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RICARDO HENRIQUE BELMIRO

USE OF DYNAMIC HIGH PRESSURE TECHNOLOGY, ACETYLATION REACTION AND ENZYMATIC HYDROLYSIS IN THE MODIFICATION AND APPLICATION OF WASTE FROM COFFEE BEAN PEELING

USO DA TECNOLOGIA DE A ALTA PRESSÃO DINÂMICA, DA REAÇÃO DE ACETILAÇÃO E DA HIDRÓLISE ENZIMÁTICA NA MODIFICAÇÃO E APLICAÇÃO DOS RESÍDUOS DO DESCASCAMENTO DO GRÃO DE CAFÉ

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Thesis presented to the Faculty of Food Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor, in the area of Food Technology.

Orientador: Dr MARCELO CRISTIANINI

Co-orientadora: Dra LUDMILLA CARVALHO DE OLIVEIRA

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ORCID do autor: https://orcid.org/0000-0003-2251-5964
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Banca Examinadora

Dr. Marcelo Cristianini

Presidente

Dra. Alline Artigiani Lima Tribst

Membro titular

Unicamp

Dra. Cinthia Baú Betim Cazarin

Membro titular

Unicamp

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À minha FAMÍLIA, dedico

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Resumo

O café é uma importante commodity e uma bebida consumida no mundo inteiro, e que para ser consumida, é necessário que o grão seja previamente descascado e torrado. Durante o descascamento dos grãos de café enormes quantidades de resíduos (RDC – resíduos do descascamento do grão de café) são geradas, os quais contém consideráveis teores de fibra alimentar e compostos antioxidantes. Para ser mais bem aproveitada pelas indústrias alimentícias, a fibra presente nestes subprodutos deve ser modificada, alterando assim suas propriedades tecnológicas, como a capacidade de retenção de água (CRA) e óleo (CRO) e a solubilidade (IS), e promovendo melhorias funcionais. Os métodos de modificação de fibra compreendem os métodos físicos, químicos e enzimáticos, porém muitos destes envolvem a utilização de altas temperaturas ou ácidos e bases fortes, o que causa impacto ambiental e pode levar à degradação de compostos bioativos e nutricionais presentes no resíduo. A alta pressão dinâmica (APD), a reação de acetiliação (ACT) e a hidrólise por celulase (ENZ) foram aplicados em diferentes níveis nas fibras do resíduo do descascamento do grão de café e suas propriedades físico-químicas foram determinadas. A aplicação destes produtos, não modificado e modificados, em biscoitos tipo cookies também foi avaliada. Todos os métodos de modificação levaram a melhorias nas propriedades tecnológicas dos subprodutos do café (até 50% de aumento na CRA e 90% na CRO). Através de microscopia eletrônica de varredura verificou-se que, em geral, os métodos de modificação causaram quebra e/ou abertura da estrutura da fibra dietética. Através da técnica de difração a laser constatou-se que a APD resultou na diminuição do tamanho de partículas, a ENZ levou a um ligeiro aumento e a ACT não causou alterações. A incorporação do RDC, não modificado ou modificado, incrementou o teor de fibras e o status antioxidante dos biscoitos, causando poucos impactos nas dimensões, propriedades físicas e atributos sensoriais, promovendo assim uma boa aceitação dos provadores. Palavras chaves: subprodutos agroindustriais, fibras alimentares, compostos antioxidantes, propriedades tecnológicas, atributos sensoriais.

Abstract

Coffee is an important commodity and a beverage consumed all over the world, which, in order to be consumed, requires the bean to be previously husked and roasted. During the processing of coffee, huge amounts of by-products (RDC) are generated, such as peel, pulp and parchment, which contain considerable amount of dietary fiber and antioxidant compounds. Intending to be better applied by the food industries, the fiber present in these by-products must be modified, thus changing their technological properties, such as the water retention capacity (CRA) and oil (CRO) and the solubility (IS), and, consequently, leading to functional improvements. Fiber modification methods include physical, chemical and enzymatic methods, however some of them involve the use of high temperatures or strong acids and bases, which in addition, cause loss of nutritional compounds and environmental impact. Dynamic high pressure (APD - physical method), acetylation (ACT - chemical method) and cellulase hydrolysis (ENZ - enzymatic method) were applied at different levels in coffee by-products and their physico-chemical properties were determined and the physicochemical properties of the modified and non-modified residues were evaluated. Moreover, these residues were added into cookies to evaluate the consequences of their use as an ingredient in bakery. All modification methods led to improvements in the technological properties of coffee by-products (up to 50% increase in CRA and 90% increase in CRO). Through scanning electron microscopy, it was found that, in general, the modification methods caused the disrupt and / or opening of the structure of the dietary fiber. Through the laser diffraction technique, it was found that APD resulted in a decrease in particle size, ENZ led to a slight increase and ACT did not cause changes. The incorporation of RDC, non-modified or modified, increased the fiber content and the antioxidant status of the cookies, causing little impact on the dimensions, physical properties and sensory attributes, thus promoting a good acceptance by the consumers. Keywords: Agro-industrial by-products, dietary fiber, antioxidant compounds, technological properties, sensorial attributes.

Lista de Figuras

Introdução

Lista de tabelas

Capítulo 1

Sumário

Introdução

O café é uma das commodities mais comercializada e uma das bebidas mais consumidas no mundo, com um volume de produção mundial de cerca de 3 milhões de toneladas de grãos em 2019 (FAOSTAT, 2021).

O fruto do café (Figura 1) é formado pelo grão ou endosperma (54% do peso do fruto, b.s – base seca.), polpa ou mesocarpo (26,5%, b.s.), pergaminho ou endocarpo (13% b.s.) e casca, ou epicarpo (10% b.s.) (BRESSANI, ESTRADA E JARQUIN, 1972).

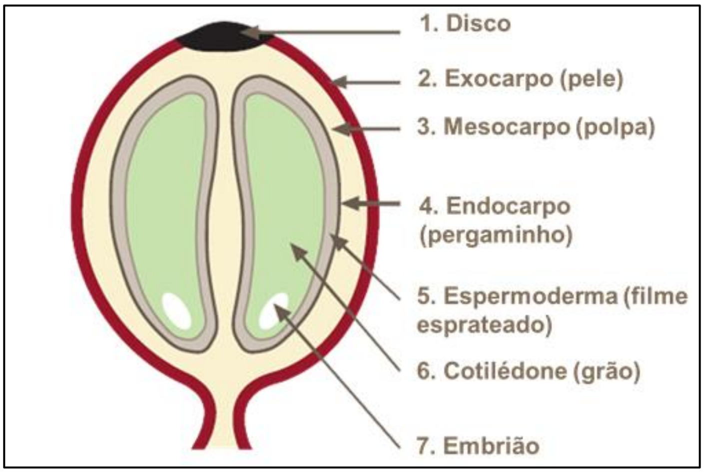

Figura 1 Morfologia do grão de café. Fonte: Yara, 2021

Para a produção da bebida apenas o cotilédone é utilizado, sendo que os demais componentes do grão, ou subprodutos da limpeza do grão de café (RDC), são retirados e descartados (Figura 2), gerando assim um volume de cerca de 1 kg de subproduto para cada 2 kg de grão de café beneficiado (BRESSANI, ESTRADA E JARQUIN, 1972). Portanto, considerando que todo o café produzido seja beneficiado, somente no ano de 2016 cerca de 4,6 milhões de toneladas de RDC foram produzidos.

Figura 2 Resíduos formados após o descascamento do grão de café. Fonte: Autor

A polpa do grão de café é normalmente utilizada como fertilizante enquanto a casca e o pergaminho são empregados tradicionalmente como combustível utilizado no processo de secagem do próprio café, como adubo e como alimento para animais. Esta aplicação é feita, porém, em quantidades limitadas, já que o elevado teor de cafeína e taninos presente neste resíduo causa estimulação do sistema nervoso do animal e os taninos podem se complexar com as proteínas, comprometendo o ganho de peso do animal (BRESSANI, R.; ESTRADA, E.; JARQUIN, 1972; VALE et al., 2007).

O RDC é rico em fibras alimentares (FA) e compostos bioativos (Belmiro et al., 2020), tais como, ácido clorogênico, ácido cafeico e taninos, os quais apresentam propriedades antioxidantes e estão relacionados à redução do nível sérico de lipídios, redução do índice glicêmico e redução do risco de doenças coronárias, mal de Alzheimer, diabetes e câncer (ABDUL-HAMID; LUAN, 2000; ROEHRIG, 1988; SHIMODA et al., 2006), dentre outros males. Portanto, constitui-se de uma potencial matéria-prima/ingrediente para o enriquecimento de formulações alimentícias.

