77	2	0.009
Δb*	-31.10	0.59	-22.16	0.70	-16.12	2	0.004
ΔE*	37.24	1.14	24.24	0.70	12.62	2	0.006
Chroma	31.15	0.63	21.96	0.70	15.89	2	0.004
°hue	82.59	0.55	88.13	0.46	-10.27	2	0.009
WHITE	L*=97.55	a*=0.18	b*=-0.21				

"Mean differences are statistically significant at p < 0.0500"

Table 6. Colour parameters of passion fruit peels flour produced by different thermal treatment.

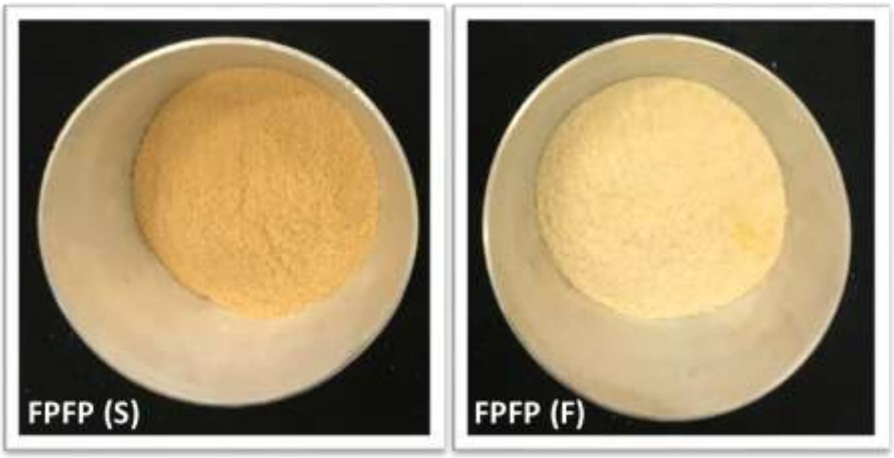

Figure 1. Passion fruit peel flour (FPFP) dried by forced air stove (S) and by freeze drying (F).

4. Conclusions

Both products are rich in nutrients like protein, calcium, potassium, iron and crude fiber in significant way to benefit human nutrition. FPFP stood out, being a better source of nutrients. According to its nutritional potential both flours could be source of important nutrients that could be exploited at vegan and vegetarian food market in order to prepared recipes or develop new food products.

For food stability, freeze dried flours showed low values of water content and, for the physico-chemical characterization, both flours demonstrated to be stable products from the microbiological point of view and supportive for a longer shelf life due to its low Aw.

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CHAPTER 2

Effect of thermal treatments on the nutritional composition of soy okara flour

Effect of thermal treatments on the nutritional composition of soy okara flour

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Abstract

The okara, also known as soybean pulp, is a by-product resulting of processing of soybeans to produce soy milk. This doughy material has a nutritional potential to the development of food rich in lipids, protein, vitamins and antioxidants compounds that could satisfy nutritional needs of vegetarian and vegan diets that, currently, attract more consumers. Normally, raw material of okara presents approximately 80% of water in its constitution and high water activity, becoming a problem considering deterioration and alterations by chemical and enzymatic reactions. An alternative to improve that condition and take an advantage of the properties of this by-product is to subject it to drying treatment, developing a nutritive flour. Thus, the aim of this research work was to obtain okara flour by convective drying (CD) in forced air stove at 65°C for 72 hours and by freeze drying (FD) and characterize the resulting products. Okara flours were characterized considering centesimal and physico-chemical composition, and also macro and micronutrients content, in order to know its potential for new products development. Both flours proved to be nutritionally rich: the main nutrient contents for freeze dried flour were 59.54 $mg.100g^{-1}$ of iron, 32.83 $mg.100g^{-1}$ of zinc, 21.93 $mg.100g^{-1}$ of boron and 9.8 $g.100g^{-1}$ of potassium and, for convective dried flour, were 58.07 $mg.100g^{-1}$ of iron, 32.15 $mg.100g^{-1}$ of zinc, 24.41 $mg.100g^{-1}$ of boron and 12.7 $g.100g^{-1}$ of potassium. The amount of crude fiber were higher for freeze dried flour than flour produced by convective drying. The protein contents were 40.68 and 27.38 $g.100g^{-1}$ for CD and FD flours, respectively, while 20.31 and 14.27 $g.100g^{-1}$ were lipids content. These values are significantly higher when compared with others vegetable sources. Both flours showed water activity about 0.3, containing strongly bound water. So, okara flours showed nutritional and microbiologically stable behaviour.

Keywords: gluten-free; nutrients; sustainability; by-product.

1. Introduction

Brazil is the world' second largest soy producer and exporter. Between 2018 and 2019, soy production was about 114.843 million tons with mean production of 3.206 kg per hectare (EMBRAPA, 2019).

The solid extract resulting from soybean processing for soy milk production is known as okara, and it is rich in protein and isoflavones. It is reported that okara has 2.8 $g.100g^{-1}$ of ashes, 37 $g.100g^{-1}$ of protein, 13 $g.100g^{-1}$ of lipids, 42.5 $g.100g^{-1}$ of dietary fiber and 35.7 mg% of total isoflavones (BOWLES & DEMIATE, 2006). The importance of the positive effect of isoflavones in preventing chronic degenerative diseases such as some cancers and heart disease makes it interesting to add this by-product in formulations for enrichment of food products.

From different soybean industrial processes, large volumes of by-products are generated, which must be properly used (TOMBINI, RONCATTI, LIMA & CUNHA, 2015). Industrially, soy by-product is processed for animal feed. Soy protein is the basis of bakery ingredients, pasta, meat products, cereals, prepared mixes, beverages, baby food, dietary foods and also used by adhesives and nutrients industry, as well as fertilizers, foam formulator, fiber manufacturing, coating and water emulsion paper for inks. The manufacture of agro-industrial by-products flours has been prominent in produce cookies, cakes, breads and used as a source of fibers, minerals, among other compounds. Microfibrillated cellulose obtained from okara has a great potential as reinforcement in eco-friendly cellulosic nanofibrillated for diversified applications (LI, WANG, HOU & LI, 2018). Soybean okara was used in sausage manufacturing, obtaining sensory acceptance of up to 92% (GRIZOTTO, ANDRADE, KIYAGUSKU & YAMADA, 2012).

The okara yield per kilogram of soy is 0.4 kilograms of dry product suitable for human consumption (LESCANO, 2009), that is a good portion of material to be used and higher percentage of proteins and lipids remains in the solid fraction during the okara obtaining (YOSHIDA, PEREIRA, CASTILHO & SEIBEL, 2014).

However, it is necessary to apply treatment to this by-product aiming its use in human food, to facilitate its addition in formulation of new products and to increase its shelf life. Reduction of water content treatments are alternatives to obtain a concentrated product with low water activity. Under specific conditions, those treatments can keep the original quality, properties and composition of the raw material, and could improve the exploitation of nutrients. Drying processes could produce encapsulation of the

proteins inside a structure of polysaccharides, allowing the preservation or improvement of the properties of some food ingredients (BUERA, SCHEBOR & ELIZALDE, 2005). Fresh okara deteriorates rapidly because of its high water activity and content (O'TOOLE, 1999). As explained, okara must be dried as soon as possible under appropriate conditions in order to keep its integrity and allow its use as flour (WACHIRAPHANSAKUL & DAVAHASTIN, 2007).

The objective of this research work was to produce okara flour applying convective and freeze drying treatments, in order to evaluate the influence of thermal treatment on nutritional composition and to obtain a nutritive food product, suitable for human intake and for addition in other food formulations.

2. Material and methods

In order to produce okara soy, 2 kg of soybeans (Camil, São Paulo-SP, Brazil) were bought at local market of Campinas, SP, Brazil. The beans were immersed in 3 L of distiller water over night. Then, every 100g of hydrated beans with 1L of distiller water were crushed by centrifugation with blades for 3 minutes. Okara was obtained filtering off by press that crushed material, until remove great aqueous portion. Okara was used to produce flours applying two kinds of thermal treatments: convective drying by forced air stove (CD) at 65°C for 72 hours and by freeze drying (FD) with vacuum chamber stabilized at the minimum 0.75 Torr along the process, freezing temperature of -22 ºC, maximum defrosting temperature of 40 ºC and total process time of 26 h. The dry material were milled and sieved (60 mesh) in order to obtain the flours. The flours were stored in hermetically sealed glass jars at 25°C.The flours characterization was carried out to know its nutritional potential according to its centesimal, physico-chemical composition, macro and micronutrients contents.

The methods described by AOAC were used to determine water and ash contents. Protein content was determined by Kjedahl method (AOAC, 2005). Lipids and crude fiber content were determined by method described by IAL (IAL, 2008); while carbohydrates were determined by difference. The nitric-perchloric acid method was used to determine macro and micronutrients contents. To determine the titratable acidity was used the method described by (CEREDA *et al*., 2001) and for the determination of the colour, pH and water activity were used specific equipment for direct reading.

The parameters collected for colour were: L*, that indicates the luminosity (ΔL*=L*treatment-L*WHITE), a*, related to red and green colours (Δa*=a*treatment-a*WHITE), b*, related to yellow and blue colours (Δb*=b*treatment-b*WHITE), total variation of colour ($\Delta E^* = ((\Delta L^{*2})+(\Delta a^{*2})+(\Delta b^{*2}))^{½}$), chroma, that represents saturation ($C = (a^{*2}+b^{*2})^{½}$) and hue angle, related to the tonality (hue= arctang (b*/a*)). The values of L*, a* and b* were obtained by digital colorimeter with light source D65 and 10 mm aperture, observation angle 10°, calibrated by the reference system of the excluded specular reflectance module (RSEX) and operating by means of the three-parameter reading system, in the CIE (International Commission of L'Eclairage) space and the equations proposed for HUNTERLAB (1997) were used to calculated the complementar paramethers.

These analyses were carried out on dry matter basis. It was used a t-test for mean comparison at confidence level of 95%.

3. Results and discussion

The flours resulting from the treatments presented conditions of colour and odour characteristic of soybeans, a homogeneous dusty material without obvious visual difference (Figure 1). However, considering the results of centesimal composition, treatments affected significantly water, ashes, lipids and crude fiber contents. While FD treatment showed the lowest water content and the highest content of crude fiber and carbohydrates, CD showed highest content of ashes, lipids, protein and water content, as shown at Table 1. Both flours presented desirable nutritive characteristics that could benefit human health. Table 1 shows that thermal treatments had significant statistical differences for the centesimal parameters.

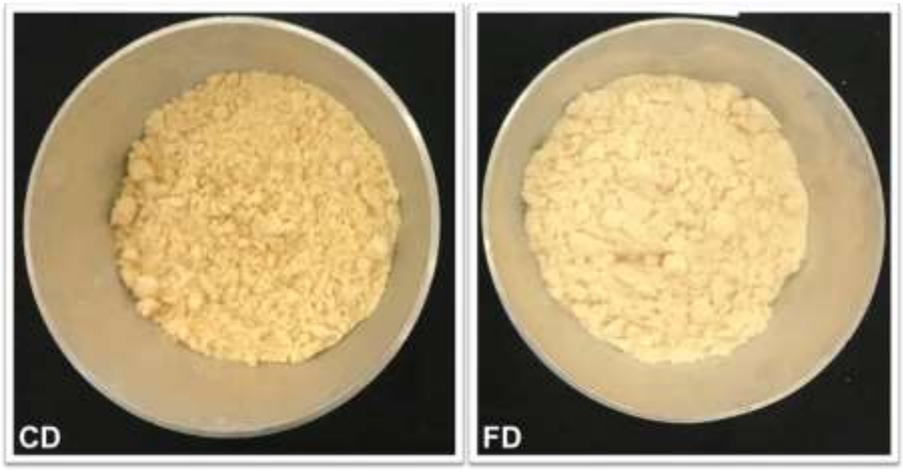

Figure 1. Okara soy flours obtained by convective drying (CD) and freeze drying (FD).

	Treatment				
	CD	FD	T-test		
	Mean/Std.Dv	Mean/Std.Dv	t	Df	p
Water content	8.21±0.03	2.52±0.05	147.653	2	0.0001
Ashes	4.54±0.09	3.16±0.11	14.497	2	0.0047
Lipids	20.31±0.17	14.27±0.31	25.904	2	0.0015
Protein	40.68	27.38	-	-	-
Crude fiber	8.49±0.90	24.11±0.70	-23.033	2	0.0019
Carbohydrates	25.98	31.08	-	-	-

Units of centesimal parameters are $g.100g^{-1}$ of dry matter. Mean differences are significant at $p < .0500$. Space with - : t test was not applied.

Table 1. Centesimal composition of okara soy flours.

Centesimal composition allows obtaining basis nutritional information; necessary to develop any product based on the studied material. Okara has been widely studied over years, because of its innumerable nutritional properties beneficial to health and because it can be used for development of gluten-free foods rich in protein. Thermal treatments, applied to transform a raw material in food, could generate changes at the flour. Research reports showed centesimal characterization of okara *in natura* (IN) and treated by flash pneumatic dryer (FP), traditional convective drying (CD) in stove at different temperatures, microwave (OM), rotatory dryer with convective airflow (OR), freeze dryer (OF) and spin-flash drying (SF). Table 2 shows the results of centesimal composition of okara flour produced by those treatments.

Considering Tables 1 and 2, water content presented variability related to the type of thermal treatment, varying from 1.38 $g.100g^{-1}$ to 17.68 $g.100g^{-1}$. The parameter with the lowest variability was ashes content, varying from 0.34 $g.100g^{-1}$ to 4.54 $g.100g^{-1}$. The 4.54 $g.100g^{-1}$ of ashes from okara *in natura* corresponds to the ashes content obtained from okara flour by CD at this present work. The values for lipids varying from 2.63 $g.100g^{-1}$ to 20.31 $g.100g^{-1}$. The highest value was shown for okara treated by CD at this work, as well as for the protein content. Protein content was higher than protein content of carioca beans after cooking (4.8 $g.100g^{-1}$) (TACO, 2011). The values for crude fiber also varied greatly, since different values were obtained for the same thermal treatment (CD). Therefore, it is possible that fiber content of okara flour does not depend just on the thermal treatment, since centesimal composition of soy could vary depending on the variety and harvest season (VIEIRA, CABRAL & PAULA, 1999).

Source	IN [1]	FP[2a]	FP[2b]	CD (65°C)[3]	CD (105°C)[4]	OM[5]	OF[5]	OR[5]	SF[6]
Water content	-	6.88	6.51	10.22	4.37	1.38	3.62	17.68	4.91
Ashes	4.54	4.01	3.93	2.58	0.34	3.44	2.24	1.80	3.40
Lipids	12.3	16.71	17.08	18.33	2.63	19.10	18.98	14.74	3.60
Protein	26.8	35.36	34.93	36.46	46.49	34.61	33.39	30.79	18.1
Crude Fiber	-	20.58	16.12	40.18	25.35	20.37	23.14	22.45	-
Carbohydrates	52.9	16.46	21.44	36.62	-	21.11	18.74	16.37	-

Units of centesimal parameters are $g.100g^{-1}$. (MA, LIU, KWOK & KWOK, 1997)[1], (GRIZOTTO, RUFI, YAMADA & VICENTE, 2010)[2], (YOSHIDA, PEREIRA, CASTILHO & SEIBEL, 2014)[3], (TOMBINI, RONCATTI, LIMA & CUNHA, 2015)[4], (OSTERMANN-PROCEL, RINALDONI, RODRIGUEZ-FURLÁN & CAMPDERROS, 2016)[5], (LI *et al*., 2019)[6].

Table 2. Centesimal composition of okara flours reported by different sources.

According to Table 3 and Table 1, the CD treatment flour showed the highest content for the majority of macro and micronutrients. It is in accordance with the fact of having presented the highest ashes content. For macronutrients, CD was a richer than the FD flour for N, P and K. Both flours showed similar contents of Mg and S, but those were still higher for CD. The FD treatment flour stood out for showed the highest content of Ca. Related to the micronutrients contents, CD treatment resulted in a flour richer in Cu, while FD was richer in Mn.

Treatment / Nutrients	Unit*	CD	FD
N	**g**	5.974	4.270
P	**g**	0.485	0.294
K	**g**	1.269	0.980
Ca	**g**	0.287	0.599
Mg	**g**	0.233	0.212
S	**g**	0.252	0.189
B	**mg**	2.441	2.193
Cu	**mg**	3.241	0.559
Fe	**mg**	5.807	5.954
Mn	**mg**	1.828	3.392
Zn	**mg**	3.215	3.283

***** for 100g of flour

Table 3. Macro and Micronutrients of okara soy flour.

However, comparing the K, Ca, Mg and Fe contents of the flours with others vegetable sources as parsley that have 0.35 g.100g^{-1} and 2 mg.100 g^{-1} of K and Fe, respectively, spinach with 0.15 g.100g^{-1} of Ca, sweet maize 0.050 g.100g^{-1} of Mg, it is possible to state that okara flours are source rich in those minerals (SIKORSKI, 2007). Despite of Zn was the mineral in the lowest amount of all flours, the Zn contents were higher than the content of Zn in bee honey, fish and meat (0.08-1.2 mg.100g^{-1}) (SIKORSKI, 2007). In addition, according to Mean Daily Intake and Recommended Dietary Allowances (RDA), 100 g of okara flours can supply the mean daily intake of Mg (0.145 g.100g^{-1}) and B (0.001-0.003 g.100g^{-1}). According to Safe and Adequate Intake (SAI), 100g or least of okara flours can supply daily intake of Mn (2-3 mg.100g^{-1}) (SIKORSKI, 2007). According to Tables 1 and 3, the high nutritional potential of okara flour was evidenced. Those results could be reinforced by some works, in which okara flour was added in a food preparation. Incorporation of okara flour in cookies showed nutritional increase and good acceptance by judges. It was reported that addition of okara flour increased protein, lipids, ashes and dietary fiber content (YOSHIDA, PEREIRA, CASTILHO & SEIBEL, 2014). Some studies also found that intake of fiber obtained from okara amend some of the high fat diet adverse metabolic effects and prevent adipose tissue accumulation (DAI, HUANG & DENG, 2019).

The thermal treatments had significant statistical differences for titratable acidity and pH of the flours, as shown at Table 4. Those parameter are related to the taste, acid organic content and conservation of the product. The CD treatment flour could be a better source of organic acids that are important for production and metabolism of vitamins. Aw of both flour was lower than the obtained for a flour treated with CD at 105°C of 0.65 (TOMBINI, RONCATTI, LIMA & CUNHA, 2015). The results for pH of CD and FD are similar (Table 4), besides, it was a significant statistical difference, and was similar to the pH of the water soluble extract of soy of 6.6 (BARROS & VENTURINI-FILHO, 2016). Considering the low flours water contents (Table1) and water activity (Table 4), it is possible to state that both products are microbiologically stable and could have an extended shelf life. Low water content inhibits microbial growth and, when Aw below 0.3, there is no water available for development of microorganisms (SILVA, BORGES & FERREIRA, 1999).

	Treatment				
	CD	FD	Test t		
	Mean/Std.Dv	Mean/ Std.Dv	t	df	p
Titratable Acidity (% citric acid)	1.24±0.01	0.72±0.01	257.673	2	0.0000
pH	6.24±0.01	6.42±0.01	-18.000	2	0.0031
Aw (decimal)	0.25±0.01	0.31±0.04	-3.097	2	0.0903

"Mean differences are significant at p < .0500"

Table 4. Physico-chemical composition of okara soy flour.

Table 5 shows colour parameters for the thermal treatments used for okara flours production. By the statistical point of view, thermal treatments made not difference for yellow coloration (b; Δb*****), saturation (chroma) and the total difference of colour (ΔE*). As showed at Table 5, it is possible to state that both treatments resulting at a clear with a yellow tonality flour. Comparing to the work described by OSTERMANN-PROCEL, RINALDONI, RODRIGUEZ-FURLÁN & CAMPDERROS (2016), in which okara was dried by microwave (OM), freeze-dried (OF) and rotatory dryer (OR), the flour of this work showed to be lighter (L*= 69.50, 74.85 and 69.53, respectively). The values for redness (a*= 4.01, 2.29 and 4.19, respectively) were similar at both works, being low values. That same behaviour was evidenced for yellowness (b*= 23.92, 19.50 and 25.17, respectively).

	Treatment						
	CD		FD				
Parameters	**Mean**	**Std. Dv**	**Mean**	**Std. Dv**	**t**	**df**	**p**
L*	85.71	1.87	83.97	1.38	5.78	2	0.029
a*	1.94	0.47	3.19	0.27	-6.70	2	0.022
b*	25.63	1.17	24.32	0.67	1.98	2	0.187
ΔL*	11.84	1.87	13.58	1.38	-5.78	2	0.029
Δa*	-1.76	0.47	-3.01	0.27	6.70	2	0.022
Δb*	-25.84	1.17	-24.53	0.67	-1.98	2	0.187
ΔE*	28.51	1.37	28.20	1.28	0.56	2	0.632
Chroma	25.70	1.19	24.53	0.70	1.75	2	0.223
°hue	85.69	0.89	82.54	0.41	9.12	2	0.012
WHITE	L*=97.55	a*=0.18	b*=-0.21				

"Mean differences are significant at p < 0.050"

Table 5. Colour parameters of okara flours produced by different thermal treatment

4. Conclusion

Nutritive flours from okara soy were obtained by convective and freezer drying treatments. Convective drying method showed the highest content of nutritive components like protein, lipids and macro and micronutrients, so it is and important product with potential to cover vegetarian diners demand. The protein and lipids content for flours of both treatment were significantly higher when compared with others vegetable sources and the flour obtained by freeze drying showed the highest content of crude fiber. Both flours showed water activity about 0.3. So, okara flours showed full nutritional and microbiologically stable behaviour. The thermal treatment resulted in flours with desirables characteristics that allow their use to develop new food products.

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CHAPTER 3

Coffee by-product processing for nutritional use

Coffee by-product processing for nutritional use

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Abstract

By-products of coffee industry are widely used as fertilizer but, at the same time, tend to be a pollution problem, because of their large volume and difficulties for proper treatment. In this way, alternatives that allow taking advantage of the by-product nutrients at human food industry are being researched. The coffee husk and pulp, for example, are by-products rich in fiber, some nutrients like potassium, iron and manganese and, besides, contain caffeine, those could promote a healthy diet for people with active life rhythms as those who enjoy practice sports. Thus, the aim of this work was to characterize coffee by-product (peels and pulp) flour obtained from wet process material by freeze drying (FD), by convective drying (CD) and material from dry process with convective drying (OD). Coffee by-product flours were characterized considering centesimal and physico-chemical composition and determination of macro and micronutrients and quantification of caffeine of aqueous extract by HPLC method. It was observed that the flours have a high concentration of potassium, iron and manganese, in which the drying method made no difference at potassium amount (2.012 $g.100g^{-1}$, 2.012 $g.100g^{-1}$ and 2.081 $g.100g^{-1}$ for OD, CD and FD, respectively). Otherwise, freeze dried flour showed higher amount of iron and manganese (13.269 $mg.100g^{-1}$ and 4.292 $mg.100g^{-1}$) when compared to the 11.25 $mg.100g^{-1}$ and 2.954 $mg.100g^{-1}$ of CD flour and the 3.588 $mg.100g^{-1}$ and 1.97 $mg.100g^{-1}$ of OD flour. The aqueous extract of the flours showed a high concentration of caffeine for a beverage (52.045 mg for FD flour, 48.226 mg for CD flour and 36.751 mg for OD flour), considering a portion of 100 mL. All the flours showed low water content, pH, acidity and water activity about 0.3, containing strongly bound water. So, the physico-chemical reactions are low, being a microbiologically stable product.

Keywords: nutrition; pollution; sustainability; waste.

1. Introduction

The culture of coffee consumption is an integral part of society's daily life, being a product of high demand worldwide. Brazil strongly influences the world supply of coffee due to its high production levels.

Since the late 1990s, world production has increased by 20%, reaching around 130 million bags for coffee year 1999/2000, corresponding to the highest quantity recorded until 2013 (FNC, 2013). And along the time production had increased as in 2018 the world coffee production was 170.22 million bags 2019/20 world coffee production is estimated at 168.86 million bags (ICA, 2020).

In 2016, Brazil broke a record in coffee exports, with sales of arabic and instant coffee reaching the highest volume since the country's exports began (PORTAL BRASIL, 2017). To make this possible, a high volume of production was required, which in turn included the production of by-products. In Brazil, research can be doing to know what happens to by-products using portals as “CONSÓRCIO Pesquisa Café” with and specific topic called “Usos Alternativos para Resíduos e Subprodutos do Café”, where it is possible to access researches being developed as silage production and the use of husk for cellulase production (CHAGAS *et al*., 2013; LIMA, MANHÃES, PESSOA, MIGUEL & SIMÕES, 2013).

Large amounts of residues are generated in coffee industry, which are toxic and represent serious environmental problems (WOLDESENBET, WOLDEYES & CHANDAVANSHI, 2015). The amount of 100 kg of fresh cherry gives about 40 kg of wet waste pulp. Coffee dispensation requires an elevated degree of processing know how and produces large amounts of processing by-products such as coffee pulp and husk, which have limited applications such as fertilizer, livestock feed, compost and such others. Biotechnological applications in the field of industrial residues management promote sustainable development of country’s economy (MURTHY & NAIDU, 2012). Properties of coffee by-products are less known and considerably less research has been conducted on the subject. By-products of coffee fruit and bean processing can also be considered as potential functional ingredients for food industry. The coffee husks and pulp are one of the main by-products of coffee agro-industry and might be a valuable material for several purposes, including extraction of caffeine and polyphenols (ESQUIVEL & JIMÉNEZ, 2012).

Coffee pulp represents between 39 and 49% of the fresh fruit mass and contains from 6 to 8% of mucilage. It is a wet waste, rich in carbohydrates, proteins and lignin

(DURÁN *et al*., 2017). Coffee fruit mucilage contains proteins, carbohydrates, sugars, vitamin E, fiber and minerals, which can be used for nutritional purposes and contains 16.7% caffeine (SOARES *et al*., 2008). Coffee husk is a waste of the chain poorly used in Brazil, with high potential in food industry, because of its dry matter content and fiber. There are reports of 0.754% and 0.81% of caffeine contents at coffee husks (FERNANDES, 2007; ANDRADE, 2009).

Vegetal raw material is mostly composed by water with a high water content and high water activity, conditions that favour microbial growth. Thus, drying treatments decrease those conditions, being an option to extend shelf life of those materials. Coffee by-products have nutritional characteristics that can be used at human nutrition, but in its raw form are susceptible to microbial growth and degradation, making difficult to exploit. By-product drying processing could allow its utilization at food industry and extending the shelf life.

Drying allow product preservation, but cause physical, chemical and biochemical changes, desirable or not, as shape, colour, flavour or texture. It defines the importance of characterization and analysis of the behaviour of the material submitted to drying process in order to state the better treatment to obtain and keep a quality product. Most of the changes are temperature dependent and highest quality parameters are generally obtained by vacuum or freeze drying (BAKER, 1997). The quality of a food product is defined as a sum of attributes that favour the consumer's satisfaction reflecting at the nutritional and safety aspects, such as contents and availability of nutritionally contents, mainly proteins, vitamins, fiber and minerals and not containing harmful microbial or compounds above the accepted concentrations (SIKORSKI, 2007).

In this context, the aim of this work was to produce flour of coffee by-products applying different thermal treatment in order to know the nutritional behaviour of the resulting product by its characterization of centesimal, physico-chemical and macro and micronutrients contents.

2. Material and methods

The material were collected from a land of southeast of São Paulo-Brazil at 22º 36'44" S of latitude and 46º 42' 02" W of longitude. The wet material of husks/pulp were collected after wet process of *Coffea arabica* beans, packed in sterilized plastic containers, which were sanitized by 10 minutes immersion of the by-products in

peracetic acid (Pac200 powder disinfectant) solution with distiller water (0.0123g.L^{-1} of active compound in water). The material was submitted to production of flours. Two kinds of thermal treatments were applied: convective drying by forced air stove (CD) at 65°C for 72 hours, and by freeze drying (FD) with the vacuum chamber stabilized at the minimum 0.75 Torr along the process, freezing temperature of -22 ºC, maximum defrosting temperature of 40 ºC and total process time of 26 hours. Coffee beans of dry process (harvesting and drying beans while still in cherry), were dried by convective drier at 60°C for 30 h. Then, the dried husks were separated from beans by husker. This treatment is defined as the other convective drying process (OD). The dry materials were milled and sieved at 60 mesh in order to obtain the flours. The flours were stored in hermetically sealed glass jars at 25°C. The flours characterization was carried out to know its nutritional potential according to centesimal, physico-chemical composition and macro and micronutrients content. These analyses were carried out on dry matter basis.

The methods described by AOAC were used to determine water and ash contents. Protein content was determined by Kjedahl method (AOAC, 2005). For the determination of lipids and crude fiber, the method described by IAL (IAL, 2008) was used; carbohydrates were determined by difference. The -nitric-perchloric acid method was used to determine the macro and micronutrients content. To determine the titratable acidity was used the method described by (CEREDA *et al*., 2001) and for the determination of the colour, pH and water activity were used a specific equipment for direct reading.

The parameters collected for colour were: L*, that indicates the luminosity (ΔL*=L*treatment-L*WHITE), a*, related to red and green colours (Δa*=a*treatment-a*WHITE), b*, related to yellow and blue colours (Δb*=b*treatment-b*WHITE), total variation of colour ($\Delta E^* = ((\Delta L^{*2})+(\Delta a^{*2})+(\Delta b^{*2}))^{½}$), chroma that represents saturation ($C = (a^{*2}+b^{*2})^{½}$) and hue angle, related to the tonality (hue= arctang (b*/a*)). The values of L*, a* and b* were obtained by digital colorimeter with light source D65 and 10 mm aperture, observation angle 10°, calibrated by the reference system of the excluded specular reflectance module (RSEX) and operating by means of the three-parameter reading system, in the CIE (International Commission of L'Eclairage) space and the equations proposed for HUNTERLAB (1997) were used to calculated the complementar paramethers.

An aqueous extract of coffee by-products were obtained by boiling of 200g of flour of each treatment mixed with 2000 ml of distiller water for 5 minutes. Then, the resulting mixture was filtered with filter paper. The filtered liquid was submitted to physico-chemical analysis of pH and soluble solids (SS) by direct reading at pHmeter and refractometer. The total titratable acidity was obtained by the titration of the liquid with 0.1M NaOH, counting the amount of titrant spent to reach pH 8.1.

Quantification of caffeine of the aqueous extract was made by HPLC method. Information on the conditions and particularities of the analysis: method name HPLC_029, column Aclaim C18, 4.6x250, mobil phase water: methanol, 75:25, 1 $ml.min^{-1}$, channel A, 20 µL, temperature of sample and column 25°C, detector UV-Vis of 272 λ nm, time injection of 17 minutes. The calibration curve presented a correlation coefficient of 99.93%, appropriate to perform the quantification of the samples.

The means results were evaluated by Tukey test at 95% of confidence.

3. Results and discussion

According to the analyses results, coffee by-products flours are rich in minerals, proteins and fiber, as shown in Table 1.Water content of a food is related to its stability, quality and composition and could affect storage, packaging and processing (CECCHI, 2003). An important quality factor for a flour is its water content that must be under 15% in order to ensure stability and shelf life. All treatments resulted in flours with less than 15% of water content with statistical significant difference between their means.

The ashes content obtained for the flours were significantly different, the highest content was showed for OD and the lowest content was for FD. The OD treatment flour presented the closer value to the reported by the literature for coffee pulp (ULLOA ROJAS, VERRETH, AMATO & HUISMAN, 2003). FD and CD treatment flours presented values between the values reported for husk/pulp in other research works (Table 1).

For the lipids contents, the difference was statistically significant just between FD and OD with the higher value for OD. The results of the present work were similar to the reported for pulp as cited in Table 1. Despite of FD, CD and OD flours presented lower values of lipids contents, they presented higher values than the reported for husk (MURTHY & NAIDU, 2012). Lipids are prominent in the protective surfaces of plant parts and its content in fruits and vegetables is lower than 1% (SIKORSKI, 2007). Therefore, the results were appropriate for flours.