Além de seu benefício à saúde, as fibras alimentares também apresentam propriedades tecnológicas importantes para a indústria de alimentos. Quando adicionadas em produtos alimentícios elas podem substituir parcialmente a farinha de trigo, o sódio e a gordura, como um agente higroscópico, sem causar impacto na textura do produto, bem como aumentar a retenção de água e óleo ou evitar a perda destes durante o processo de cocção em produtos com redução no teor de sódio (ELLEUCH et al., 2011; FERRÃO et al., 2016; SPOTTI; CAMPANELLA, 2017). Para que a aplicação do RDC seja viável economicamente, pode ser necessário que as características funcionais das fibras presentes, tais como capacidade de retenção de água (CRA), capacidade de retenção de óleo (CRO) e índice de solubilidade sejam melhoradas, através da modificação da fibra alimentar (seu principal componente), porém sem causar perda nutricional nestes resíduos do café.

Métodos de modificação de fibra consistem em métodos físicos, mecânicos e enzimáticos. A alta pressão dinâmica (APD) (método físico), a reação de acetilação (método químico) e a modificação com celulase (método enzimático) são métodos relativamente simples e que por não utilizarem altas temperaturas e nem reagentes orgânicos fortes (OZYURT E OTLES, 2016; YANG et al., 2017), podem garantir maior retenção das propriedades dos compostos bioativos presentes nas matrizes alimentícias e, portanto, são métodos promissores para a modificação de fibras.

A APD é uma tecnologia emergente que consiste em submeter alimentos líquidos, ou suspensões, através de um orifício estreito, da ordem de micrômetros, causando um elevado aumento na pressão, seguido de uma abrupta queda até a pressão ambiente (Figura 3). Este processo ocasiona fenômenos de cavitação, cisalhamento e turbulência, fenômenos estes que podem levar ao rompimento de partículas e da parede vegetal e a quebra de ligações glicosídicas (FLOURY et al., 2004; MCCRAE, 1994), como as presentes em fibras alimentares. A quebra das ligações glicosídicas diminui o tamanho das partículas da FA, o que facilita a entrada de água e óleo entre as cadeias do polímero, aumentando assim a CRA, a CRO e a solubilidade (BUGGENHOUT et al. 2015).

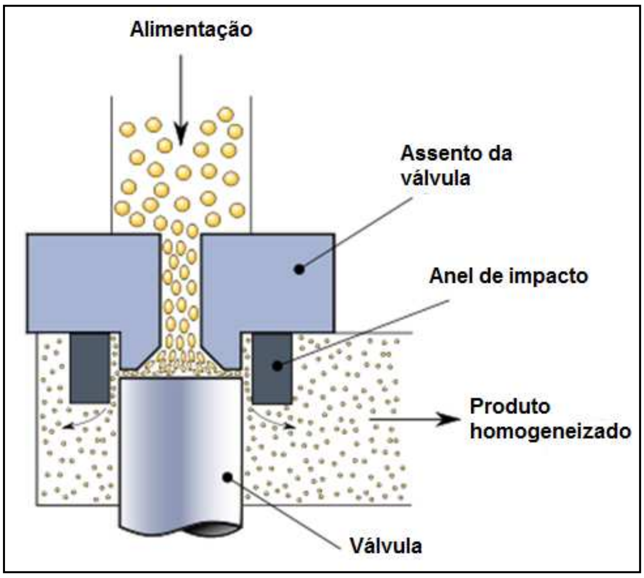

Figura 3 Esquema de funcionamento do homogeneizador a alta pressão. Adaptado de Genizer (2017).

A acetilação é um método comumente utilizado para a modificação de amido e, recentemente, alguns estudos relatam a modificação de fibras alimentares pela reação de acetilação para a fabricação de compósitos, uma vez que esta modificação promove uma maior aderência entre a fibra alimentar e o polímero sintético, devido à mudança na polaridade da fibra, resultando em um aumento na resistência do material. Este método se baseia na substituição de terminais hidroxilas do polissacarídeo por terminais acetil, utilizando ácido acético ou anidrido acético como reagente e hidróxido de sódio como catalisador (AČKAR et al., 2015; HAN et al., 2012).

Uma vez que os grupos acetil são mais volumosos que os grupos hidroxilas, originalmente presentes nas FA, e devido a sua polaridade, estes grupos impedem a interação entre as cadeias de fibras, facilitando assim a entrada e a retenção de água, ou óleo em seu interior e, consequentemente, aumentando sua CRA, sua CRO e sua solubilidade (ACKAR et al., 2015).

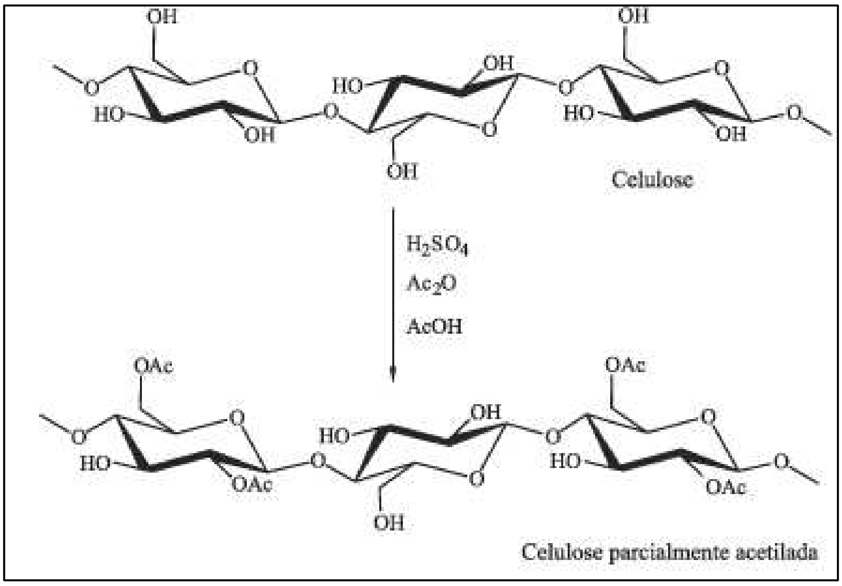

Figura 0-4 Esquema de acetilação da celulose. Fonte: Autor

A modificação enzimática com celulase se baseia na quebra das ligações α-1,4 da cadeia de celulose pela enzima. As reações enzimáticas usam condições reacionais brandas e possuem forte especificidade e, portanto, há tipicamente pouca destruição da composição e estrutura da fibra (OZYURT; ÖTLES, 2016). Uma vez que a modificação enzimática promove uma quebra na cadeia de celulose e consequente diminuição do tamanho de partícula da fibra, há um aumento na área superficial facilitando a entrada de líquido no seu interior e aumentando a CRA, a CRO e a solubilidade da FA (YI et al., 2014).

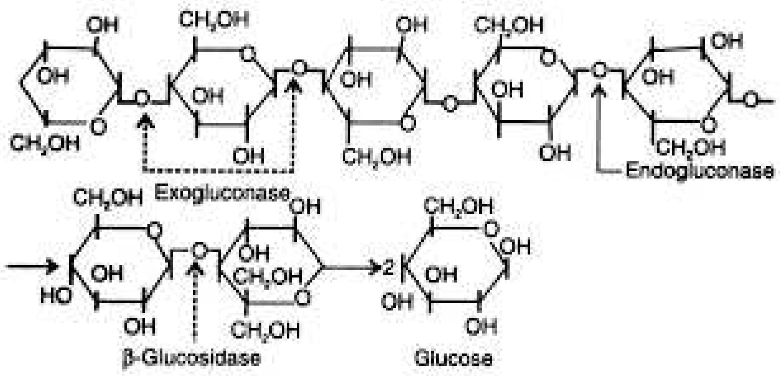

Figura 0-5 Esquema de atuação da celulase. Fonte: IFGOIANO, 2021

Objetivos

Objetivo geral

O presente estudo teve como objetivo principal avaliar o impacto de três métodos de modificação estrutural de fibras, nas propriedades tecnológicas dos resíduos do descascamento do grão de café.

Objetivos específicos

Avaliar as propriedades de capacidade de retenção de água e de óleo e a solubilidade dos produtos obtidos

Avaliar o efeito dos processamentos nos teores de fibra alimentar insolúvel e solúvel

Avaliar a modificação nas estruturas das fibras por meio de microscopia eletrônica de varredura e por tamanho de partícula;

Avaliar o efeito das modificações no potencial antioxidante *in vitro* dos compostos fenólicos livres presentes no resíduo;

Avaliar a funcionalidade tecnológica dos produtos obtidos em biscoitos tipo cookie com substituição parcial da farinha de trigo pelo resíduo do descascamento do grão de café

Determinar as propriedades tecnológicas e sensoriais do biscoito.