A different behaviour was evidenced for protein contents, as the highest value was presented by CD treatment flour, which was in accordance with the values reported for pulp and husk (Table 1). The lowest content of protein was shown for OD flour. However, the values were higher than some other vegetable sources. In general, the protein content in vegetables is lower than 3% (SIKORSKI, 2007).

Source	FD	CD	OD	Pulp[1,2,3,4]	Husk[2,3]
Water content	3.15±0.04[a]	9.90±0.29[b]	14.80±0.34[c]	12.6	-
Ashes	5.60±0.05[a]	6.60±0.03[b]	8.09±0,15[c]	7.3-8.9	5.4-6.2
Lipids	1.51±0.03[a]	2.27±0.48[a,b]	2.63±0.12[b]	2-7	0.3-2
Protein	10.72	12.59	6.64	7.5-15	7-9.2
Crude fiber	21.25±1.04[a]	14.49±0.52[b]	22.84±0.45[a]	21-60.5	24-30.8
Carbohydrates	60.92	64.05	59.80	21-32	57.8-72.3

The units of the centesimal parameters were at g.100g^{-1}. **[1]** (ULLOA ROJAS, VERRETH, AMATO & HUISMAN, 2003)**,** [2] (MURTHY & NAIDU, 2012)**,** [3] (DURÁN *et al*., 2017)**,** [4] (BRAHAM & BRESSANI, 1979),– value not informed.

Table 1. Centesimal composition of coffee husk/pulp flours by different thermal treatments and some literature sources.

Comparing to the literature, a discordance were evidenced as pulp should present 60 g.100g^{-1} and none of the flours treatment showed that crude fiber content, but they were similar to the reported for husk (ULLOA ROJAS, VERRETH, AMATO & HUISMAN, 2003; MURTHY & NAIDU, 2012; DURÁN *et al*., 2017). The treatment FD and OD did not presented significant difference between them and CD was statistically significant different from FD and OD, presenting the lower crude fiber content. For carbohydrates even in high amounts compared to other nutrients may contain dietary fibers and indicates that the flours are highly caloric.

However, it was possible to obtain flours rich in proteins and fibers that could be exploited at food industry like a nutritive flour or as constituent of a food preparation, and it could be state that the product treated by CD resulted in a more balanced flour related to its centesimal composition.

Treatment		FD	CD	OD
Nutrients	Unit*			
N	**g**	1.661	1.814	0.905
P	**g**	0.085	0.078	0.103
K	**g**	2.081	2.012	2.012
Ca	**g**	0.617	0.347	0.275
Mg	**g**	0.168	0.146	0.06
S	**g**	1.15	0.181	0.108
B	**mg**	2.481	1.919	1.35
Cu	**mg**	0.842	0.835	1.125
Fe	**mg**	13.269	11.25	5.388
Mn	**mg**	4.292	2.954	19.7
Zn	**mg**	0.679	0.537	0.292

*** for 100g**

Table 2. Macro and Micronutrients of coffee husk/pulp flours

Table 2 shows the macro and micronutrients contents of the flours with different thermal treatments. FD treatment presented the highest value of K at the macronutrients and Fe at the micronutrients. For FD, the macronutrient in the least amount was P and the micronutrient was Zn. Despite Zn was the one with the least amount for FD, was the highest when compared to CD and OD. The CD treatment presented the same content pattern for highest and least amount, i.e., K and Fe for the highest values of macro and micronutrients, P and Zn for the least. The content of N for CD treatment was higher than for FD and OD. The macronutrient in greater amount for OD was K. Mg of OD was the one with the lowest concentration. The flour of OD treatment showed the highest Mn amount among the micronutrients composition and was higher than the amount showed for FD and CD. Zn was the micronutrient in least concentration at OD flour and it was the lowest value among the treatments. The OD flour showed higher amount of P and Cu comparing with the other treatments. Concluding, thermal treatments showed different concentrations of macro and micronutrients.

Considering the content of some macro and micronutrient of dehydrated coffee pulp, FD flour showed Ca content higher than 0.554 $g.100g^{-1}$, OD showed a value close to 0.116 $g.100g^{-1}$ of P, none of the treatments showed values close to 15 $g.100g^{-1}$ of Fe and all the treatments showed values of K higher than 1.765 $g.100g^{-1}$ (BRAHAM & BRESSANI, 1979).

However, comparing the K, Ca, Mg and Fe contents of the flours with others vegetable sources as parsley that have 0.35 $g.100g^{-1}$ and 2 $mg.100\ g^{-1}$ of K and Fe, respectively,

spinach with 0.15 g.100g^{-1} of Ca, sweet maize 0.050 g.100g^{-1} of Mg, it is possible to state that coffee by-product flours are source rich in those minerals (SIKORSKI, 2007). Despite of Zn was the mineral in the lowest amount of all flours, the Zn contents were higher than the content of Zn in bee honey, fish and meat (0.08-1.2 mg.100g^{-1}) (SIKORSKI, 2007). In addition, according to Mean Daily Intake and Recommended Dietary Allowances (RDA), 100 g of FD and CD flours can supply the mean daily intake of Mg (0.145 g.100g^{-1}) and B (0.001-0.003 g.100g^{-1}). According to Safe and Adequate Intake (SAI), 100g or least of FD, CD and OD flours can supply daily intake of K (2 g.100g^{-1}) and Mn (2-3 mg.100g^{-1}). Flours of FD and CD can be source of Fe in order to supply daily intake, according to the SAI recommendation of 10-15 mg.100g^{-1} (SIKORSKI, 2007).

According to Table 3, the results of titratable acidity and water activity were statistically different. As the results of titratable acidity are presented as percentage of citric acid equivalents, it represents the presence of organic acids that are related to vitamins, the treatment by CD showed the highest amount. The differences on the treatments for pH were not statistically significant and showed values similar to 4.5, pH value reported for pulp dried by oven at 60°C (ULLOA ROJAS, VERRETH, AMATO & HUISMAN, 2003). Despite of the Aw values were statistically different, the observed values were close to 0.3 or below, being a complementary characteristic for a microbiologically stable flour and with a longer shelf life, which are desirable quality parameters for a human food.

Treatment	**Titratable Acidity** (%citric acid)	**pH**	**Aw** (decimal)
FD	2.67±0.04^{a}	4.67±0.15^{a}	0.29±0.01^{a}
CD	2.98±0.01^{b}	4.49±0.05^{a}	0.35±0.01^{b}
OD	2.43±0.05^{c}	4.70±0.01^{a}	0.28±0.01^{c}

Table 3. Physico-chemical characterístics of coffee husk/pulp flours.

Figure 1. Coffee pulp/husk flour obtained by freeze drying (FD), convective drying after wet process (CD), convective drying after dry process (OD).

The visual colour of the resulting flours was lighter than roasted coffee powder, although, the flour showed the characteristic brown coloration of a coffee product (Figure 1).

Table 4 shows results of the colour parameters for the coffee by-products treated by freeze drying (FD), convective drying (CD) and the resulting material of dry process (OD). It was possible to state that the thermal process affect significantly the luminosity, according to the values of L and ΔL*. All flours resulted in dark material and FD and CD treatments were darker than OD, that could be related to the higher protein and carbohydrates content of FD and CD, and because of the different origin of those materials. So, by-products from wet process of coffee tend to result at darker flours than those from dry process. Low positive values of a* and Δa* indicated a red tonality with statistically significant difference among the treatments. Related to the yellow/blue coordinate (b*, Δb*), there was statistically significant difference among the treatments, indicating a tendency to yellow colour. A low value of chroma shows a low saturation and hue confirmed the colouration between red and yellow indicated by a* and b*.

	Treatment					
	FD		CD		OD	
Parameters	**Mean**	**Std. Dv**	**Mean**	**Std. Dv**	**Mean**	**Std. Dv**
L*	40.38[a]	0.29	38.76[a]	0.62	52.59[b]	2.02
a*	12.56[a]	0.03	11.13[b]	0.46	10.22[c]	0.08
b*	24.02[a]	0.07	22.29[b]	0.67	28.81[c]	0.56
ΔL*	57.17[a]	0.29	58.79[a]	0.62	44.96[b]	2.02
Δa*	-12.38[a]	0.03	-10.95[b]	0.46	-10.04[c]	0.08
Δb*	-24.23[a]	0.07	-22.50[b]	0.67	-29.02[c]	0.56
ΔE*	63.32[a]	0.023	63.89[a]	0.88	54.46[b]	1.45
Chroma	27.10[a]	0.07	24.91[b]	0.80	30.57[c]	0.51
°hue	62.40[a]	0.02	63.43[b]	0.26	70.46[c]	0.44
WHITE	L*=97.55	a*=0.18	b*=-0.21			

Table 4. Analyses of colour parameters of husks/pulp coffee flours.

Concluding, brown flours were produced with different tonalities, depending on the luminosity, saturation and hue. OD treatment presented the highest luminosity, saturation and hue values, while CD treatment had the lowest luminosity and saturation.

An aqueous extract from the flours were obtained and analysed showing that thermal treatment could have an effect on some properties of coffee by-product beverage. Table 5 shows the results of those analyses. For caffeine content, it had not statistical difference between FD-CD and CD-OD. However, a statistical difference was showed between the highest and the lowest content that were showed for FD and OD, respectively. This results could be related with the water content. It means that, at lower water content, some components are concentrated.

The titratable acidity of the aqueous extract presented a lower concentration when compared to its flour with significant differences between CD and OD, but keeping the behaviour presented by the flours, i.e., the hierarchy from highest to lowest. The aqueous extract showed similar pH value to its original flour. The relation between ºBrix and titratable acidity indicates the sweet-acid balance of foods, being an evaluation of their quality. In this way, a range between 12 and 18 indicates organoleptic balance, in which just aqueous extract of FD flour fits. It means that the extract was not very diluted and not very acidic (MAPA, 1986). Thus, due to it high caffeine content and its organoleptic balance, the aqueous extract of flour obtained by FD treatment seems to be an appropriate energetic beverage.

Treatment	Caffeine (mg.100mL^{-1})	Titratable Acidity (%citric acid)	pH	SS (°Brix)	SS/Titratable acidity
FD	52.05±4.21^{a}	0.151±0.003^{a,b}	4.25±0.00^{a}	2.00±0.00	13.3
CD	48.23±0.65^{a,b}	0.164±0.007^{a}	4.25±0.00^{a}	1.92±0.11	11.7
OD	36.75±0.45^{b}	0.141±0.005^{b}	4.48±0.01^{b}	3.00±0.00	21.3

Table 5. Physico-chemical composition of aqueous extract of coffee by-product

Statistically FD and CD do not showed difference for caffeine content, but both were higher than the caffeine content of OD, so, by-products from wet process of coffee beans could have higher caffeine content. The higher content showed for FD could be explained by the caffeine volatility at high temperature. Caffeine content of different beverages like the 22.64 mg.100mL^{-1} from coffee husk, the range of 17.4 to 540 mg.100mL^{-1} from different preparations of coffee beverages and the range of 5 to19 mg.100mL^{-1} from silverskin tea, showed that the aqueous extract obtained from the treated flours had higher values of caffeine content than the silverskin tea and the husk. Aqueous extract from FD, CD and OD showed values between the range of the different coffee preparations, confirming it aptitude to be a caffeine source (HEEGER, KOSIN´SKA-CAGNAZZO, CANTERGIANI & ANDLAUER, 2017).

4. Conclusion

The results showed a high nutritional composition for all coffee by-product flours due to their protein, fibers and micronutrients contents, besides obtaining an aqueous extract with significant amount of caffeine and organoleptic balance. It was possible to obtain nutritive flours submitting the coffee by-products to different thermal treatments. The flours were rich in protein and crude fibers. Treatment CD resulted in a more balanced flour related to its centesimal composition. FD treatment was obtained a flour rich in Fe. Flour of CD treatment showed to be rich in N and OD was richer in Mn. All the flours showed low water content, pH and acidity, besides water activity about 0.3, containing strongly bound water. So, the physico-chemical reactions are low, being a microbiologically stable product. The colour of the flour obtained by OD was the clearest, however, all flours showed brown coloration similar to coffee products. The flours resulting from the thermal treatments contain nutritional value for consumption or addition in the preparation of new foods and they can also be used for the preparation of energy beverages with caffeine content.

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CHAPTER 4

Edible films and nutritive gel for agro-industrial waste management

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Edible films and nutritive gel for agro-industrial waste management

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Abstract

Food over production generates a large volume of waste, being that most of the food products are packed with synthetic constituents, e.g. plastic-based packings, and, together, are responsible for environment pollution, resulting in a food safety problem. In recent years, nutritional international organizations and environmental protection associations has been motivated to the development and production of healthy foods aiming to reach the needs of growing population and reduce the adverse effects that inappropriate management of large-scale production could impact on the environment, soils and food quality. Development of edible packaging has proven to be a viable solution to decrease food deterioration and reduce the use of plastic packaging. On the other hand, some agro-industrial wastes showed nutritional potential as functional properties that made them able to animal and human nutrition. Thus, films based on potato and cassava starch were developed for suitable use as part of a food packaging, besides a gel-shaped food developed from some agro-industrial nutritive by-products from orange, passion fruit, coffee and soy bean that are richer in fiber, protein and calories. Thereby, the objective was to establish appropriate formulation for the production of a film by casting method, formulation of a gel using agro-industrial by-products and evaluate its shelf life using the film as part of the packaging. The films were subjected to physical, physico-chemical and morphologic analysis, showing strong structural and thermal characteristics able for their used at food packing. The appropriate formulation for film production was concentration of 4% starch and 15% plasticizer for the two types of starch. The nutritive gel was made based on the by-products flours, using extract of orange and coffee husks as a gel matrix. On the other hand, for the analysis of shelf life, the food developed was subjected to physico-chemical and microbiological analyses. So, a nutritive gel with a shelf life of, at least,

13 days was developed, while starch films lid showed to be able to keep food quality as a part of the food packaging, reducing plastic use.

Keywords: food; packing; pollution; sustainability; waste.

1. Introduction

Nowadays, people are being more aware about what they eat, how it is produced and how it affects their health, the environment and their pockets. This awareness could be acquired by the increase of food waste generation due to the rapid urbanization and industrialization that incited to employ novel techniques for waste management in order to reduce to a minimum or convert them into some valuable products (PUNNAGAIARASI, ELANGO, RAJARAJAN & PRAKASH, 2017). The increasing amount of food packaging waste is perceived as a problem in urgent need of solution in all industrialized countries (KUMAR, IRSHAD & RAJARAJAN, 2016). Whence, it is imperative to research focused on mitigating those problems, finding effective uses for waste and developing new products that can be used in industry instead of plastic packaging. Source reduction, reuse and recycle are the most powerful and effective implementation that can be used to manage waste (KUMAR, IRSHAD & RAJARAJAN, 2016).

Analysing agro-industrial waste in Brazil, logistics problems for harvesting and post-harvesting of agricultural products increase losses and decrease the earnings of producers (BATISTA, 2018). Some waste derived from these losses could be turned into a nutritive material, able for processing and consuming. There are a lot of reports about peels flours, some components extracted from those wastes are used as additive in food preparation or used for other applications, e.g. water filtration (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018; BARRAGÁN, TÉLLEZ & LAGUNA, 2008; BOWLES & DEMIATE, 2006; BRAHAM & BRESSANI, 1979; CAZARIN, SILVA, COLOMEU, ZOLLNER & JUNIOR, 2014).

Reduce costs and optimize production processes is important to recognize the potential of the use of by-products at different areas of food and non-food consumption because of its nutritional characteristics and other functional properties (bioenergy production, composting, pharmaceutical, among others). This could be seen as an innovation, since industries are increasingly trying to use co-products and by-products to add nutritional/functional value and avoid a greater environmental impact on their waste generation (BALDISSERA, BETTA, PENNA & LINDNER, 2011).

In recent years, the consumers have shown greater interest in functional foods characterized by offering many health benefits in addition to the nutritional value inherent to their chemical composition, which may play a potentially beneficial role in

reducing the risk of degenerative chronic diseases such as cancer and diabetes, among others (FERRÃO, 2012; CARDOSO & OLIVEIRA, 2008). The US Food and Drug Administration (FDA) subdivides the term "functional food" into two subcategories: "Medical Foods" and "Foods for Special Dietary Use". Other organizations such as the American Dietetic Association (ADA), the International Food Information Council (IFIC) and the Institute of Food Technologists (IFT) have developed definitions based on providing additional health benefits, as disease risk reduction and/or promote optimal health. In Europe, for the European Commission Concerted Action on Functional Food Science, functional foods, in addition to reducing the risk of disease and/or promoting optimal health, must demonstrate their effects under amounts that are normally expected to be consumed in the diet. Japan is the only country that legally recognizes functional foods as a distinct category. This category legally provides effects for certain diets and use aimed at maintaining and regulating specific health conditions (BALDISSERA, BETTA, PENNA & LINDNER, 2011; ROBERFROID, 2000).

Brazilian law stipulates that functional property is that related to the metabolic or physiological role that the nutrient or non-nutrient has in the growth, development, maintenance and other normal functions of the human organism. Any kind of claim referring to cure or disease prevention is not allowed (ANVISA, 1999). The National Health Surveillance Agency (ANVISA) regulated functional foods by Resolution RDC n°. 02 of January 7, 2002, which approves the technical regulation of isolated bioactive substances and probiotics with functional or health claims (ANVISA, 2002).

In this way, taking advantage of agro-industrial waste, it is possible to develop new products with functional properties and earned value, ensuring full exploitation of the productive chain and contributing to the mitigation of the environmental pollution problem.

Besides, plastic materials are widely used for food packaging and pollution by plastic waste is being recognized as a big problem that besides affecting the environment, which is affecting the marine trophic chain. A framework calculated that 275 million metric tons (MT) of plastic waste was generated in 192 coastal countries in 2010, with 4.8 to 12.7 million MT entering the ocean. From those countries, Brazil is on the top 20 countries ranked by mass of mismanaged plastic waste at 16th position (JAMBECK et al., 2015). Considering the growing concern with health, the environment and the quality of food products, development of biodegradable/edible packaging from

starches has been an alternative for the development of films with higher degradation rate and characteristics that made them able to use at food packaging (FAKHOURI et al., 2012; SARTORI & MENEGALLI, 2016; EMBUSCADO & HUBER, 2009).

Edible film use has expanded rapidly for retaining quality of a wide variety of foods, due to solve quality problems related to the increased transportation distribution systems, storage needs, and advent of ever larger supermarkets and warehouse stores; because it takes considerable time for a food product to reach the final consumer (EMBUSCADO & HUBER, 2009). Any type of material used for enrobing food to extend shelf life of the product that may be eaten with food with or without further removal could be considered as edible film or coating (KUMAR, IRSHAD & RAJARAJAN, 2016). To replace the use of plastic in packaging industry with edible films, there are some important parameters that should be properly studied for its application and, among the natural polymers able to form edible films, starch and gelatin are potential sources (FAKHOURI, MARTELLI, CAON, VELASCO & MEI, 2015). Starch is made up of alpha-D-glucose polymers, smaller components from amyl pastes, limiting membrane of amyloplasts and material deposited on the surface of the granules during tissue disintegration. Some of those components are amylose and amylopectin (CEREDA et al., 2001).

A film or coating can be made from any type of starch that contains amylose. Gelatinization occurs over a range of temperatures and is dependent upon the type of starch and its modification (KRAMER, 2009). The packaging technique, in conjunction with the choice of a packaging material endowed with appropriate gas and water barrier properties, aims to prevent destruction of food by microbial and insect attack (KUMAR, IRSHAD & RAJARAJAN, 2016). Several studies have shown that films containing cassava starch and potato starch in their formulation can have advantages in their use in food products, because they can be integrated with other compounds and because of their physico-chemical, thermal and mechanical characteristics (FARIAS, FAKHOURI, PILER & ASCHERI, 2012; FAKHOURI et al., 2012; MORENO, ATARÉS & CHIRALT, 2015; ZAVAREZE et al., 2012).

A way to analyse the prevention of microbial hazard is to test the material as a part of the food packaging and evaluate its shelf life. Shelf life is defined as time period whereby a product is not only safe to eat, but still has acceptable taste, texture and appearance after being removed from its natural environment (EMBUSCADO & HUBER, 2009). Shelf life assessment is a tool for gaining information that determines

the period a product preserves its ideal consumer characteristics, crucial information for marketing planning.

The objective of this work was to establish appropriate formulation of edible films from cassava and potato starches and sorbitol using the casting method, develop of a nutritive gel using agro-industrial by-products and evaluate its shelf life using the edible film as part of the packaging. The films were subjected to analysis of water vapour permeability (WVP), thickness, water content, solubility, water activity (Aw), mechanical properties, Scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The nutritive gel was made based on the nutritional content of the characterized flours produced with agro-industrial waste, using extract of orange peel and coffee husks as a gel matrix. On the other hand, for the analysis of shelf life, the food developed was subjected to determination of water content, water activity (Aw), titratable acidity, pH, soluble solids (°Brix), colour and microbiological analyses. One formulation from each starch material was selected to use as part of the nutritive gel, because they showed the better characteristics on the analysed parameters. A plastic lid was used as a control reference for the shelf life of the product and the nutritive gel began to show strong signals of deterioration at the 13th day after production.

2. Material and methods

The experiment was developed at the Laboratory of Postharvest Technology of School of Agricultural Engineering at the University of Campinas. For the films development, the material was potato (allotment G18BRPP241, Yoki, São Bernardo do Campo-SP, Brazil) and cassava (allotment EA163, Casa do Naturalista, Amparo-SP, Brazil) starches, from local market. For gel-shape food dry formulation, orange and passion fruit peels flours and okara soy flour were used, produced by convective drying and previously characterized. An aqueous extract of orange peel and coffee husks flour were obtained and used for development of the gel matrix.

2.1 Starch films formulation for food packaging

An experimental central composite rotatable design (CCRD) with 4 axial and 3 central points, resulting in 11 experiments was used to obtain a second-order model for prediction of water vapor permeability, thickness, water content, solubility and water activity as function of two variables: concentration of starch and concentration of plasticizer related to the starch amount. Table 1 presents the statistical design and

coded and real values of these variables. The analysis of variance (ANOVA) was calculated with a confidence interval of 90% and 95%, according to each case. The Tukey test was used to determine the differences between edible films mechanical properties in the range of 95% confidence. All experiments were performed randomly, and data were treated by STATISTICA®, version 9.0.

Experimental runs	Encoded Starch concentration (x)	Encoded Sorbitol percentage (y)	real x ($g.100mL^{-1}$ of water)	real y (%)
1	-1	-1	2	15
2	-1	1	2	20
3	1	-1	4	15
4	1	1	4	20
5	-1.41	0	1.59	17.5
6	1.41	0	4.41	17.5
7	0	-1.41	3	13.975
8	0	1.41	3	21.025
9	0	0	3	17.5
10	0	0	3	17.5
11	0	0	3	17.5

Table 1. Encoded and real values of CCRD.

2.1.1 Edible film

The films were produced using casting method. Filmogenic solution were obtained by weighed the amount of starch and plasticizer as Table 1. The plasticizer used was liquid sorbitol at 70%. Initially, starch was hydrated in 100 mL distilled water. Then, it was taken to thermostatic bath at 80°C for 4.5 min with constant manual agitation. After that, sorbitol was added and homogenized. At 150x15 mm petri dishes, 27 mL of filmogenic solution were added and, then, dried at 25 °C in a room with air conditioning system. Drying time for both kind of films were different. Potato starch films dried for 36 hour and the cassava starch films dried for 48 hours (FAKHOURI *et al*., 2012).

2.1.2 Water content and solubility of films

The samples for water content and solubility determination were subjected to humidity control (55% ± 3 of RH) for 2 days before the analyses procedure.

For water content, samples were conditioned at glass crucibles. The initial weight was determinate before submitted to drying at 105 °C in stove without air circulation for 24 h. Water content was determined by difference between the initial and final weight,

expressed in g.100g^{-1} (AOAC, 1990). Then, solubility test was determined using dried samples. Samples were immersed in beckers with 50 mL of distilled water at 25 °C disposed at thermostatic bath for 24 h with stirring at 115 rpm. Samples were withdrawing from the water by slow drainage and tweezers. The samples were placed in the glass crucibles and taken to stove without air circulation at 105 °C for 24 h. Solubility was calculated by difference between resultant dry matter and initial dry matter (GONTARD, GUILBERT & CUQ, 1992).

2.1.3 Water vapor permeability (WVP) of films

Water vapour permeability (WVP) was determined by standard E96/96M-13 method, with adaptations. Testing acrylic cells sealed with O-ring and lid in acrylic with aperture in the centre fixed with screws were used. The analysis was performed in triplicate, for both potato and cassava starch films. Thickness measurement was expressed as the mean of 15 measures with a digital micrometer at different points of the samples from centre to edge. In the testing cell, the desiccant material was placed so that it remained 6 mm away from the sample. The film was placed on testing cell, fixed with O-ring and lid with opening in top of plate, marking the area of the sample exposed to vapour pressure and, held with screws. Then, cells with samples were weighed, stored in desiccators at 25 °C and relative humidity of 75% ± 3. Water vapour transferred through the film was determined by mass gain of the calcium chloride, measured every 60 minutes until complete 12 measures (ASTM, 2013). The effect of air space between region below film and the surface of the calcium chloride in test cells was not considered for the calculation of the water vapour transmission rate (MCHUGH & KROCHTA, 1994; GENNADIOS, WELLER & TESTIN, 1993).

2.1.4 Thickness and water activity (Aw)

The thickness measurement was determined with a digital micrometer in fifteen points of 5 cm diameter disk of starch films, from different parts of the samples from centre to edge to calculate the mean, it was performed in triplicate. The water activity was determinate by direct read of 3.6 cm disks of starch films using Aqualab equipment in five replicates. The samples were subjected to relative humidity control (55% ± 3 RH) for 2 days before the analyses.

2.1.5 Mechanical properties

Tension test was applied at five selected formulations that were evaluated as appropriate according to the CCRD of the parameters analysed. The tensile strength

and elongation at break of films were determined by texture analyzer (TA.TX Plus Texture Analyzer), using “Texture Exponent 32” software (Stable Micro Systems, Surrey, UK), according to the standard method D882-12 (ASTM, 2012) with modifications. An average of eight determinations was taken each analysed film formulation. The films samples were adapted into 2.5 cm wide and 10 cm long strips. The initial grip separation and the crosshead speed were set at 8 cm and 1.0 mm/s, respectively. The tensile strength (force/initial cross sectional area) and the elongation at break were computed directly from the curves of strength vs elongation curves by using “Texture Exponent 32” software. Young's modulus was calculated as the slope of the initial linear portion of this curve (SARTORI & MENEGALLI, 2016). From the results of this test, two formulations were selected as appropriated for packaging to analyse its structure and thermal characteristics and to use as part of food packaging.

2.1.6 Scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC)

The film samples were adapted to 2 x 2 cm square samples and subjected to relative humidity control (55% ± 3 RH) for 48 h before the analyses.

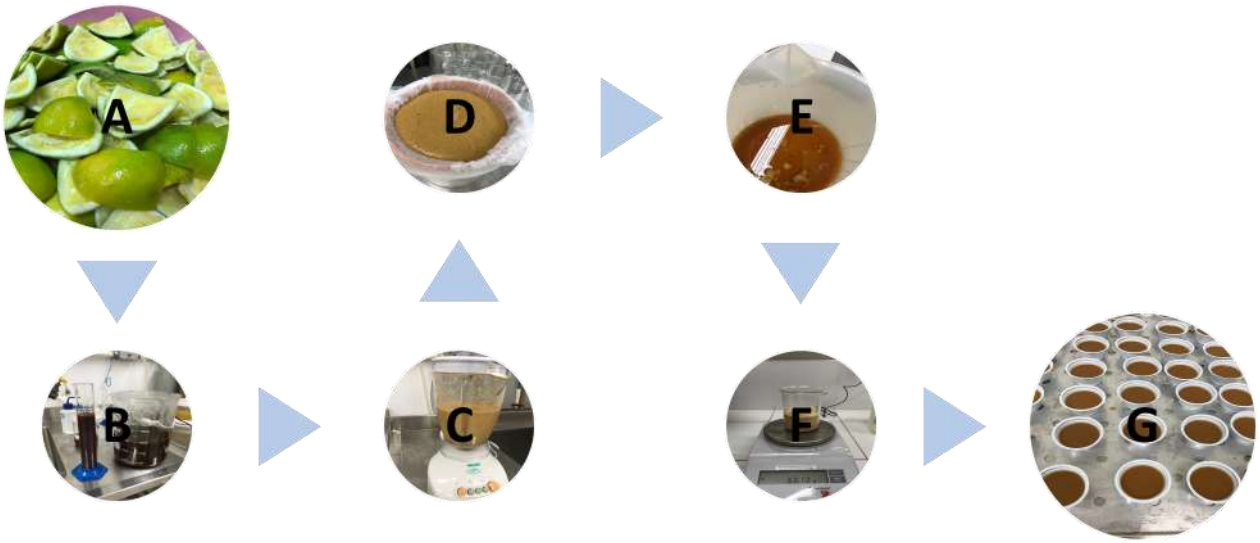
SEM analysis aided the evaluation of the film surface and cross-section. Samples were fractured by application of liquid nitrogen, to afford small fragments. Samples of these fragments were fixed on aluminium stubs by means of a double-sided tape and coated with a gold layer (Sputter Coater POLARON, model SC7620), to improve conductivity. The coated samples were viewed under a scanning electron microscope (LEO, model LEO 440i, Cambridge, England) operating at an acceleration voltage of 15 kV.

The X-ray diffraction analyses were performed on an X-ray diffractometer (Bruker, model D8 advance, Germany) operating at a voltage of 40 kV and a current of 40 mA; the target was Cu. The diffraction data were collected over an angular range from 5 to 70° (2θ), at a scanning rate of 0.0166 °/s.

The determination of the glass transition temperatures and the melting enthalpy variations of films were made by DSC, using a calorimeter (TA Instruments, TA 2010 model, USA) with liquid nitrogen cooling module. The measurements were performed in an inert atmosphere of ultra-dry nitrogen gas chromatographic grade, to the same feed flow rate and the drag of 50 mL/min. The tests were started at 25 °C and then samples were heated at rate of 10 °C/min until 160 °C. The material reference for this analysis was the atmospheric air.

2.2 Nutritive gel

The materials where sanitized by 10 min immersion in peracetic acid (Pac200 Powder Disinfectant) solution with distilled water (0.0123g.L^{-1} of active compound in water), distilled water and alcohol 70%. The films were adapted in disks of 6 cm diameter and submitted to 15 min of UV radiation for sanitation in a laminar flow hood for microbiology (TROX-SERIE 2245). Figure 1 shows the summarized steps for preparation and packaging of the gel.



Preparation and packing: Orange peels *in natura* (A), aqueous extract of coffee by-products (B), mixture of A and B processing by blender (C), filtration for obtain aqueous extract of orange peels (D), orange peel aqueous extract (E), by-products flour (F), nutritive gel packaging (G).

Figure 1. Flowchart of the nutritive gel preparation and packing.

2.2.1 Components extraction and dry formulation

An aqueous extract of coffee pulp flour was obtained by a preparation of 1:10 g/mL of coffee by-product flour and distiller water by boiling for 5 minutes and, then, the resulting liquid was filtered with filter paper.

An aqueous extract of orange peel was obtained by processing in a blender with 1:3 g/mL of orange peel and aqueous extract of coffee pulp flour for four minutes. Then, the liquid was filtered in a sieve coated with thin polypropylene fabric and was supplemented with 1 part of natural orange juice.

As a nutritive dry part, flours of okara soy, orange and passion fruit peels and sugar in 1:1:1:5 portions were homogenized. The nutritional composition of the final dry product was determined by linearly proportional relationship using the characterization of each flour and its portion at the total product.