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Capítulo 1

Modification of fiber-rich agro-industrial by-products by physical, chemical and enzymatic methods and the stability of their antioxidant compounds: A review

Submetido ao jornal: Renewable Agriculture and Food Systems

Modification of fiber-rich agro-industrial by-products by physical, chemical and enzymatic methods and the stability of their antioxidant compounds: A review

Ricardo Henrique Belmiro1, Ludmilla de Carvalho Oliveira1, Marcelo Cristianini[1],

[1]Corresponding author. Address Monteiro Lobato, 80, School of Food Engineering, University of Campinas, Postal code: 13083-862, Campinas, SP, Brazil. Phone n° +55 19 3521-4008. Fax n° +55 19 3521-0202. E-mail: olecram@unicamp.br (Marcelo Cristianini); ludmillacoliveira@outlook.com (Ludmilla de carvalho Oliveira)

Abstract

The public demand for healthier and clean label foods increases the interest in the agro-industrial by-products worldwide. These could be referred to residues source of dietary fiber (DF) and antioxidant compounds (AC) and their intake may prevent many diseases, such as diabetes, coronary heart disease and bowel inflammatory disease. The use of rich-in-fiber by-products by the food industry strongly depends on their technological properties, related to the DF. Therefore, modifications of the DF by physical, chemical or enzymatic methods are suggested in order to improve its technological properties and make it more suitable for application. However, such modifications can cause change in the phenolic content and antioxidant activity present of the agro-industrial by-products, thus reducing their functional properties. There are several recent works that have evaluated the effect of modification methods on dietary fibers obtained from agro-industrial waste, evidencing the relevance of this topic, but few of them have considered the influence of the methods applied on the antioxidant status of these by-products. Thus, this work reviews the influence of the modification methods on the technological properties and antioxidant activity of agro-industrial by-products.

Keywords: Residue, dietary fiber, technological properties, phenolic compounds, emerging technologies.

1. Introduction

Agro-industrial by-products are the biomass waste generated in large amount by food processing industry (Vilar et al., 2018). However, these residues have been progressively recognized as a rich source of bioactive compounds like dietary fibers (DF) and antioxidants, thus revealing the great potential of using them in the fortification of industrialized and homemade food. In addition, it is expected that these bioactive compounds may contribute to the enhanced food stability and shelf life, and improved consumers' health (Mateo & Maicas, 2015; Nunes et al., 2016). The increased intake of DF has been associated to the prevention of diabetes, bad cholesterol and bowel diseases (Makki et al., 2018; Müller et al., 2018), while antioxidant properties could have effect on body weight reduction, anti-inflammatory response, anti-bacterial activity, and cancer, coronary and Alzheimer diseases prevention (Shahidi & Ambigaipalan, 2015; Tungmunnithum et al., 2018).

Examples of agro-industrial by-products already applied as ingredients in the food industry includes protein from the soybean oil-processing (Preece et al., 2017), whey protein from cheese-making processing (Królczyk et al., 2016) and fiber-rich material from the residue of citrus juice processing (Chavan et al., 2018). However, the feasibility of the above-mentioned by-products application strongly depends on their technological properties, such as solubility, water and oil holding capacity, viscosity, among others (Belmiro et al., 2018; Ozyurt & Ötles, 2016). To date, by-products generated during the coffee, wheat, wine and coconut processing, for example, have been reported to be a rich source of fiber and antioxidant compounds (Wang et al., 2020; Zheng & Li, 2018), but their technological properties are limited compared to the citrus fiber ones, for example (Table 1-1). Studies have shown that the modification of the fiber, the major component found in such residues, can improve its technological properties, and then extend the use of agro-industrial by-products by the food industry (Ozyurt & Ötles, 2016; Yang et al., 2017). When choosing a method of modification, it should be considered the intended changes and the stability of the bioactive or nutritional compounds present in the residue in order to retain them.

Studies have reviewed the modification of agro-industrial by-products focused on the extraction of bioactive compounds (Lai et al., 2017; Naziri et al., 2014; Strati & Oreopoulou, 2014) or the modification of isolated fibers from by-products (Abdul Khalil et al., 2014; Garcia-Amezquita et al., 2018; Karaki et al., 2016; Ozyurt & Ötles, 2016; Spotti & Campanella, 2017; Yang et al., 2017). In this regard, the present review work seeks to assemble, as a whole material, some valuable agro-industrial by-products that stand out both for their DF and antioxidant compound contents. Furthermore, we attempt to discuss recent literature about the possible methods to modify the fiber-rich by-products focusing on food application, and how the stability of their antioxidants may be affected as well.

2. Agro-industrial residues as source of dietary fiber and antioxidant compounds

According to the Food and Agriculture Organization of the United Nations (FAO, 2020), around 9.2 billion tons of vegetables, fruits and other crops were harvested in the world in 2018. In view of this, it is presumable that a large quantity of these foods is processed and agro-industrial by-products (i.e., peel, seed and pulp) are increasingly disposed. Table 1-1 shows the DF content and the physic-chemical properties of some of those industrial residues. Those crops are source of bioactive compounds, such as DF and antioxidants, which in turn are mostly retained in the agro-industrial residues after processing. This way, there is potential and interest in converting these by-products into functional food ingredients, thus contributing to its valorization and sustainable production systems.

Table 1-1 Dietary fibers of agro-industrial by- products from different sources

Source	By-product	SDF/IDF	SDF (g/100 g db)	IDF (g/100 g db)	TDF (g/100 g db)	WHC (g/g db)	OHC (g/g db)	SP (g/g db)	Reference
Clementine	Peel	0.82	34.70	42.50	77.30	10.80	3.30	–	(He et al., 2020)
Orange	Peel	0.39	16.08	40.95	57.03	8.32	2.12	8.08	(Huang et al., 2021)
Banana	Peel	0.21	11.50	54.10	65.60	6.50	1.70	–	(He et al., 2020)
Pineapple	Peel	0.20	7.70	37.60	45.20	6.10	3.50	–	(Crizel et al., 2016)
Pineapple	Peel	0.20	7.6	37.6	45.2	6.6	3.4	–	(Crizel et al., 2016)
Soybean	Okara	0.20	13.90	70.88	76.28	10.33	5.03	4.58	(Chen et al., 2019)
Cumin	Whole	0.17	12.30	71.90	84.20	6.30	5.70	6.80	
Blackcurrant	Pomace	0.12	8.10	68.70	76.90	3.50	1.70	–	(He et al., 2020)
Potato	Peel	0.10	5.90	59.30	65.20	6.30	3.30	–	(He et al., 2020)
Wheat	Bran	0.09	4.10	45.40	46.00	4.90	2.10	–	(He et al., 2020)
Olive	Peel, pulp and seed	0.09	4.40	49.30	53.70	3.60	2.60	–	(Crizel et al., 2016)
Papaya	Peel	0.06	1.90	30.30	32.20	8.90	3.80	–	(Crizel et al., 2016)
Lemon	Seed	0.06	5.00	80.00	85.00	6.46	3.89	23.60	(Karaman et al., 2017)
Grapefruit	Seed	0.06	5.00	85.0	90.00	7.06	4.19	23.00	(Karaman et al., 2017)
Blueberry	Peel, pulp and seed	0.03	1.60	46.00	50.60	4.00	3.20	-	(Crizel et al., 2016)
Oat	Hull	0.02	1.70	74.50	76.30	3.00	1.90	–	He., et al 2020
Foxtail millet	Bran	0.02	1.70	77.50	79.20	3.24	–	2.06	(Zhu et al., 2018)
Rice	Bran	0.02	1.50	75.20	76.70	3.60	2.70	1.40	(Wen et al., 2017)

Soluble dietary fiber/insoluble dietary fiber ratio (SDF/IDF), insoluble dietary fiber (IDF), soluble dietary fiber (SDF), total dietary fiber (TDF), water holding capacity (WHC), Oil holding capacity (OHC) and swelling power (SP)

2.1. Dietary fibers

According to the Codex Alimentarius (2009), DF are defined as carbohydrate polymers with ten or more units of monomers, not digestible by the endogenous enzymes of the small intestine of humans. DF are classified as soluble or insoluble. Soluble dietary fibers (SDF) include pectic substances, gums, mucilage and some hemicelluloses, while cellulose, lignin and other types of hemicelluloses are included in the insoluble dietary fiber (IDF) fraction (Carlson et al., 2018; Poutanen et al., 2017). The soluble and insoluble nature of DF involves differences in their technological functionality and physiological effects. SDF are related to lowering blood cholesterol levels, protecting against bowel cancer, delayed glucose absorption and reduced gastric emptying, while IDF are supposed to increase the fecal bolus, regulate bowel function and prevent intestinal constipation (Carlson et al., 2018).

In addition to their health benefits, DF impart important technological properties for the food industry. When added in certain food products they may partially replace flour and fat without impacting the texture of the product, as well as increasing the water and oil retention or preventing them from being lost during the cooking process in products with reduced sodium content (Spotti & Campanella, 2017).