2.2.2 Gel preparation and packaging

The dry part was homogenized with the aqueous extract of orange in a preparation of 9:40 g/mL by manual stirring with glass rod for four minutes. Then, 25 mL of the homogenized material were deposited in plastic (PVC) vessels with 30 mL capacity. The vessels were covered with films of potato or cassava starch, lids diameter were 6 cm and average thickness of 0.068 mm for potato starch and 0.030 mm for cassava starch. The lids were attached to the vessels with non-toxic solid glue. For each type of film, 24 vessels were prepared with starch film samples and other 24 vessels were prepared using plastic (PVC) transparent lids with an average thickness of 0.153 mm as a traditional packaging comparison standard. Finally, the packed material was left to gel at 10 °C for 18 hours.

2.3 Nutritive gel shelf life analyses

The vessels were stored at 10°C along analyses time. After gelling, the physico-chemical and microbiological analyses were initiated, which were repeated every 4 days in triplicate until the 13th day after preparation.

2.3.1 Physico-chemical analyses

For water content, samples were dried at 105 °C in force air circulation stove for 24 h and water content was determined by difference between the initial and final weight expressed in $g.100g^{-1}$ (AOAC, 1990). The total titratable acidity was obtained by the titration dilution of 10g of gel in 100 mL of distilled water with 0.1M NaOH, counting the amount of titrant spent to reach pH 8.1 (AOAC, 1990). For the determination of pH, soluble solids (SS), water activity (Aw) and colour parameters were used a specific equipment for direct reading. The parameters collected for colour were: L*, that indicates the luminosity, a*, related to red and green colours, b*, related to yellow and blue colours, chroma that represents saturation ($C= (a^{*2}+b^{*2})^{1/2}$) and hue angle, related to the tonality (°hue= arctang (b*/a*)). The values of L*, a* and b* were obtained by digital colorimeter with light source D65 and 10mm aperture, observation angle 10°, calibrated by the reference system of the excluded specular reflectance module (RSEX) and operating by means of the three-parameter reading system, in the CIE (International Commission of L'Eclairage) space and the equations proposed for HUNTERLAB (1997) were used to calculated the complementar paramethers.

2.3.2 Microbiological analyses

Samples were submitted to total coliforms, total aerobic, mesophilic and psychrotrophic plate count, mold and yeast count to evaluate the hygienic-sanitary conditions of the food. For sample preparation, 25 g of sample were mixed with 225 ml of peptone water and, then, used for inoculation. For microbiological evaluation purposes, the microorganism count of the samples at the day after gelling were considered as initial population and the microorganism count after samples stored time as final population.

2.3.2.1 Total coliforms and thermotolerant

The most probable number method (MPN) was used, including the presumptive test with Lauril Sulfate Tryptose Broth (LST) tubes and the confirmation test with Bright Green Broth (GB) and *E. Coli* Broth (EC) tubes at 45ºC (SILVA, JUNQUEIRA & SILVEIRA, 2007).

2.3.2.2 Total Aerobic Mesophilic and Psychrotrophic Count

For sample preparation, 25 g of sample were mixed with 225 ml of peptone water inoculating in depth and surface, for mesophiles and psychrotrophic, respectively, in Plate Count Agar (PCA) culture medium by plating and counting per Colony Forming Unit per gram of sample (CFU g^{-1}) (SILVA, JUNQUEIRA & SILVEIRA, 2007).

2.3.2.3 Mold and Yeast

Using 25 g of sample mixed with 225 ml of peptone water, Dichloran Rose Bengal Chloramphenicol (DRBC) culture medium was inoculated superficially by plating and counting per Colony Forming Unit per gram (CFU g^{-1}) (SILVA, JUNQUEIRA & SILVEIRA, 2007).

3. Results and discussion

The results were organized and showed in two parts. The first part showed the results of the development, formulation and determination of the adequate starch based film to produce lids for a food packaging. The second part describes the preparation of a nutritive gel based on flours of agro-industrial waste and analyses of shelf life and degradation behaviour of the product over time by physico-chemical and microbiological analyses.

3.1 Edible films

As an edible film must provide protection to prevent moisture losses, controlled gases exchange, provide surface sterility and prevent loss of other important components, a CCRD experimental design was established to analyse some basic parameters of different films formulations based on cassava and potato starches in order to discover which formulation has better conditions to reach edible film requirement. The responses of the analyses are shown at Table 2, in which 'x' represents the coded values of starch concentration and 'y' represents coded values of sorbitol percentage.

Potato starch						
x	**y**	**WVP** (g.mm/ m^2day.kPa)	**Thickness** (mm)	**Water content** (g.100g^{-1})	**Solubility** (g.100g^{-1})	**Aw** (decimal)
-1	-1	4.39	0.033	20.36	17.74	0.539
-1	1	3.12	0.032	27.06	20.17	0.493
1	-1	4.86	0.068	15.95	11.48	0.436
1	1	5.82	0.049	10.32	5.29	0.429
-1.41	0	4.33	0.024	29.94	16.90	0.538
1.41	0	2.64	0.057	12.11	3.13	0.416
0	-1.41	6.80	0.042	23.35	11.90	0.517
0	1.41	4.70	0.042	19.63	12.33	0.518
0	0	5.78	0.045	18.26	15.76	0.517
0	0	5.68	0.045	21.62	16.27	0.497
0	0	6.31	0.042	20.33	24.04	0.516
Cassava starch						
x	**y**	**WVP** (g.mm/ m^2day.kPa)	**Thickness** (mm)	**Water content** (g.100g^{-1})	**Solubility** (g.100g^{-1})	**Aw** (decimal)
-1	-1	8.02	0.034	13.65	9.96	0.440
-1	1	2.95	0.030	13.26	16.53	0.441
1	-1	3.26	0.030	12.38	5.41	0.533
1	1	2.27	0.032	15.47	11.35	0.529
-1.41	0	4.42	0.023	7.95	10.50	0.489
1.41	0	3.33	0.057	15.03	11.04	0.436
0	-1.41	3.80	0.036	4.10	15.73	0.471
0	1.41	3.24	0.032	6.19	18.39	0.464
0	0	2.42	0.024	10.21	5.44	0.457
0	0	2.42	0.032	11.45	3.39	0.429
0	0	2.40	0.034	11.40	3.06	0.447

Table 2. Physico-chemical analysis results for potato and cassava starch films.

According to the obtained responses with the experimental design and the ANOVA results for potato starch films (Table 3), it was possible to obtain mathematical models for some parameters that were expressed as shown at Equations 1, 2, 3 and 4.

$WVP = 5.83 - 1.21x^2 - 0.41y + 0.56xy$ Equation 1 with R^2= 0.70

$Thickness = 0.044 + 0.012x - 0.003y - 0.004xy$ Equation 2 with R^2=0.94

$Water\ content = 19.9 - 5.8x - 3.08xy$ Equation 3 with R^2=0.91

$Aw = 0.51 - 0.042x - 0.022x^2$ Equation 4 with R^2=0.88

Solubility showed one significant factor and R^2= 0.55. Considering that, it was not possible to obtain a model to describe the experimental solubility results. The mathematical models were calculated using the encoded values of x and y.

	SS	df	MS	Fcalc	Ftab (10%)
WVP					
Regression	11.58	3	3.86	5.27	3.07
Residue	5.13	7	0.73		
Lack of Fit	4.89	5	0.98	8.52	9.29
Pure error	0.23	2	0.12		
Total	16.71	10			
Thickness					
Regression	0.0013	3	0.00045	33.37	3.07
Residue	9.39E-05	7	1.34E-05		
Lack of Fit	0.00009	5	1.75E-05	5.41	9.29
Pure error	0.00001	2	3.23E-06		
Total	0.00144	10			
Water content					
Regression	306.58	2	153.29	39.03	3.11
Residue	31.42	8	3.93		
Lack of Fit	25.67	6	4.23	1.49	9.33
Pure error	5.74	2	2.87		
Total	337.995	10			
Aw					
Regression	0.0173	2	0.0086564	28.14	3.11
Residue	0.0025	8	0.0003076		
Lack of Fit	0.0022	6	0.000367	2.84	9.33
Pure error	0.0003	2	0.000129		
Total	0.0198	10			

Table 3. ANOVA table for potato starch films - WVP, Thickness, Water content and Aw.

Figure 2a represents the WVP responses that had a positive quadratic relation with the starch concentration and a negative linear relation with sorbitol percentage. That means that the increase at starch concentration tend to increase the WVP of the films and the increase of sorbitol tend to result in a WVP decreasing.

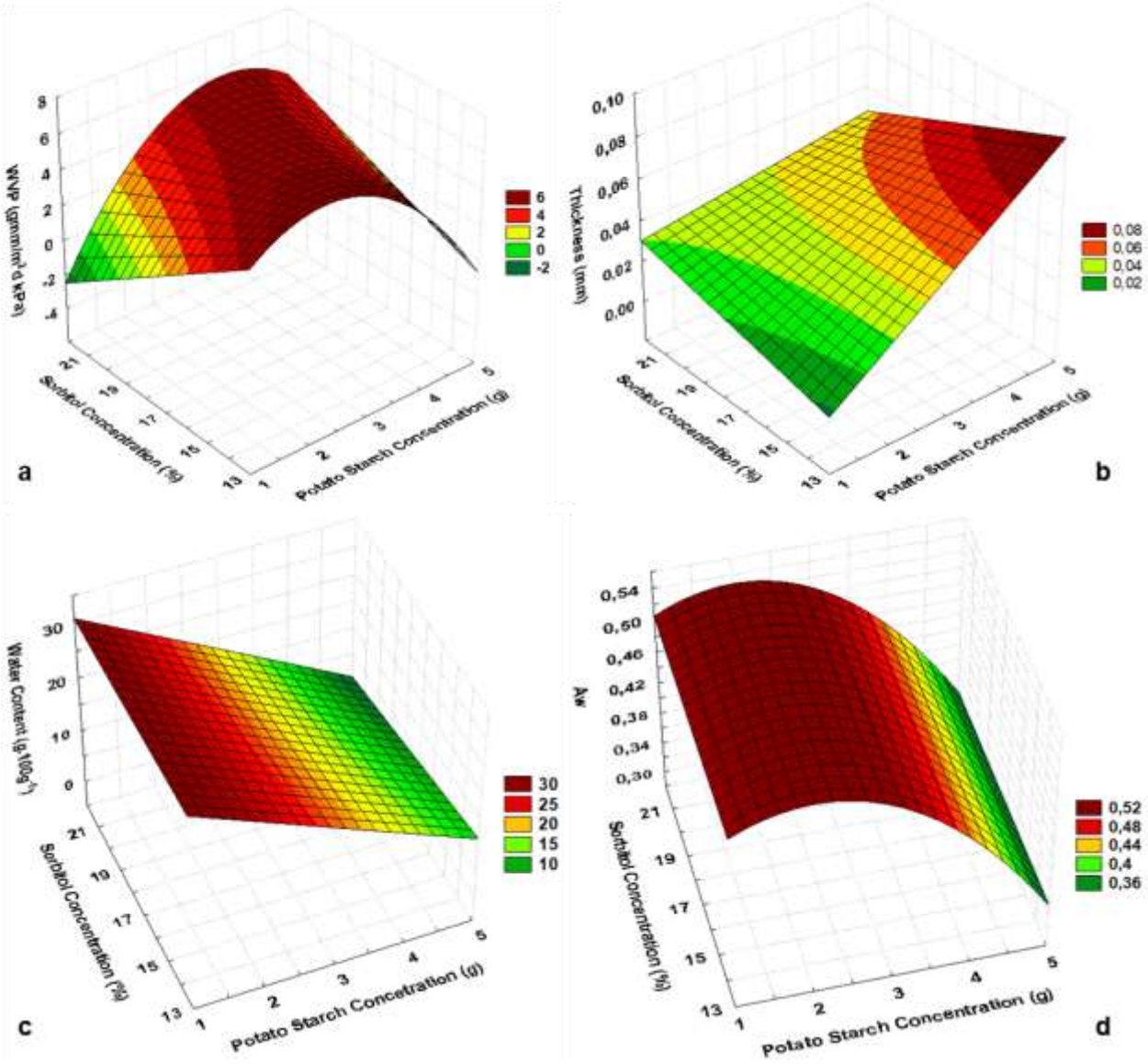


Figure 2. Response surfaces for WVP, Thickness, Water Content and Aw of Potato Starch films.

However, analysing the interaction where was used the highest concentration of starch with the central point of sorbitol, the samples showed the lower WVP, that is because besides the influence of each factor individually, their interaction affect the behaviour and that is supported by the quadratic relation between them. So, in this case, high starch concentration related to a fixed sorbitol concentration could result in films with lower WVP and to verify that behaviour it is recommended to run another kind of experimental design, using other method for the films preparation in order to avoid homogenization problems of the filmogenic solution and films surface that could occur because of the increase of density related to a higher starch concentration. For packaging material, low WVP are desirables. Some reported WVP values for both native and modified potato starch films vary between about 5 to 10 g.mm/m^2.day.kPa

and, in this research work, lower values from 2.68 to 6.80 gmm/m^2.day.kPa was observed (ZAVAREZE *et al*., 2012). In addition, a value of 4.22 g.mm/m^2.day.kPa was reported for films made of gelatine with native potato starch (FAKHOURI *et al*., 2007). According to MORENO, ATARÉS & CHIRALT (2015), the thickness of potato film is related to the starch content, that behaviour was showed by the surface response of the thickness where a positive linear relation between thickness and starch content at the Figure 2b (MORENO, ATARÉS & CHIRALT, 2015). Also, films with thickness vary between 0.06 and 0.168 mm have been reported and, at this work, there were obtained some lower values varying from 0.024 to 0.068 mm as showed at Figure 2b (MORENO, ATARÉS & CHIRALT, 2015; ZAVAREZE *et al*., 2012).

For potato starch films, the responses showed a negative linear relation between water content and starch concentration, while sorbitol percentage seems to not affect this parameter, so, increasing on starch concentration would be a restrictive factor for water content (Figure 2c), being a desirable characteristic of edible films for food in order to inhibit microorganism development that could affect food quality, but use of high starch content is a factor that increase the WVP that is an undesirable and according to the method used for film production it could be a operation problem too. For Aw, it was obtained a positive quadratic relation with starch concentration, while sorbitol percentage seems not to affect it (Figure 2d), so, at the film composition, the starch will control the available water that could influence physiological process of the microorganisms or the food packaging with this material. Lower water content and Aw are desirables for those parameters at packaging materials.

The solubility of potato starch films varied from 3.13 to 24.04 g.100g^{-1}, being lower than reported of 27.53 % of potato starch with gelatine (FAKHOURI *et al*., 2007). However, closer values were reported varying between 14.26 and 19.87% for films of native potato starch films (ZAVAREZE *et al*., 2012).

According to the statistical analyses and mathematical models, optimal results are obtained at the region nearly to 4 g.100mL^{-1} of water of potato starch concentration and 15 % of sorbitol percentage (Table 3; Figure 2). However, at higher concentrations of potato starch, operational difficulties arise that result in films with an uneven surface and require more time to dry. Thus, concentrations of 4 g of starch with 15 and 20% of sorbitol were selected as films with the best conditions for using as part of food packaging.

For cassava starch films, the effect estimates of thickness showed that just the linear effect of x was significant. In that way there was few parameters for a model and R^2= 0.44. For Aw, the effects were not significant. Effect estimates for water content showed more significant, but R^2<0.5 and lack of fit was present (Table 4). Thus, it was not possible to obtain a model that represents the experimental results in order to choose an appropriate formulation for cassava starch edible films. However, according to the responses obtained with the experimental design, it was possible to obtain a mathematical model for some parameters of cassava starch films that were expressed as showed at Equations 5 and 6 (in coded values).

$$WVP = 2.42 - 0.87x + 0.84x^2 - 0.86y + 0.66y^2 + 1.02xy \quad \text{Equation 5}$$

$$Solubility = 3.96 + 2.63x^2 + 2.03y + 5.77y^2 \quad \text{Equation 6}$$

Both mathematical models with R^2=0.8.