2.2. Antioxidant compounds

The agro-industrial by-products have been characterized by a high antioxidant activity, which is mainly attributed to the presence of phenolic compounds (Belmiro et al., 2021; Lai et al., 2017; Wang et al., 2020; Zhao et al., 2015). Phenolic compounds have, as a common characteristic, the presence of at least one hydroxyl-substituted aromatic ring. These bioactives are commonly bounded to other molecules, such as DF (glycosyl residue) and proteins, and it may influence their extraction and antioxidant activity (Jakobek, 2015; Jakobek & Matić, 2019). They can be classified into different groups depending on the number of phenol rings they contain and the structural elements that bind these rings: phenolic acids, stilbenes, coumarins, lignans, tannins and flavonoids, among others (Tungmunnithum et al., 2018). Phenolic compounds have numerous biological effects, their antioxidant capacity being the most recognized (Dai & Mumper, 2010; Reis Giada, 2013). Table 1-2 summarizes the total phenolic content and the antioxidant activity of agro-industrial by-products from different sources.

Table 1-2 Antioxidant status of different sources of agro-industrial by-products.

Source	By-product	TPC (mg/g)	ORAC	DPPH	ABTS	FRAP	Reference
Banana	Peel	9.0	-	65.0***	90.0***	-	(He et al., 2020)
Carrot	Pomace	8.5	-	3.5*	-	-	(Yu et al., 2018)
Acerola	Peel and seed	7.9	47.0**	53.2*	-	-	(Albuquerque et al., 2019)
Sesame	Bran	6.2	-	4.9.0*	39.0*		(Görgüç et al., 2019)
Blackcurrant	Pomace	5.5	-	85.0***	90.0***	-	(He et al., 2020)
Orange	Peel and seed	4.3	13.6**	10.8*	-	-	(Albuquerque et al., 2019)
Potato	Peel	3.0	-	30.0***	40.0***	-	(He et al., 2020)
Blueberry	Peel, pulp and seed	23.6	-	4.6*	-	-	(Crizel et al., 2016)
Olive	Prunnning biomas	2.9	-	22.0*	48.0*	32.0*	(Gullón et al., 2018)
Olive	Leaves	2.8	-	27.0*	48.0*	28.0*	(Gullón et al., 2018)
Oat	Hull	2.0	-	10.0***	20.0***	-	(He et al., 2020)
Papaya	Peel	15.3	-	23.5*	-	-	(Crizel et al., 2016)
Tomato	Peel and seed	13.4	144.4*	25.8*	-	-	(Perea-Domínguez et al., 2018)
Pineaple	Peel	12.3	-	23.9*	-	-	(Crizel et al., 2016)
Mango	Peel and pulp	10.9	61.6**	224.5*	-	-	(Albuquerque et al., 2019)
Olive	Peel, pulp and seed	10.0	-	19.2*	-	-	(Crizel et al., 2016)
Passion fruit	Peel and seed	1.2	46.9**	36.6*	-	-	(Albuquerque et al., 2019)
Clementine	Peel	4,5	-	15.0***	40.0***	-	He., et al 2020
Wheat	Bran	2,5	-	10.0***	25.0***	-	He., et al 2020

Total phenolic content, oxygen radical absorbance capacity (ORAC), Diphenyl-1-picrylhydrazyl assay (DPPH), 2, 2-azinobis (3ehtylbenzothiazoline-6-sulfonic acid) diamonium salt assay (ABTS) and ferric reducing antioxidant power (FRAP)

*(µmol Trolox/g by-product)

**(µmol Trolox/L of extract)

***scavenging value(%)

Various methods have been used to measure the antioxidant activity of vegetal tissues such as DPPH (Diphenyl-1-picrylhydrazyl), FRAP (Ferric Reducing Antioxidant Power), ORAC (The Oxygen Radical Absorbance Capacity) and ABTS [2, 2-azinobis (3ehtylbenzothiazoline-6-sulfonic acid) diammonium salt] (Moniruzzaman et al., 2012).

3. Effect of modification methods on the dietary fiber and antioxidant compounds

Agro-industrial by-products with small SDF/IDF ratio (i.e., below 0.1) usually show limited physical-chemical properties, especially regarding water holding capacity (WHC) and swelling power (SP), as Table 1-1 shows. This way, various modification principles (physical, chemical, enzymatic) can be applied to the whole material intending to open/disrupt the DF structure (Figure 1-1), thereby improving its capability to retain water and oil. However, such modification can also lead to change in the antioxidant compounds and on its activity. The modulation of the physical-chemical properties of DF in by-products as well as the extent of impact in the antioxidants depend on both the principle behind the modification method and the food matrix (Dawidowicz & Typek, 2010; Reis Giada, 2013; Spotti & Campanella, 2017) and were discussed below.

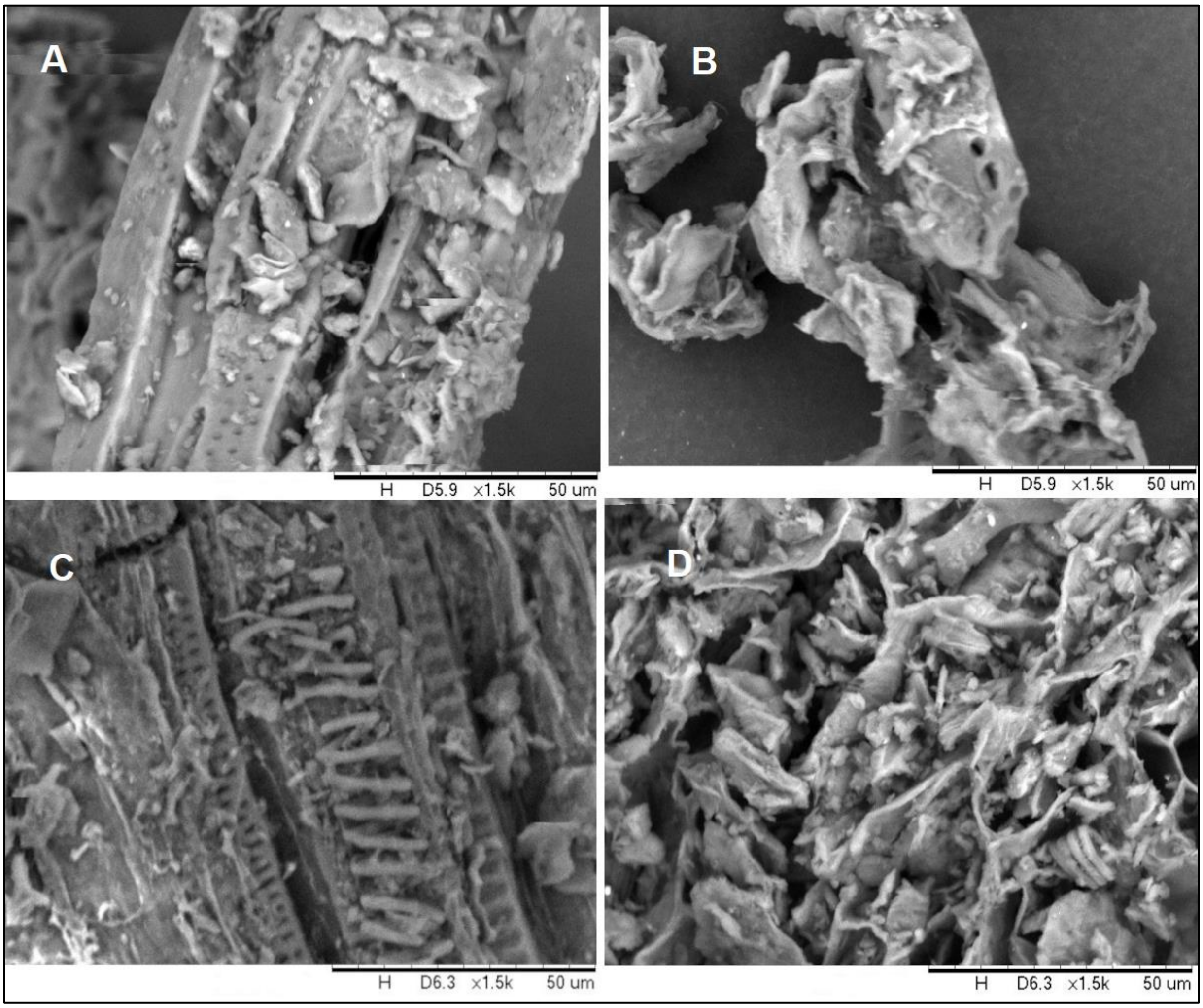

Figure 1-1 Scanning electron microscopy (SEM) of the coffee by-products at 1.5K: Não modificado (A), modified by dynamic high pressure (B), modified by acetylation (C), modified by cellulase (D). Source: Authors.

3.1. Dietary fiber modification

The techno-functional properties of DF, such as WHC, oil holding capacity (OHC) and SP, are defined by the chemical composition and structure, Different processes can alter fibers composition and structure, modulating their properties (Belmiro et al., 2018; Ozyurt & Ötles, 2016; Yang et al., 2017). In other words, the interaction between DF and water or oil depends on water or oil penetration/retention in the glycosidic chains of the polysaccharide. Modifications at these binding sites will lead to changes on the ability of the mentioned interactions. Thus, the more easily water or oil penetrates, the greater will be the WHC, OHC and SP of the fiber (Ozyurt & Ötles, 2016).

From a sensorial point of view, the enhancement of the interaction between fiber and water or oil in food systems play a role in controlling oil and moisture loss (Barretto et al., 2015), thus improving in-mouth sensory sensation and chewability of the product. Adding fiber with increased WHC to food formulation may also control syneresis phenomenon. In foods formulated with high fat content, ingredients with high OHC are required to act as emulsifiers (Abbasi et al., 2019; Spotti & Campanella, 2017).

In the above context, methods of modification have been applied to DF and changes are reported as follows: open/disruption of the fiber structure (Figure 1-1) redistribution of IDF to SDF; replacement of hydrophobic groups at the hydroxyl ends of the glycoside; and arrangement of the fibers in the amorphous and crystalline regions, which open the fiber channels, facilitating the water/oil entrance and improving the WHC, SP, OHC and solubility of the fiber (Feng et al., 2017; Ozyurt & Ötles, 2016). Table 1-3 summarizes some recent works that investigated the effect of modifications on DF extracted from agro-industrial sources and a brief explanation about these methods of modification is related below. For a more in-depth reading on the mechanisms of the modification of DF, the following works can be consulted: Ozyurt & Ötles (2016); Spotti & Campanella (2017); Yang et al. (2017).

Table 1-3 Different methods of modification of dietary fiber (DF) from different sources

modification method	Technology	Source of DF	Reference
Physical	extrusion	Barley	(Djurle et al., 2016)
		Barley	(Honců et al., 2016)
		Orange	(Huang & Ma, 2016)
		Rye	(Andersson et al., 2017)
		Wheat	(Andersson et al., 2017)
		Wheat	(Oliveira et al., 2015)
	Dynamic high pressure	Coffee	(Belmiro et al 2021)
		Orange	(Van Buggenhout et al., 2015)
		Purple potato	(Xie et al., 2017)
	High hydrostatic pressure	Carrot	(Yu et al., 2018)
		Okara	(Pérez-López et al., 2016)
		Purple potato	(Xie et al., 2017)
		Sugar beet	(Peng et al., 2016)
	Griding	Barley	(Djurle et al., 2016)
		Carrot	(Yu et al., 2018)
		Coconut	(Zheng & Li, 2018)
		Grape	(Zhao et al., 2015)
		Okara	(Ullah et al., 2017)
Chemical	Acid	Coconut	(Zheng & Li, 2018)
		Coffee	(Belmiro et al 2021)
		Orange	(Wang et al 2015)
	Alkali	Abaca	(Cai et al., 2015)
		Cucumber	(Senthamaraikannan & Kathiresan, 2018)
Enzymatic	Cellulase	Coffee	(Belmiro et al 2021)
		Okara	(Huang et al., 2015)
		Soy	(Huang et al., 2015)
	Xylanase	Sugar cane	(Saelee et al., 2016)
		Wheat	(Santala et al., 2014)

3.1.1. Physical modifications

The physical modification of fibers includes mainly thermal modification, thermoplastic extrusion and dynamic high-pressure (Ozyurt and Otles, 2016; YANG et al., 2017).

3.1.1.1. Thermal modification and thermoplastic extrusion

Thermal modifications can change the technological properties of dietary fibers by turning IDF into SDF and changing the total fiber content. In general, high temperatures break glycosidic bonds in the polysaccharide, which can lead to the release of oligosaccharides and, thus, increase the amount of SDF. At higher temperatures, drying dietary fiber can degrade some SDF components and alter their hydration properties and fat adsorption capacity (Ozyurt & Ötles, 2016).

The thermoplastic extrusion subjects the material to high temperature, high pressure and high shear force, causing the internal moisture of the material to evaporate quickly and, consequently, modify the spatial structure of the fiber at an intermolecular and intramolecular level. During extrusion, the molecular structure of the material is altered and forms a porous state (Yang et al., 2017). This modification method has a positive effect on total and soluble dietary fiber, and, in general, the IDF content is decreased, probably due to the disruption of covalent and non-covalent bonds of the polysaccharide, leading to smaller and more soluble molecular fragments (Rashid et al., 2015). Additionally, the water solubility index can be increased by varying the extrusion temperature and extruder thread speed (greater shear force) (Huang & Ma, 2016).

3.1.1.2. Griding

In the grinding equipment, there is a static and a rotating grind stone or a blender in which the dietary fiber is crushed. The mechanism of the DF modification is to break down of hydrogen bond and cell wall structure by shear forces, reducing its size. Reduction in particle size may influence the structure, porosity and surface structure of DFs, resulting in modification of physical-chemical and functional properties (Abdul Khalil et al., 2014; Zheng & Li, 2018b).

3.1.1.3. Dynamic high pressure

Dynamic high pressure is a technology in which a fluid, or a suspension, is pumped and forced through a narrow gap, on the order of micrometers, under high pressure. After passing throughout, there is a pressure drop (from working pressure to ambient pressure), causing cavitation, turbulence and high shear (Kleinig & Middelberg, 1997). These effects are capable of promoting severe changes in the product, promoting the rupture of the wall and compartments of plant cells and / or turning IDF into SDF (Belmiro et al., 2018; Ozyurt & Ötles, 2016).

3.1.2. Chemical modifications

Chemical methods use chemical reagents, such as acid and alkali, to degrade dietary fiber. By controlling the amount of acids and alkalis, temperature and reaction time, some IDF are converted to SDF, thus increasing WHC, OHC and solubility (Yang et al., 2017).

In general, the chemical modifications break the inter and intramolecular bonds between cellulose, hemicellulose and lignin. However, the acidic medium does not disrupt the internal structure of lignin, but the β-glycosidic bonds of the cellulose and hemicellulose polysaccharides. In this process it is possible to dissolve amorphous fractions of cellulose releasing glucose monomers, however, the acid or alkali concentration and reaction conditions must be controlled to avoid degradation of the monomers to furans, acids, alcohols or other by-products. In addition, a high concentration of reactant is not indicated because it is toxic and highly corrosive (Lee et al., 2014; Ozyurt & Ötles, 2016).

3.1.3. Enzymatic modifications

The enzymatic modification causes the degradation of dietary fiber, decreasing the IDF content and increasing the SDF content. Enzymatic reactions use mild reaction conditions and have strong specificity and, therefore, there is typically little destruction of the fiber composition and structure. The enzymes used in the modification of dietary fiber are mainly xylanase and cellulase (Ozyurt & Ötles, 2016).

Enzymatic modification with cellulase cleaves the β-glucosidic bonds of the cellulose and this has been shown to be effective in improving the quality of DF by modifying its structure (Ma & Mu, 2016; Santala et al., 2014; Sousa et al., 2011; Zheng & Li, 2018).

for a more in-depth reading on the mechanisms of the modification of DF, the following works can be consulted: Ozyurt & Ötles (2016); Spotti & Campanella (2017); Yang et al. (2017).

3.2. Effect in the phenolic compounds

A few recent studies have investigated the effect of thermal and chemical processes on the stability of isolated phenolic compounds and some of which are discussed below.

The temperature has showed to be a crucial factor, responsible for causing physical and chemical changes that affect the stability of phenolic compounds. Reports about the temperature effects on these compounds in foods were first linked to the reduction of the antioxidant activity due to degradation or isomerization of phenolic compounds (Dawidowicz & Typek, 2010; Réblová, 2012). On the contrary, it can improve the bioavailability of bound phenolics by releasing them from the DF complex, resulting in increased phenolic concentration. Temperature can also cause an acceleration of the initiation reactions of phenolics, and hence a decrease in its activity (Dawidowicz & Typek, 2010; Réblová, 2012).

Bryngelsson et al. (2002) studied the influence of thermal processes on oat grains and found that steaming and flaking of dehulled oat groats resulted in moderate loss of caffeic acid content, while ferulic acid and vanillin increased. In this work, autoclaving the whole grains (including the hulls) caused increased levels of vanillin, ferulic and p-coumaric acids, whereas caffeic acid was almost eliminated.