In spite of Anova, the model of WVP showed lack of fit. All the effects were significant and the value of mean relative deviation was 0.145 that was considered as low and in this case. The model satisfactorily describes the behaviour of the results within the range studied. The mathematical models were calculated using the encoded values of x and y.

Considering the responses showed at Table 2 for cassava starch, the values of WVP varied from 2.27 to 8.02 g.mm/m^2day.kPa in a negative quadratic relation with starch concentration, as showed at Figure 3a. There are reports of rate of 3.91-7.45 g.mm/m^2.day.kPa for films of native cassava starch with gelatine and sorbitol, and rate of 4.57–6.64 g.mm/m^2.day.kPa for modified cassava starch with gelatine and sorbitol. So, there were lower values reported at this work because of the use of different starch concentration (FAKHOURI *et al*., 2012). The thickness of cassava starch films varied from 0.024 to 0.057 mm, while FAKHOURI *et al*. (2012) reported values of 0.034 and 0.050 mm for films with 3 and 5g of starch concentration, respectively. FARIAS, FAKHOURI, PILER & ASCHERI (2012), who compared concentration of glycerol and pulp fruit at cassava starch films, showed that it was a positive quadratic relation between thickness and fruit pulp concentration.

	SS	df	MS	Fcalc	Ftab (10%)
WVP					
Regression	21.15	5	4.23	3.69	3.45
Residue	5.74	5	1.15		
Lack of Fit	5.74	3	1.91	9180.07	9.16
Pure error	0.00042	2	0.00021		
Total	26.89	10			
Solubility					
Regression	226.55	3	75.52	9.44	3.07
Residue	56.01	7	8.002		
Lack of Fit	52.69	5	10.54	6.34	9.29
Pure error	3.33	2	1.66		
Total	282.56	10			

Table 4. ANOVA table for cassava starch films - WVP and Solubility.

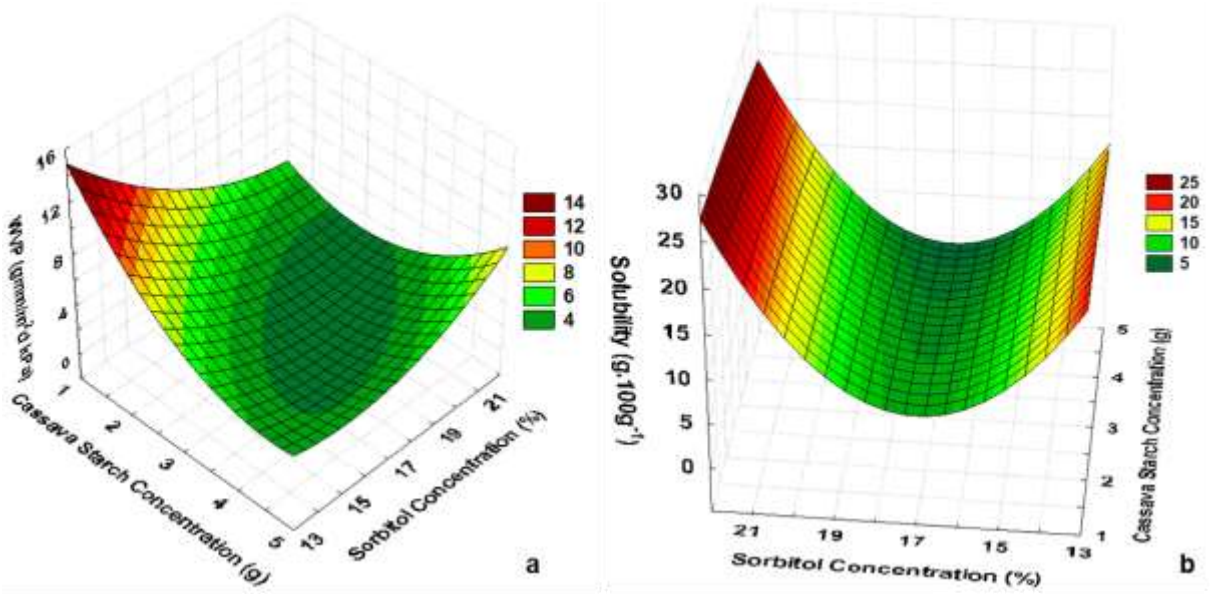


Figure 3. Response surfaces for WVP and Solubility of cassava starch films.

Therefore, it is possible that, for cassava starch films, concentration of starch and plasticizer did not influence significantly thickness and the obtained values are among the expected for this kind of film.

The water content of cassava starch films varied from 4.10 to 15.47 g.100g^{-1} and showed lower values than the potato starch films, that could be related to the different structure of each starch, showing that potato starch has a higher capacity of retain water in this this after gelatinization and that is why takes a longer time to dry potato starch films (Table 2). Figure 3b shows that solubility had a negative quadratic relation with sorbitol concentration with rate values varying from 3.06 to 18.39 g.100g^{-1} and cassava starch concentration showed not influence to the solubility, so, according to

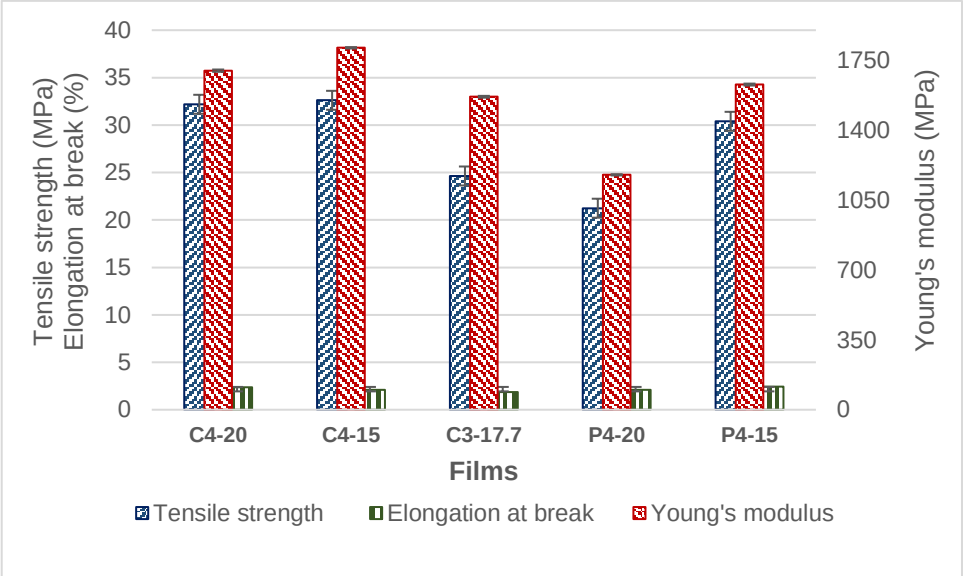
the interaction the use of 15 to 20% of sorbitol would result in low soluble films. Comparing the films of potato and cassava, cassava star films showed lower solubility values than potato starch films, that it another indicative of cassava starch is less hydrophilic than potato starch under the operational parameters of films production on this work. Higher values were obtained in films of native and modified cassava starch with values between 20.81 to 39.41%, because of gelatine content at formulation (FAKHOURI *et al*., 2012). In a work with addition of fruit pulp at cassava starch films formulation were obtained values of solubility between 16.8 to 52.9%, in which the pulp concentration influenced significantly, when higher concentration of pulp, then, lower the solubility was (FARIAS, FAKHOURI, PILER & ASCHERI, 2012).

According to the statistical analyses and mathematical models, optimal results are obtained at the region nearly to the central region including 3 to 4 g of cassava starch for WVP with sorbitol concentration higher than 13 % (Table 4; Figure 3a). However, for sorbitol concentration higher than 20 %, solubility is affected, became inadequate for food packaging (Figure 3b). Thus, in order to test the better formulation of cassava starch films for food packaging, the central point and the formulations with 4 g of starch with 15 and 20 % of sorbitol were selected.

The selected formulations were submitted to tensile strength and elongation at break evaluations, obtaining the results showed at Figure 4. The mechanical properties for the selected films of cassava and potato films are shown at Figure 4.

For packaging materials, it is important to evaluate mechanical properties of polymer films, since only strong enough films can undergo high external forces and protect inner articles perfectly (HU, CHEN & GAO, 2009).

There were not statistical difference ($p > 0.05$) for elongation at break values for all films formulations, while these values varied between 1.9 and 2.4%, which implied that the films were rigid. Similar values of elongation at break were reported for films of potato starch and gelatine (2.86±1.20 %) (FAKHOURI *et al*., 2007). Elongation at break depends on the flexibility of the molecular chain and it could be reduced by increasing starch concentration. High values of elongation at break were reported for potato starch with glycerol films from 58.33 to 85.20%, but lower values for tensile strength of 3.53 to 5.25 MPa and Young`s modulus of 3.95 to 9.23 MPa (ZAVAREZE *et al*., 2012).



First number accompanying the capital letter indicates the concentration of starch (g) and the second indicates sorbitol percentage.

Figure 4. Mechanical properties of the selected films formulations. C=Cassava starch; P=Potato starch.

HU, CHEN & GAO (2009), working with oxidized potato starch films, reported decreasing on elongation at break and tensile strength related to the increase of glycerol, in which the maximum value of tensile strength was 12.82 MPa that is lower than the obtained in present work. Films of potato starch with antioxidant and antimicrobial incorporation, showed values of tensile strength between 5 and 40 MPa depending on different relative humidity (RH) and storage time. In this present research work, the tensile strength was approximately between 20 and 35 MPa, similar to the results of the films storage at 33%RH for 1 week (MORENO, ATARÉS & CHIRALT, 2015). Comparing potato starch films using Tukey test at 95% of interval of confidence, there was significant statistical difference for Young`s modulus and tensile strength evidenced that the formulation with 4 g of potato starch and 15% of sorbitol (P4-15) was a more resistant formulation than P4-20 (Figure 4).

The highest tensile strength was obtained for C4-15 and C4-20 (32.611 and 32.192 MPa) that was higher than the reported for cassava starch films at different concentration of sorbitol (about 2 to 30 MPa) obtained by (SHIMAZU, MALI & GROSSMANN, 2007). It was reported that an increase in the plasticizer concentration reflects in tensile strength reduction, but increases the elongation at break because of the flexibility properties adding with the plasticizer (SHIMAZU, MALI & GROSSMANN, 2007; BERGO *et al*., 2008; LAGOS, VICENTINI, DOS SANTOS, BITTANTE & SOBRAL, 2015). FAKHOURI *et al*., (2012) obtained elongation at break values for

cassava starch films with gelatine and sorbitol showed from 3.81 to 11.52%, higher than the obtained in this present work, while the tensile strength was even higher varying from 70 to 170.31 MPa. Comparing cassava starch films among its formulations using Tukey test at 95% of interval of confidence, central point (C3-17.5= 3 g of starch and 17.5% of sorbitol) was statistically different for tensile strength and showed the lowest values for Young`s modulus and elongation at break. For cassava starch films, there was not significant difference for Young`s modulus. Between C4-15 and P4-15, cassava starch samples showed higher tensile strength. Cassava starch films showed the lowest values for water content, solubility in water and water vapour permeability than potato starch films and, since water is a parameter that usually decreases the tensile strength of the film by weakening intermolecular forces (KRAMER, 2009), that explains why C4-15 resulted in a material more resistant to tensile strength.

Commercially, low-density polyethylene (LDPE) is widely used to pack food and presented values of tensile strength about 10 to 30 MPa, depending on the increase at thickness (RENNERT *et al*., 2013). Therefore, cassava and potato starch films had good resistant characteristics for food packaging when related to LDPE. Then, according to the statistical analysis and looking for the more resistant formulation, C4-15 and P4-15 were selected to produce films for a food packaging and were submitted to SEM, XRD and DSC analyses in order to describe their structural and thermal properties.

Figure 5 shows images of the surfaces and cross sections of the edible films of cassava and potato starches. Films structure and the differences in structuring the filmogenic matrix of both materials can be observed. The edible films showed a regular and homogeneous surface, without bubbles or cracks (Figure 5). C4-15 (Figure 5a, b), showed a surface similar to the reported for a modified cassava starch film of low viscosity (HENRIQUE, CEREDA & SARMENTO, 2008). However, P4-15 (Figure 5c, d), showed small irregularities in the relief (elevations and inequalities of the film surface/thickness) which are marked with arrows, resulting in not uniform in shape and size films as the reported for native potato starch films (ZHANG, WANG & CHENG, 2018). That irregularities could be adjusted using a vibration table to spread the filmogenic solution along the plates. The homogeneity of the films was confirmed by observing the analyses of XRD and DSC (Figure 6 a,b). Between other visual characteristics of the films, potato starch films were more opaque than cassava starch

films that were more transparent and both showed white hue angle. Edible films can provide either clear or milky (opaque) coatings, but consumers generally prefer invisible, clear coatings (PAVLATH & ORTS, 2009).

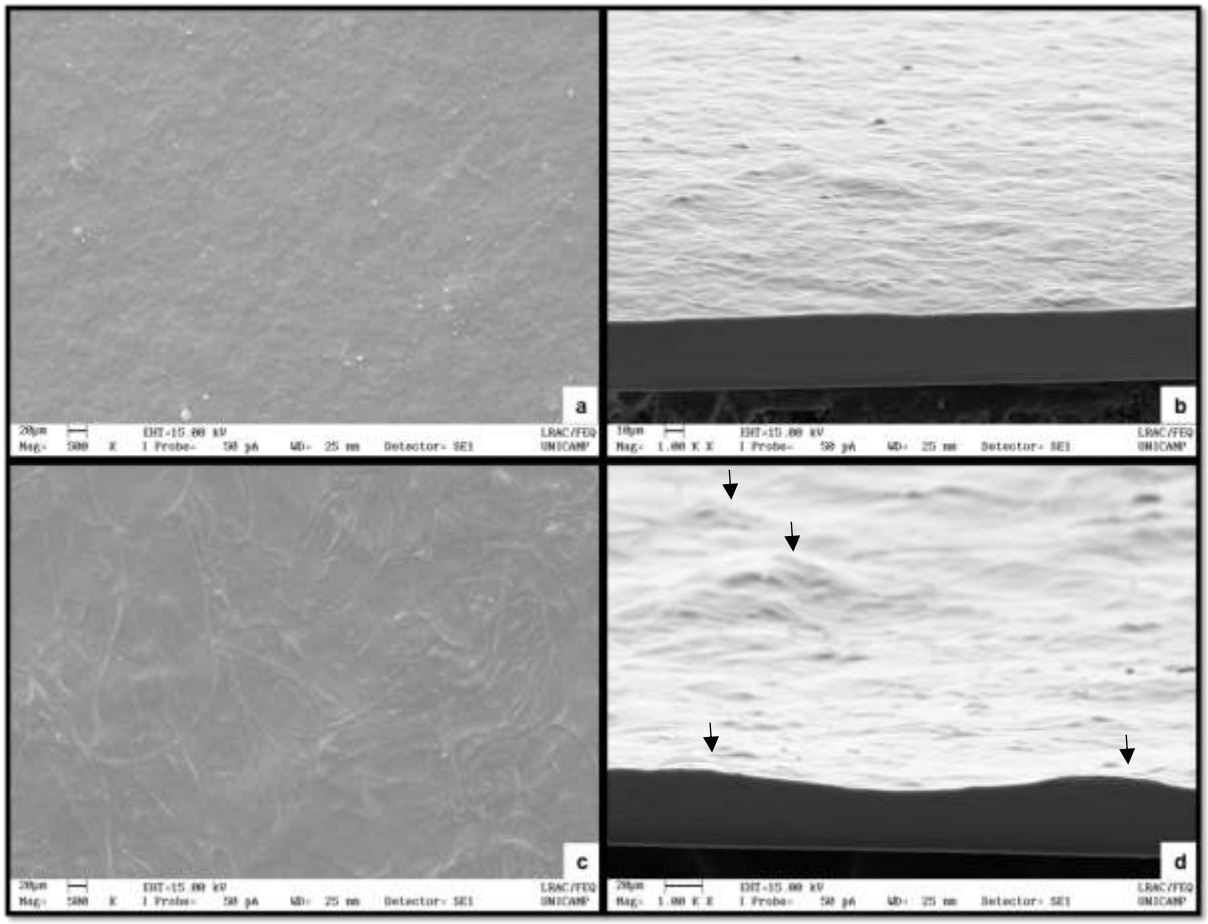
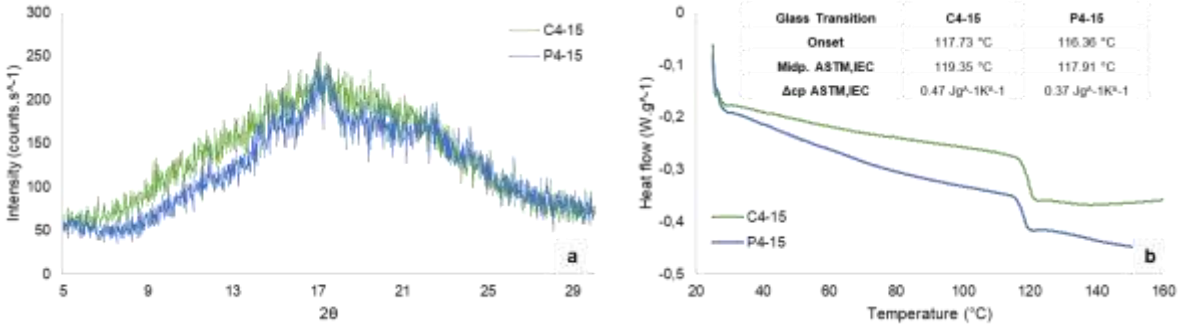


Figure 5. Scanning electron micrographs for surfaces (a,c) and cross-sections (b,d) of cassava (a,b) and potato (c,d) starch films.