The main chlorogenic acid in coffee, 5-O-caffeoylquinic acid, is unstable at high temperatures and its heating in the range of 100-200 °C causes its degradation and isomerization (Dawidowicz & Typek, 2010). However, 3-O-caffeoylquinic and 3,5-dicarbonylic acids are stable under acidic conditions, whereas at neutral and basic pH values the isomerization of different chlorogenic acids, including 5-O-caffeoylquinic, occurs rapidly (Dawidowicz & Typek, 2010; Xue et al., 2016). Extreme conditions such as high temperature and acidic or basic conditions have a great influence on the stability of some chlorogenic acid and may therefore adversely affect their antioxidant activity (Giada, 2013). Nardini et al. (2002) reported that caffeic, dihydrocaffeic and homogentisic acids were more susceptible to degradation under alkaline conditions when compared to coumaric, ferulic, vanillic, sinapic and syringic acids, which were stable against the alkaline hydrolysis. Dihydroferulic acid was slight less stable than ferulic acid, showing that the stability of phenolic compounds depends on their chain length, conformation and presence of functional groups.

Ultrasound processes (20 kHz – 1.7 MHz; 30 – 850 W; 30 min – 5 hours) can lead to the degradation of phenolic compounds, being this degradation dependent on the phenol presence, frequency, power and time of exposure. It was reported that this degradation follows both a thermal decomposition (pyrolysis of carbonyl linkages), mainly for thermolabile phenol compounds, and a free radical reaction mechanism (OH side by side reacts), mainly for less volatile or nonvolatile phenol compounds (Chowdhury & Viraraghavan, 2009).

Belmiro et al. (2021) found that the modification of coffee by-products by the dynamic high pressure (50 and 100 MPa, 1, 2 and 3 cycles of pressure and 25 °C) lead to a slight loss of the phenolic compounds, mainly chlorogenic and caffeic acids. It was stated that this loss was probably due to formation of dietary fiber-phenol complex during the modification.

4. Effect of modification techniques on the bioactive compounds found in agro-industrial by-products

Recent studies have investigated the modification of the agro-industrial by-products as a whole material, without any isolation or purification of the DF or antioxidant compounds. Information from the available literature confirms the feasibility to modify different agro-industrial by-products that are sources of DF (coffee, wheat, grape, coconut by-products) by different methods (dynamic high pressure, acetylation, enzymatic hydrolysis, extrusion, gridding, acidification), with the purpose of improving their techno-functional properties, as reviewed below. Moreover, there has been interest about the modification techniques' possibility of preventing the loss of phenolic compounds and its antioxidant activity.

The effect caused on the agro-industrial by-products by the modification methods depends upon the source of the dietary fiber, the method applied and the process parameters. The physical methods (dynamic high pressure, extrusion and griding) led to a reduction in the particle size and increase in the WHC and OHC, except for griding, but the effect on IDF and SDF levels and antioxidant activity varied according to the source and method used. Physical modification methods have the advantage of not using organic reagents in their processing, which makes them ecologically friendly, but they require robust equipment, especially DHP and thermoplastic extrusion.

The chemical methods (acetylation and hydrochloric acid) caused a slight reduction in the particle size and a more pronounced loss in the antioxidant activity while the technological properties varied for both methods. The enzymatic hydrolysis was more dependent on the agro-industrial by-product source, showing different results for the coffee and coconut. Both the chemical and enzymatic methods have the advantage of not requiring the use of robust equipment, however the chemical methods use reagents that can cause damage to the environment (i.e. strong acids and bases) and the enzymatic methods use relatively expensive substrates. In both cases, the post-wash step can cause leaching of phenolic compounds, decreasing the nutritional value of agro-industrial by-products.

The choice of the method to be utilized will depend upon the by-product available and the final product desired. However, more studies that consider the effect of the modification of agro-industrial by-products as a whole are necessary for a better understanding of the possible applications of these methods. It is important to emphasize that the ability to analyze antioxidant activities of the *in vitrol* methods may not represent the real antioxidant status of the agro-industrial byproducts, requiring, thus, the *in vivo* assay, which allows the bioavailable and bioaccessibility to these products.

Table 1-4 summarizes the effect of the modification methods on different agro-industrial by-products.Table 4 summarizes the effect of the modification methods on different agro-industrial by-products.

4.1. Coffee by-products

Coffee processing generates 1 ton of by-product (skin, mucilage parchment and silver skin) per two tons of coffee processed. Considering the coffee world production in 2018 (10.3 million tons) (FAO, 2020), potentially 5.1 million tons of coffee by-product could have been produced. Coffee by-products contain predominantly IDF, and are source of antioxidant compounds, mainly chlorogenic and caffeic acids and tannins (Belmiro et al., 2021; Kovalcik et al., 2018).

Coffee by-products modified by dynamic high pressure (DHP - 50 and 100 MPa, 1, 2 and 3 cycles of pressure and 25 °C), acetylation (10 and 30% of anhydride acetic for 30, 60 and 120 min) and enzymatic hydrolysis (5 and 15U of cellulase for 30, 60 and 120 min) (Belmiro et al., 2021), showed an increase in the WHC (up to 53%), SP (up to 85%) and OHC (up to 90%), but no significant change in the IDF and SDF. Authors showed that DHP led to a reduction in the particle size and dispersion due to a drastic disruption of the fiber aggregates, while acetylation caused reductions in the particle size and the disruption of the aggregates was less pronounced. The enzymatic method did not disrupt the fiber aggregates but resulted in the opening of the inside channels, causing an increase in the porosity. It was stated that those changes promoted an improvement in the technological properties of the coffee by-products. DHP led to a reduction in the phenolic content and slight reduction in the antioxidant activity, and this reduction was probably due to formation of DF-phenol complex after the modification. Acetylation and enzymatic processes led to a drastic reduction in the phenolic content and antioxidant activity, probably due to the formation of fiber-phenol complex and the leach effect of the pos-washing process of both modification methods, according to the authors.

4.2. Wheat by-products

Wheat is the third most cultivated crop in the world, with a total production of 734 million tons in 2018 (FAO, 2020). Approximately 80% of the whole wheat grain is comprised of endosperm and the remaining 20% is by-product (wheat bran). Wheat processing potentially generated 147 million tons of residue in 2018. Wheat by-product is rich in fiber, mainly insoluble, and ferulic acid, a natural antioxidant. The main applications of wheat by-product are in the animal feed and as fuel in the drying process of wheat.

Wang et al. (2020) evaluated the effect of the twin-screw extrusion process (20 and 25% of moisture content, 100 RPM and 100 °C) on the physicochemical properties and antioxidant activity of the wheat bran. Authors showed that the modification by cooking extrusion increased the WHC (40%), SP (81%) and OHC (65%). Extrusion process promoted a disruption on the fiber aggregates, decreasing the particle size, increasing the surface area and opening the inside channels. They also observed that the IDF content was decreased and the SDF increased, due to the extrusion process. Authors stated that the observed increase in the technological properties was due to the disruption of the particle and IDF/SDF redistribution. DPPH radical scavenging and hydroxyl radical scavenging activities of wheat bran increased from 6.8% to 18.4% and from 5.3% to 15.9%, respectively, but no explanation was provided about these results.

4.3. Grape by-products

Grape processing generates agro-industrial residues, comprising peel, seed, stalk, and residual pulp, referred to as grape pomace and corresponding to approximately 20% of the fruit (Spanghero et al., 2009). About 79.1 million tons of wine were produced in 2018 (FAO, 2020), which generated approximately 15.8 million tons of grape pomace. Grape by-products are rich in IDF and polyphenols, being mainly catechin, gallic acid epicatechin (Beres et al., 2016; Cappa et al., 2015).

Zhao et al. (Zhao et al., 2015) applied the superfine gridding on grape pomace as a modification method. Processing caused a reduction on the particle size of grape pomace, and then a decrease in the fluidity and an increase in the solubility. The authors suggested that the reduction in the particle size promoted an increase in the surface area, facilitating the contact of the water with soluble molecules and shortening the time of dissolution. They also showed that the effects on the particle size and solubility described here have affected positively the antioxidant activity. Therefore, the total polyphenol and flavanol contents and antioxidant activity were found to increase.

4.4. Coconut by-products

Also known as coconut cake or copra cake, the coconut by-product is the residue obtained after the commercial milling and extraction of coconut oil and approximately 1 ton of coconut produces 370 kg of copra cake. In 2018, the world production of coconut was about 65 million tons (FAO, 2020), potentially generating 24 million tons of copra cake. Coconut by-product contains about 85% of DF, mostly IDF, and are source of polyphenols, principally gallic and chlorogenic acids and catechin (Seneviratne et al., 2016; Zheng & Li, 2018).

Zheng & Li (2018) evaluated the effect of the enzymatic hydrolysis by cellulase (0.3 g of cellulase at 50 °C for 1h) and acid modification (HCl 1 M, at 60 °C, for 30 min.) on the physicochemical and technological properties of modified coconut cake. Acid modification led to a reduction in the IDF and SDF, while the cellulase hydrolysis promoted an increase in the SDF and a reduction in the IDF content, due to the disruption of the DF structure. WHC and SP of the coconut cake was decreased by cellulase hydrolysis and acid modification, whereas OHC remained unchanged when compared to the control (coconut cake defatted). The griding process caused the reduction of both WHC and OHC. Those changes were attributed to the break of β-linkage of glycoside bonds and destruction of hydrogen bonds, leading to the destruction of the fiber matrix, and due to change in the hydrophobicity. The polyphenol content was totally lost due to both modification methods, but no further explanation was presented (Zheng & Li, 2018).