The viscosity at the filmogenic formation was visual and physically different. Cassava starch filmogenic solution was less viscous than potato starch solution and was easier to mix. That is explained because of the most apparent change upon starch gelatinization is an intense increase in viscosity related to heating. Gelatinization steps were used to characterize different starches (KRAMER, 2009).

By X-ray diffraction, it was observed the crystalline region of cassava and potato starches edible films. Such crystalline region is clearly observed in the defined peaks from 5 to 25°, approximately. There were observed peaks after 5°, 14°, 17° and between 21° and 25°. Those peaks match with B type starches, since strong bands appeared at 5.6, 14.4, 17.2, 22.2 and 24.0º (ZOBEL, 1994). Those starches, as the films produced in this present work, have a semicrystalline morphology.

The X-ray results showed films with semicrystalline behaviour related to their main starch. So, the sorbitol addition did not affect the starch crystallinity. Comparing both films, it was concluded that there was not big difference in relation to the formation of observed crystalline regions and to intensity. C4-15 showed higher peaks, but P4-15 had the highest value at point 17.07 of 2θ with 255 of intensity (Figure 6a).



Tg is the glass transition temperature, Midp. Is the midpoint and Δcp is the delta of specific heat capacity.

Figure 6. X-ray diffraction (XRD, a) and Differential Scanning Calorimetry thermogram (DSC, b) of cassava (M4-15) and potato (P4-15) starch edible films.

Similar results were reported for potato starch films which characteristic diffraction peak appeared clearly around 20°, noting that increasing of glycerol concentration resulted in decreasing on the crystallinity (ZHANG, WANG & CHENG, 2018; HU, CHEN & GAO, 2009). For cassava starch films with 30 and 45% of glycerol, tendency to crystalline peaks around 20° were reported, coinciding with data obtained at this present work for cassava starch film with 15% of sorbitol (BERGO *et al*., 2008).

By the DSC analysis (Figure 6b), it was observed that the glass transition temperature (Tg) of the materials were between 116.36°C and 119.35°C with higher values for the cassava starch edible film (C4-15), because of potato starch films had a water content a little higher (15.95 g.100g^{-1}) than cassava starch films (12.38 g.100g^{-1}). C4-15 also showed a higher value of specific heat capacity, that explain why the filmogenic solution of potato starch showed a denser solution faster than the cassava starch solution at same temperature. Cassava starch films presented Tg values between reported values for films of cassava containing 0% and 15% (97.9°C and 131.9°C, respectively) by (BERGO *et al*., 2008), who observed Tg decreasing with the glycerol increase. However, potato starch films presented Tg values lower than reported values for potato starch films with incorporation of antioxidant and antimicrobial proteins, which varied from 125.9 °C to 161.8 °C (MORENO, ATARÉS & CHIRALT, 2015). So, the formulation of 4 g of starch and 15% of sorbitol for cassava and potato starch

resulted in homogeneous films, thus they are suitable for using as edible lids for food packaging.

3.2 Nutritive gel

Considering the characterizations of based flours and its portion at the dry part using linear proportion, the nutritional composition of the mixed flour considering 100g of product was obtained and showed at Table 5. The aqueous extract of coffee by-product flour used to the development of the gel presented 48.2 mg.100mL^{-1} of caffeine. Table 5 shows nutritional composition corresponding to an agro-industrial by-product in flour shape produced with agro-industrial waste. Orange and passion fruit peel were the principal source of crude fiber and okara soy was the source of protein. A fiber intake of, at least, 30 g per day as well as the variety of fiber source foods (fruits, vegetables, whole grains and bran) are relevant factor for achieving health benefits (BERNAUD & RODRIGUES, 2013).

Nutrients Composition		Caloric Composition (kcal)
Carbohydrates (g)	82.869	331.476
Protein (g)	6.240	24.960
Lipids (g)	2.563	23.070
Crude Fiber (g)	5.453	
P (g)	0.077	
K (g)	0.536	
Ca (g)	0.417	
Mg (g)	0.048	
S (g)	0.055	
B (mg)	0.602	
Cu (mg)	0.442	
Fe (mg)	1.076	
Mn (mg)	0.340	
Zn (mg)	0.570	

Table 5. Nutritional composition of dried flour used in formulation of nutritive gel (considering 100 g of dried product).

However, besides those nutrients, it was evident the input of other important macro and micronutrients. The nutritive gel dry mass has higher protein content than some animal sources as cooked marrow jam (2.1 g), natural yogurt (4.1 g), or vegetal source as cooked carioca beans (4.8 g); cooked lentil and tofu has similar content with 6.3 g and 6.6 g of protein, respectively (TACO, 2011). The nutritive gel dry mass has higher content of K than parsley (0.35g), more Ca than spinach (0.15g) and could be a source

of Zn, if compared with some animal source as bee honey, fish and meat (0.08-1.2mg) (SIKORSKI, 2007). In addition, according to Mean Daily Intake and Recommended Dietary Allowances (RDA), 100 g of dry part of the nutritive gel can supply the range of mean daily intake of B (0.001-0.003 $g.100g^{-1}$) (SIKORSKI, 2007). Some images of the materials used for producing the nutritive gel and the final packed product are illustrated at Figure 7. The aqueous extract of coffee pulp flour resulted to be a dark liquid similar to coffee beverage with an aromatic smell that remains ripe coffee beans (Figure 7a). The sanitized orange peels were meticulously selected in order to use just healthy peels, without spots or rotten parts that could affect flavour or smell. In order to have a stable gel shape, it is recommended to use fresh materials with not longer than 4 days of storage at low temperature and without freezing (Figured 7b).

Preparation: Aqueous extract of coffee pulp flour (a),sanitized orange peel (b), blender with a and b (c), a and b after crushed prepared to be filtered (d), orange natural juice (e), orange peel aqueous extract (f), base flour and sugar mix (g), nutritive gel portion (h). Packaging and storage: edible cassava and potato starch based lids (i), packed nutritive gel (j), disposition of gel packages for storage and shelf life analysis at 10°C (k).

Figure 7. Nutritive gel preparation, packaging and storage.

Figure 8 shows results of the colour parameters behaviour over time of the samples of nutritive gel submitted to different lid materials. By Tukey test and homogeneous groups tests at 95% interval of confidence, it was possible to determine that the plastic lid showed statistical significant difference over time and over the starch lid materials.

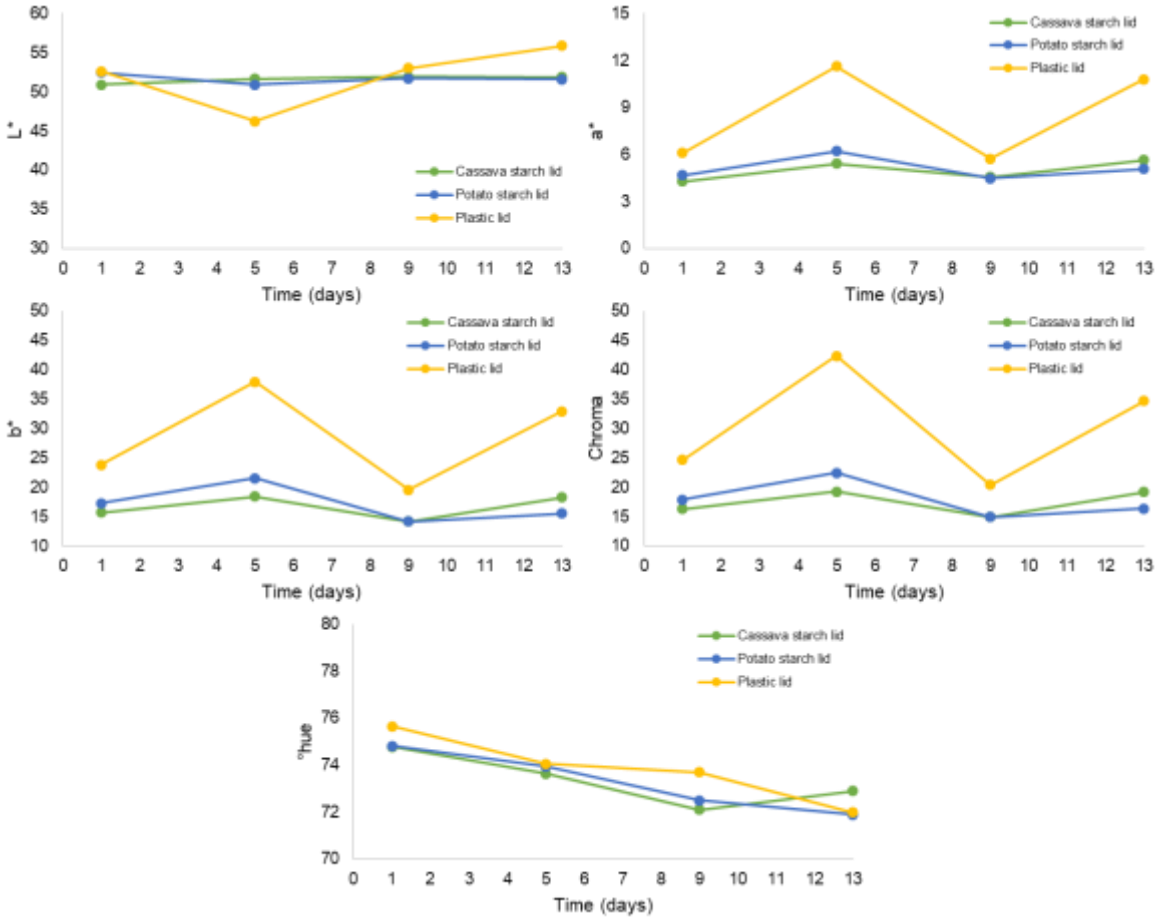


Figure 8. Results of colour parameters of nutritive gel surface along time submitted to different lid materials and stored at 10 °C

There was not statistical significant difference among the samples of cassava starch lids and potato starch lids for colour parameters. The results showed that the nutritive gel was dark, with low brightness and an intermediate colour between the coordinates a* and b* (dark orange or brown colour). Luminosity (L*) and tonality (°hue) were the colour parameters with less variability over time. Low positive values of a* indicated a dark red tonality, while b* low positive values indicated a tendency to yellow colour and low values of chrome mean low saturation. This behaviour was showed equally by samples with cassava and potato starch lids. For samples with plastic lids, at 5 and 13 days, there was significant difference with higher positive values of those parameters. The values of °hue confirmed colour between red and yellow, indicated by a* and b*

with decreasing behaviour from a more yellow tonality to red tonality. Concluding, colour parameters showed low variability related to lid materials, but with normal changes over time and significant difference for plastic lids that could occurred due to external factors. So, lid materials did not affect surface colour of the nutritive gel.

The nutritive gel was submitted to physico-chemical analyses at 1, 5, 9 and 13 days in order to evaluate the effects of different lids on shelf-life. These results are shown at Table 6. Using Tukey and homogeneous group tests at 95% of confidence interval, it was identified statistically significant differences between the lids materials and along the days for water content, Aw, total acidity and pH. Water content and Aw were high, so, it was susceptible to the development of microorganism, explaining its shorter shelf life. Thus, the nutritive gel is susceptible to microbiological development. For water content, the differences between cassava and potato starch lids were statistically significant from plastic lid at days 9 and 13, since starches lids has a higher WVP it was expected. The plastic lid was better to keep water content of the product along time, but at this condition of a food with high potential of microbiological development, it creates a beneficial environment for microbiological growth and fermentation. The Aw behaviour along the time showed to be related to the loss of water content, the variation was less than 2% from day 1 to day 13 for samples with starch based lids that were significant different from plastic lid at days 9 and 13. Plastic lids samples showed no difference for water content and Aw along time.

Acidity and pH of a food are related to the deterioration of food due to the activity of microorganisms, stability and texture of gels, taste, smell and quality (CECCHI, 2003). It was observed that, while pH was decreasing, acidity was increasing. This fact evidences deterioration of the gel due to microorganism development and/or fermentation. The increase in acidity from day 9 to day 13 was greater than in the previous days, which may be an indication of food shelf-life is approximately 9 days; since the changes in physico-chemical properties are more significant from that day. At 13 day, the samples of plastic lid showed lower pH and higher water content that explain a loss in gel consistency and higher level of deterioration due to fermentation process.

The changes at samples soluble solids were mostly not statistically significant. Soluble solids represent the content of sugars, glucose, fructose and sucrose, organic acids and other constituents, and are a parameter used to estimate fruit harvesting point (CTC, 2011). In this work, soluble solids was used as a parameter of nutritive gel

quality and deterioration. It was evident that, according to the loss of water content, soluble solids were concentrated along time for samples with the starches lids. For the samples with plastic lids where were not water content losses but where other physical changes like loss of gel shape and odour, the soluble solids could be related to organic acids derived from sugar fermentation because of the high water content, high Aw and microbiological growth and low oxygen atmosphere along the days. The changes of soluble solids on food samples could be a signal of flavour changes, which is related to the quality of a product and must be considered an undesirable characteristic.

However, the results support that cassava and potato starch films could be used as part of packaging of products which need water vapour permeability in order to keep its quality as fresh vegetables. The WVP could reduce fermentation rate due to water content loss to the environment that results in a decreasing on Aw too.

Lid material	**Time (days)**			
	1	**5**	**9**	**13**
Water content (g. 100g^{-1})				
Plastic	77.18a	76.35a	76.62a	75.61ab
Cassava starch film	76.86a	74.30ab	70.58bc	67.80cd
Potato starch film	76.78a	74.18ab	70.76bc	64.23d
Aw				
Plastic	0.9828a	0.9824a	0.9803ad	0.9800ad
Cassava starch film	0.9832a	0.9770cd	0.9739bc	0.9699be
Potato starch film	0.9851a	0.9822a	0.9737bc	0.9673e
Total titratable acidity (%citric acid)				
Plastic	0.44a	0.47ab	0.46a	0.47ab
Cassava starch film	0.50abc	0.50abcd	0.57d	0.67e
Potato starch film	0.50abc	0.52bcd	0.55cd	0.68e
pH				
Plastic	4.59d	4.31cf	4.17ab	4.12a
Cassava starch film	4.60d	4.49g	4.21be	4.16ab
Potato starch film	4.60d	4.36c	4.37c	4.28ef
Soluble solids (°Brix)				
Plastic	19.8a	20.2a	22.2a	21.5a
Cassava starch film	20.6a	22.8a	25.5ab	24.5ab
Potato starch film	20.2a	22.7a	23.5ab	31.3b

(means followed by the same letter has not significant difference).