Table 1-1-4 Physical-chemical properties of some agro-industrial by-product from different source

		Before modification						After modification						
Modification method	By-product	Mean diameter (µm)	IDF	SDF	WHC	OHC	AA	Mean diameter (µm)	IDF	SDF	WHC	OHC	AA	Source
Dynamic high pressure	Coffee husk, pulp and silverskin	195.0	58	5	5.8	3.6	22.8*	96.2	57	4	8.9	6.8	16.9*	Belmiro et al 2021
Extrusion	Wheat bran	251.3	38.6	3.1	3.2	2.4	6.8*	125.2	37.4	8.6	4.5	2.9	16*	He., et al 2020
Griding	Grape pomace	283.2	-	-	-	-	4.5**	107.7	-	-	-	-	4.8**	Zhao et al., 2015
	Coconut cake	235.0	-	-	13.1	9.9	-	148.0	-	-	11.6	6.1	-	Zheng & Li, 2018)
Acetylation	Coffee husk, pulp and silverskin	195.0	58	5	5.8	3.6	22.8*	156.3	72	1	8.7	5.4	8.5*	Belmiro et al 2021
Hydrochloric acid	Coconut cake	235.0	65.2	19.3	13.1	9.9	2.4*	224.7	67.3	2.2	3.7	9.7	2.0*	Zheng & Li, 2018)
Enzymatic hydrolysis	Coffee husk, pulp and silverskin	195.0	58	5	5.8	3.6	22.8*	246.1	73	2	8.6	5.6	9.8*	Belmiro et al 2021
	Coconut cake	235.0	65.2	19.3	13.1	9.9	2.4*	233.0	56.2	29.9	8.4	6.7	7.6*	Zheng & Li, 2018)

Insoluble dietary fiber (IDF – g/100g d.b.), Soluble dietary fiber (SDF – g/100g d.b.), whater holding capacity (WHC - g/g d.b.), oil holding capacity (OHC – g/g d.b.) and antioxidant activity (AA).

* mg of GAE/100g

** DPPH radical scavenging activity

5. Conclusion

The use of fiber-rich agro-industrial by-products as ingredients by the food industries depend on their physical-chemical properties such as WHC, OHC and SP. The modification of the structure and content of DF by physical, chemical and enzymatic methods can be applied intending to improve those technological properties and making the by-products more suitable to the industries, but the choice of the method will depend on the final product intended and the type of antioxidant compound present. There are, however, scarce studies on the modification of the agro-industrial by-product as a whole and the influence of such modification in the antioxidant content and activity. According to the studies available, all methods (physical, chemical and enzymatic) are able to modify the physical-chemical properties of the DF and the physical methods showed a better retention of the phenolic compounds. In this way, physical emerging technologies, such as dynamic high pressure, may be interesting modification methods to improve the physical-chemical of the DF at same time that retains the antioxidant status of the agro-industrial by-products. Due to the environmental, nutritional and technological importance of the agro-industrial by-products, more studies should be conducted with other different sources. Exploiting the impact of different techniques and conditions of modification on the physicochemical and nutritional and functional characteristics of by-products can contribute for the sustainable application of these material in food industry.

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Ethical Guidelines

Ethics approval was not required for this research

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Capítulo 2

Modification of coffee coproducts by dynamic high pressure, acetylation and hydrolysis by cellulase: A potential functional and sustainable food ingredient

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Modification of coffee coproducts by dynamic high pressure, acetylation and hydrolysis by cellulase: A potential functional and sustainable food ingredient

Running title: Modification of coffee coproducts

Ricardo Henrique Belmiro[a], Ludmilla de Carvalho Oliveira[a], Marina Vilar Geraldi[b], Mário Roberto Maróstica Junior[b], Marcelo Cristianini[a]

a Department of Food Technology (DTA), School of Food Engineering (FEA), University of Campinas (UNICAMP), Monteiro Lobato, 80. PO Box 6121, 13083–862, Campinas, S.P. Brazil. belmiro.rh@gmail.com, ludmillacoliveira@outlook.com, mcristianini@unicamp.com.

b Department of Food and Nutrition (DEPAN), School of Food Engineering (FEA), University of Campinas (UNICAMP), Monteiro Lobato, 80. PO Box 6121, 13083–862, Campinas, S.P. Brazil. mmarosti@unicamp.br, marinavilar35@gmail.com.

Abstract

Coffee coproducts (CCP) are significant sources of dietary fiber (DF) and phenolic compounds. Dynamic high-pressure (DHP), acetylation (ACT) and enzymatic hydrolysis with cellulase (ENZ) were investigated as methods to change the technological properties of CCP. The impact of the methods on DF structure and phenolic antioxidants was also assessed. DHP, ACT and ENZ have improved the Water Holding Capacity, Swelling Power and Oil Holding Capacity of CCP by up to 1.50, 1.80 and 1.90 times, respectively. DHP caused the most severe effect in disrupting the DF of the CCP, reducing the particle size. Total and Insoluble DF of CCP (0.63 and 0.58 g/g CCP, respectively) decreased significantly after ACT and ENZ. DHP only caused a minor impact on chlorogenic acid of CCP, leading to a smaller reduction in the antioxidant capacity as compared to that of ACT and ENZ. A potential functional and sustainable food ingredient from CCP with improved technological properties and partial maintenance of its antioxidant status was obtained.

Industrial relevance text

More than a tendency, the management of agro-industrial waste/coproducts in the development of a sustainable food system is a priority. The conversion of coproducts into food ingredients has great potential, contributing, on the one hand, to reduce the negative effects of their disposal in the environment and, on the other hand, to improve the nutritional and functional quality of the industrialized food. Modification of these coproducts should be applied to improve their technological properties, making them more suitable for industrial use. Dynamic high pressure, acetylation and enzymatic hydrolysis are environmentally friendly methods to modify agro-industrial coproducts and may yield interesting results which were not previously studied for coffee coproducts. Vegetable fiber ingredients have been widely used in bakery formulations (cookies, cakes and breads) and meat products (hamburger and sausages). Amongst the benefits of its incorporation in these formulations are the enrichment with dietary fiber, texture and yield improvement, and a reduction in sodium, fat and gluten. In addition, it could be a new source of income, especially for small producers, by adding value to these coproducts.

Keywords: high pressure homogenization, acetic anhydride, dietary fiber, technological properties, antioxidant.

1. Introduction

The consumers demand for healthier food, especially during the pandemic caused by the novel corona virus SARS-CoV 2, has made the food industry look for new sources of bioactive compounds, such as the dietary fibers and the polyphenol compounds (Galanakis, 2015, Galanakis 2020).

Coffee coproducts (CCP - husk, pulp, parchment and silverskin) are a rich source of dietary fiber, which comprises about 60% of its weight (dry basis) (Ballesteros et al., 2014). The fiber present in the CCP is mostly in the insoluble form and consists of cellulose, hemicellulose and lignin. It is also a source of phytochemicals with high antioxidant activity, including chlorogenic and caffeic acids, tannins and cyanidins (del Castillo et al., 2019; Esquivel & Jiménez, 2012; Murthy & Naidu, 2012). Despite the large amount generated and its nutritional and functional values, CCP is little used, being employed mostly as fuel for the coffee roasting process or as an adulterant for soluble coffee production (Briandet et al., 2002; Vale et al., 2007).

Based on the attractive characteristics mentioned above, CBP has the potential to be incorporated into food formulations as an ingredient, in such a way as to improve the nutritional value and antioxidant status of industrialized foods. In general, the application of coproducts by the food industry depends on their technological properties, such as swelling power (SP), water and oil holding capacity (WHC and OHC, respectively) and the solubility index (SI) (Elleuch et al., 2011; Meuser, 2000; Mudgil & Barak, 2013; Ozyurt & Ötles, 2016). In practice, the incorporation of CCP in its native form in a food formulation may promote undesirable technological and sensory changes to the final product (Ates & Elmaci, 2018), mainly when applied in higher concentrations. The intrinsic techno-functional characteristics of the fiber in the CCP matrix restricts its wide use in foods with improved nutritional value.