Table 6. Physico-chemical properties of nutritive gel along time, submitted to different lid materials and stored at 10 °C

The microbiological analyses results along time are shown in Figure 9. The count of total coliforms and thermotolerants were zero for all samples and days, agreeing the

Sanitary Microbiological Food Standards of The Brazilian Health Regulatory Agency (ANVISA, 2001). Tukey and homogeneous group tests at 95% of confidence interval identified statistically significant differences regarding to microbiological counts. According to the results, both lid materials and time affected the mesophilic growth, while the samples of cassava starch lid showed the lowest mesophilic growth over time. Considering the limit of molds and yeasts for purees and jams in paste or similar, including jams, not commercially sterile; syrup candies, not commercially sterile (in bulk), the maximum tolerance for representative sample is 10^4 (ANVISA, 2019). That maximum value was reach by plastic and potato starch lids at day 9, while at day 13, the representative sample was 10^5, exceeding the limit allowed.

For psychrotrophic count at day 1, there was not colony forming units per milligram ($CFU.mL^{-1}$), and for samples of cassava starch films, it was not possible to count at day 13 because of external contamination. At day 5, the principal difference was between cassava starch and plastic lid. Cassava starch lid samples showed the lowest values. For day 9, there was significant difference among all samples. At day 13, plastic lid showed lower psychrotrophic growth than potato starch lid. Related to molds, the principal difference was shown at cassava starch lid samples that presented lower values of molds growth at the beginning and the last 2 counts. On the other hand, potato starch and plastic lid samples showed the same growth behaviour over time, confirmed by non statistical significant difference. Finally, at the first count of yeast, the statistical analyses presented significant differences between cassava starch lid samples and potato starch and between cassava starch lid samples and plastic lid. However, there was not significant difference between potato starch lid samples and plastic lid. Cassava starch lid showed lower values than the other materials. The second count presented a decrease in log $CFU.mL^{-1}$ for potato starch and plastic lid, that were significant different from cassava starch lid samples. At the third count, samples of starch lid materials were statistically equals, but different of the plastic lid samples, which showed the highest values. At the final count, it was not significant difference between the samples for yeast growth. However, cassava starch lid samples showed the best results regarding to low microbial growth along time, proving to be a material able to keep nutritive gel's microbiologic quality for longer period.

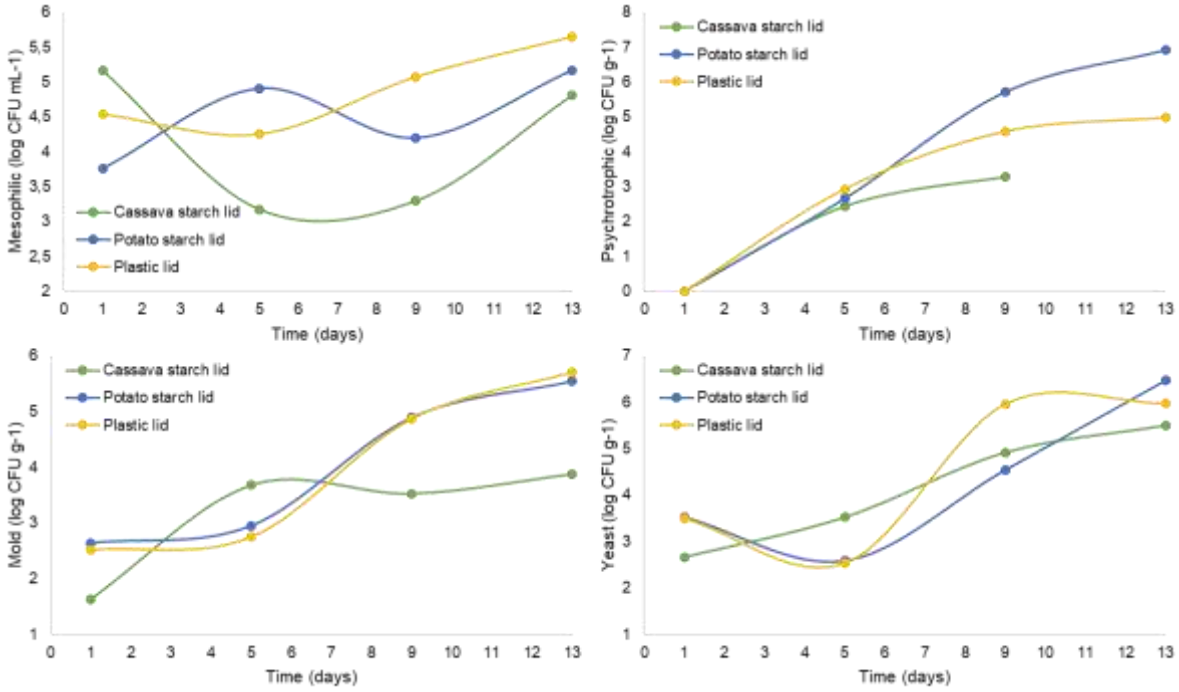


Figure 9. Microbiological count results for nutritive gel along time, submitted to different lid materials and stored at 10°C

When oxygen level drops below 3%, anaerobic respiration will start replacing the Krebs cycle, with the resulting glycolytic pathway releasing unacceptable flavours and causing other problems, such as changes in colour and texture (PAVLATH & ORTS, 2009). Fruits and vegetables native to tropical climates experience harmful chilling effects such as damage to cell membranes at temperatures of 10–12°C. In addition, some cold-tolerant pathogenic microorganisms are able to grow even under refrigeration (PAVLATH & ORTS, 2009).

According to the results, the principal difference among lids materials was the capacity of natural gases exchange demonstrated by the water content loss. Besides the material, the tight and thick of the layer interfered with natural gas exchange which affect physiological deterioration of the product, resulting in lower quality products (EMBUSCADO & HUBER, 2009). This effect was proven by the microbiological growth that is related to food quality and deterioration. Microbiological growth was lower at samples with cassava starch film lids. This film material has lower thickness than the other two materials, lower water content and solubility, higher tensile strength and allow natural gases exchange. Thus, the characteristics listed above define the films based on cassava starch as materials suitable for using as part of the food packaging, managing to maintain the quality of products with low microbiological growth, contributing to the mitigation of plastic waste problem.

For practical purposes, a period of at least 2 weeks is required for processed food to remain wholesome, allowing for packaging, transportation, distribution, and display prior to consumption (EMBUSCADO & HUBER, 2009).

4. Conclusion

As conclusion, the best formulation for edible films was 4 g.100mL^{-1} of water of starch with 15% of sorbitol for both materials which showed a similar behaviour for mechanical, structural and thermal properties with resistance and homogeneity. The films showed resistance to tensile strength, semi-crystalline morphology and Tg above 100°C according to the x-ray diffraction and DSC analyses, transparency and homogeneity from visual observation analyses. MEV also showed a homogeneous surface without cracks. Although both potato and cassava starch films showed similar thermal, morphological and mechanical characteristics and both material can be considered suitable for food packaging, lids of cassava starch showed better nutritive gel conservation, indicated by a higher water content food and consequent higher Aw, even better than plastic lid, Concluding, starch films has suitable characteristics for edible films lids for food packaging. Besides, a portion of the nutritive gel can be a source of protein, fiber, some macro and micronutrients and energy. It presented shelf life lower than 13 days. After that, it clearly presented physico-chemical and microbiological deterioration indications.

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GENERAL DISCUSSION

Flours of orange peel, passion fruit peel, soy okara, coffee pulp and husk were obtained by convective drying and freeze drying. The results of the flours characterization by centesimal composition, physico-chemical analyses and macro and micronutrient contents were detailed in Chapters 1, 2 and 3 and in the article entitled “Caracterización de subproductos agroindustriales: naranja y maracuyá” (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018).

According to Table 1, thermal treatments influenced some nutrient concentration of flours, regarding to t-test analysis on 95% of confidence interval, when orange and passion fruit by-products were subjected to CD (convective drying using forced air circulating stove at 65 °C for 72 h) and FD (freeze drying). Statistically, the treatments did not influenced at ashes, lipids and crude fiber contents for orange by-products and just influenced water content. According to those results, any treatment will produce a nutritive flour for orange by-products, but a lower water content will stimulate a longer shelf life. For passion fruit by-products, the treatments were statistically different for water content, ashes, lipids and crude fiber contents. Ashes and lipids contents were higher for CD, while FD showed better values for water (lower) and crude fiber (higher) contents.

This behaviour was evidenced for okara, i.e., the treatments were statistically different for water and crude fiber contents were better for FD and ashes and lipids that were better for CD (Chapter 2).

For coffee by-products, the treatments were statistically different for water and ashes contents, showing that FD was better to reach a lower water content (OD presented the highest water content values), while OD presented higher ashes content (Chapter 3).

So, it will depend on the desired nutritive conditions of the final product to choose the appropriate treatment.

Emphatically, freeze drying was more rigorous treatment for water content and Aw. It means that each type of material showed the lowest water content and Aw when subjected to freeze drying. However, all treatments presented water content below the 15%, tolerable for this type of product.

	Treatment				
FOP	**CD**	**FD**	**t-test**		
	Mean/Std deviation	**Mean/Std deviation**	**t**	**df**	**p**
Water content	12.77±0.08	6.60±0.04	177.384	2	0.0001
Ashes	3.84±0.30	3.37±0.01	2.745	2	0.1110
Lipids	1.71±0.30	1.37±0.31	0.956	2	0.4399
Protein	7.73	4.23	-	-	-
Crude fiber	10.92±0.66	12.37±0.67	-2.185	3	0.1168
Carbohydrates	66.12	78.66	-	-	-
FPFP	**CD**	**FD**	**t-test**		
	Mean/Std deviation	**Mean/Std deviation**	**t**	**df**	**p**
Water content	10.31±0.09	2.76±0.04	157.389	2	0.0001
Ashes	7.80±0.22	6.00±0.52	5.032	2	0.0373
Lipids	1.05±0.10	0.48±0.12	4.993	2	0.0378
Protein	7.76	5.44	-	-	-
Crude fiber	29.67±1.20	39.10±3.40	-4.8246	3	0.0170
Carbohydrates	53.72	48.98	-	-	-

Centesimal composition are expressed in $g.100g^{-1}$. Mean differences are significant at $p < .0500$. Space with - : t-test was not applied.

Table 1. t-test of orange peels flours (FOP) and passion fruit peels flours (FPFP) produced by convective drying (CD) and freeze drying (FD).

Flours with the highest ashes content were those of passion fruit and coffee by-products, with values between 6 and 8.9 $g.100g^{-1}$ (Chapter 1 and 3) (Table 1). Soy okara flours stood out for its high lipid and protein content ranging from 14.3 to 20.3 $g.100g^{-1}$ for lipids and between 27.4 and 40.7 $g.100g^{-1}$ for proteins (Chapter 2). Passion fruit by-products flours stood out for its high crude fiber content (29.7-39.1 $g.100g^{-1}$), while orange by-products flours because of its high carbohydrates content that rate between 66.12 and 78.66 $g.100g^{-1}$ (Chapter 1) (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018).

About macro and micronutrients contents, okara flour was the richest, showing the highest content of nitrogen, phosphorous, magnesium and copper (Chapter 2). Coffee by-product flours stood out because of the highest concentration of iron and manganese (Chapter 3). Passion fruit peel flours showed the highest values for calcium and Zinc (Chapter 1) (ARIAS, SILVA, OLIVEIRA & FAKHOURI, 2018). However, it could be a source of those nutrients and, according to the physico-chemical analyses, all the flours showed stable conditions in order to keep inhibitor conditions for microbial growth due to its low Aw and pH.

Regarding to colour, treatments affected or not the final colour of the flours (Chapter 1, 2 and 3). Statistically, thermal treatment did not influenced yellow coloration (b*; Δb*) and saturation (chrome) for okara and orange by-product flours. It is possible to state that orange, passion fruit and soybeans by-products flours resulted in clear yellow tonality. FPFP resulted in a clear flour, but with significant difference for all the colour parameters. CD treatment produced the darkness flour and FD resulted at luminous, pale, yellow flour. A clear, bright and light yellow is a desired colour for ripe fruits of orange and passion fruit (PEREIRA, MACHADO & COSTA, 2014; REOLON, 2008), considering that it is a desired colour for a representative product of those fruits. Therefore, good colours characteristics were obtained for those FOP, FPFP and okara flours, but FPFP colour components were more sensitive to thermal treatment (Chapter 1 and 2).

Different of those clear flours, coffee by-products resulted at darkness products with low positive values of a* and Δa*, indicating a red tonality with yellow colour tendency and different tonalities depending on the luminosity of each treatment.

Characterized materials of Chapters 1, 2 and 3 were used for developing an energetic functional product, which had gel-shaped due to the used of aqueous extract of fresh orange peel. Orange peel aqueous extract acted like a gel matrix at refrigeration, allowing the gel formation of food mixture.

As food products need packing and plastic is the most common material used for that purpose, in this study, films were developed from organic materials and analysed for using as part of food packaging. Films made from cassava and potato starches could act as protection when used as part of the food packaging, because gel food showed few differences of deterioration signals, comparing to samples stored in total plastic packages (Chapter 4).

In order to stablish the films formulation used for lids packaging, optimal parameters for concentrations of starch and sorbitol were found by CCRD. The optimal parameters were submitted to mechanical properties analyses, which obtained more resistant starch films for both materials the formulation using 4 g.100mL^{-1} of water and 15% of sorbitol. XRD and DSC supported those results.

Experimental runs chosen on optimal parameters values were used for validation of the mathematical models obtained for several responses (Table 2).

For cassava starch films, the predicted values of WVP model (Equation 5 – Chapter 4) were similar to the validation results. The model for solubility (Equation 6 – Chapter 4) showed a higher value than the experimental results. The other parameters did not presented a mathematical model statistically valid.

For potato starch films, the models for WVP and thickness (Equations 1 and 2) showed values similar to the experimental results. The models for water content and Aw (Equations 3 and 4) showed different values comparing to the experimental results.

	Cassava starch films				
	WVP ($g.mm/m^2.day.kPa$)	**Thickness** (mm)	**Water content** ($g.100g^{-1}$)	**Solubility** ($g.100g^{-1}$)	**Aw** (decimal)
Experimental results CCRD	3.26	0.030	12.38	5.41	0.533
CCRD model	2.87	*	*	10.33	*
Experimental results for validation	3.96	0.035	15.15	6.40	0.424
	Potato starch films				
	WVP ($g.mm/m^2.day.kPa$)	**Thickness** (mm)	**Water content** ($g.100g^{-1}$)	**Solubility** ($g.100g^{-1}$)	**Aw** (decimal)
CCRD Experimental results	4.86	0.068	15.95	11.48	0.436
CCRD model	4.47	0.063	17.19	*	0.444
Experimental results for validation	5.09	0.050	14.08	15.06	0.530

*Indicates that there was not results for respective response.

Table 2. Validation of CCRD for cassava and potato starch films for Run 3

GENERAL CONCLUSION

In conclusion, agricultural by-product generated by orange, passion fruit, soybeans and coffee showed functional nutritive compositions, because they are rich in protein, lipids, fiber and carbohydrates, beside high content of some macro and micronutrients like K, Mg, B, Fe, Mn and Zn, mainly. Those nutrients can be consumed using the resulting flour for food preparation.

Thermal treatments can affect nutrient content of the flours obtained from by-products, showed good physicochemical stability, resulting in products with functional characteristics, stable from the microbiological point of view and with extended shelf life. The obtained flours can be use in preparation of new food products or as an enriching component on a pre-existent recipe. And according to their nutritional potential, these by-product could be widely exploited for food industry, reducing the problem of waste generation at agriculture industry and no longer being a pollution problem.

It was possible to develop a gel-shaped food with functional and energetic characteristics, taking advantage of agro-industrial by-products and contributing to the good management of waste. The development of new food products based on by-product can generate economic benefits, avoiding environmental problems by the consequent reduction of waste disposal from the agro-industrial chains production.

It is possible to reduce plastic packaging using potato and cassava starches films because of their physico-chemical characteristics, their homogeneous and strong structure, its thermal properties and their ability to protect food products deterioration. The use of starches films for pack production is an alternative strategy to reduce the use of plastic in the packaging of food industry.

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