Physical, chemical and enzymatic methods are well known technologies used to modify the physicochemical properties of macromolecules such as dietary fiber (Ozyurt & Ötles, 2016; Phillips & Willians, 2009; Spotti & Campanella, 2017; Yang et al., 2017). The changes in the technological properties of DF as a result of various modification techniques have been widely studied: mechanical, as cooking extrusion (Andersson et al., 2017; Djurle et al., 2016; Honců et al., 2016; Y. L.; Huang & Ma, 2016; Oliveira et al., 2015), dynamic high pressure (Li et al., 2014; Ulbrich & Flöter, 2014; Van Buggenhout et al., 2015; Xie et al., 2017; Castro et al., 2020), high hydrostatic pressure (Castro et al., 2020; Peng et al., 2016;Pérez-López et al., 2016; Xie et al., 2017; Yu et al., 2018) steam explosion (Boonterm et al., 2016; Deepa et al., 2011; Kaushik & Singh, 2011), microwave (Mhiri et al., 2018; orange - Talens et al., 2017) and milling (Djurle et al., 2016; Ullah et al., 2017; Yu et al., 2018; Zhao et al., 2015; Zheng & Li, 2018); chemical, as acid (Du et al., 2016; Tibolla et al., 2014; Wang et al., 2015; Zheng & Li, 2018) and alkali (Cai et al., 2015; Janker-Obermeier et al., 2012; Senthamaraikannan & Kathiresan, 2018) and enzymatic (Beltramino et al., 2018; Huang et al., 2015; Saelee et al., 2016; Santala et al., 2014; Yi et al., 2014).

Dynamic high pressure (DHP) is an emerging physical technology capable of modifying the structure of fibers (Belmiro et al., 2018; Ozyurt & Ötles, 2016) due to the phenomena of high cavitation, turbulence and shear stress (Middelberg, 1995). Acetylation (ACT) is a chemical method originally used to modify starches destined for the food industry and more recently to produce composites (Ackar et al., 2015). To the knowledge of the authors, ACT has not previously been reported in the literature for the modification of fiber-based foodstuffs. The premise is based on esterification of the fiber (lignin, hemicellulose and amorphous cellulose) using acetic acid or acetic anhydride as the reagent, aiming to substitute the hydroxyl groups (OH) by acetyl groups (CH3OH) (Ackar et al., 2015; Han et al., 2012). On the other hand, enzymatic hydrolysis (ENZ) with cellulase cleaves the β-glucosidic bonds of the cellulose (main compound in CCP fiber) and this has been shown to be effective in improving the quality of DF by modifying its structure (Ma & Mu, 2016; Santala et al., 2014; Sousa et al., 2011; Zheng & Li, 2018). Also, emerging technologies are being applied to recover bioactive compounds of the agro-industrial coproducts (Barba et al., 2014, Barba et a 2015; Deng et al., 2015; Galanakis, 2012, Galanakis 2013; Galanakis et al., 2018) and only few studies has used the coproducts as a whole (Fan et al., 2020; Wang et al., 2020; Zhao et al., 2015; Zheng & Li, 2018).

In an attempt to improve the technological properties of the DF and overcome the limitations of the CCP as related to food technological requirements, this study investigated the use of DHP, ACT and ENZ as potential methods to modify CCP, with the advantage of being carried out at mild temperatures and pH values and without the use of strong organic reactants, thereby preventing the loss of phenolic compounds and making them environmentally friendly.

2. Material and methods

2.1. Material

Ripe and sun-dried coffee cherries (*Coffea arabica* var ruby – Anexo A) were donated by a local Brazilian farmer (22°11'39.4" S 46°53'54.4"W). The cherries were peeled using a manual machine, separating the epicarp (husk), mesocarp (pulp), endocarp (parchment) and testa (silverskin) from the endosperm (coffee grain) and storing them in polyethylene bags. The CCP was washed in a 200 ppm chlorine solution, freeze dried at -40°C for 48h, ground using a plate grinder followed by a basic analytical mill (IKA model-A11, Germany), and then sieved to pass through a 0.250 mm sieve (mesh 60 – Anexo B). The samples were vacuum packed and stored in the dark until processed. The composition of the CCP was 63% of TDF, 21% of non-complex carbohydrates (calculated by difference), 12% of proteins and 4% of lipids, on a dry weight basis (d.w.b.). The control sample was defined as unprocessed (DHP, ACT or ENZ) CCP.

2.2. Methods

2.2.1. Modification of CCP

2.2.1.1. Dynamic high-pressure process

CCP (8.0 g, d.w.b.) was suspended in 200 mL of distilled water and stirred for 30 min. The suspension was processed using a high-pressure homogenizer (Panda GEA Niro Soave, Italy) at 50 or 100 MPa for 1, 2 or 3 cycles of pressure (Table 1). The inlet temperature for all processes was 25°C. The samples were then freeze dried and vacuum packed. All processes were carried out in triplicate.

2.2.1.2. Acetylation reaction

Acetylation was carried out according to Han et. al (2012) with some modifications. 8.0 g (d.w.b.) of CCP were suspended in 200 mL of distilled water and stirred for 30 min. The temperature was adjusted to 30°C and the pH to 8.2, (0.5M NaOH) and acetic anhydride at 10 or 30% (v/v) was added dropwise and the reaction maintained for 30, 60 or 120 min. The solution was neutralized with 0.5M NaOH, washed twice with distilled water and centrifuged at 3500 g for 10 min. The supernatant was frozen and freeze dried. All processes were done in triplicate. The acetyl content (%Ac) was determined by titration with 0.1N HCl and calculated according to Equation 1. The degree of substitution (DS) was estimated according to Equation 2.

$$\%Ac = ((Vb - Va).\ MHCl.\ 0.043.\ 100\%).\ Ws\text{-}1 \qquad \text{Equation 1.}$$

$$DS = (162.\ \%Ac).\ (4300 - (43 - \%Ac))\ \text{-}1 \qquad \text{Equation 2.}$$

Where Vb is the volume of the blank, Va is the volume of the sample and Ws is the weight (dry basis) of the sample.

The values calculated for %Ac and DS were 1.97 ± 0.12 and 0.08 ± 0.01, respectively.

2.2.1.3. Enzymatic modification

Enzymatic modification was carried out according to Huang et al. (2015) with some modifications. 8.0 g of CCP were suspended in 200 mL of phosphate buffer (pH 5.0) and stirred for 30 min. The temperature was adjusted to 50°C, 5 or 15U of cellulase were added and the reaction maintained for 30, 60 or 120 min. The solution was neutralized with 0.5M NaOH, washed twice with distilled water and centrifuged at 3500 g for 10 min. The supernatant was frozen and freeze dried. All processes were done in triplicate.

Table 2-1 Description of the dynamic high pressure, acetylation and hydrolysis by cellulase processes

Process	Description
Control	Non-processed sample
DHP501c	Sample processed at 50 MPa and 1 cycle
DHP502c	Sample processed at 50 MPa and 2 cycles
DHP503c	Sample processed at 50 MPa and 3 cycles
DHP1001c	Sample processed at 100 MPa and 1 cycle
DHP1002c	Sample processed at 100 MPa and 2 cycles
DHP1003c	Sample processed at 100 MPa and 3 cycles
ACT1030	Sample processed with 10% (v/v) of acetic anhydride for 30 min.
ACT1060	Sample processed with 10% (v/v) of acetic anhydride for 60 min.
ACT10120	Sample processed with 10% (v/v) of acetic anhydride for 120 min.
ACT3030	Sample processed with 30% (v/v) of acetic anhydride for 30 min.
ACT3060	Sample processed with 30% (v/v) of acetic anhydride for 60 min.
ACT30120	Sample processed with 30% (v/v) of acetic anhydride for 120 min.
ENZ0530	Sample processed with 5U of cellulase for 30 min.
ENZ0560	Sample processed with 5U of cellulase for 60 min.
ENZ05120	Sample processed with 5U of cellulase for 120 min.
ENZ1530	Sample processed with 15U of cellulase for 30 min.
ENZ1560	Sample processed with 15U of cellulase for 60 min.
ENZ15120	Sample processed with 15U of cellulase for 120 min.

2.2.2. Technological properties of CCP

The WHC, OHC and SI assays were derived from the AACC method nº 88-04 (2012). The sample (1.0 g, d.w.b.) was placed in a 50 mL falcon tube and 20 mL of distilled water or soy oil added for the WHC and OHC assays, respectively. After standing for 30 minutes, the samples were centrifuged at 3000 g and 25°C for 10 min. The supernatant was placed in a petri dish and dried overnight and the tubes then weighed. The values for WHC, OHC and SI were calculated according to equations 3, 4 and 5, respectively.

SP was determined according to Femenia et.al (1997). The sample (1.0 g, d.w.b.) was placed in a graduated tube and the volume recorded. 20 mL of distilled water were added to the tube and gently stirred. After standing for 24h, the sample volume was recorded again and the SP calculated according to equation 6. All assays were done in triplicate.

$$WHC = (Wtw - Wti) \cdot Ws^{-1} \qquad \text{Equation 3.}$$

$$OHC = (Wto - Wti) \cdot Ws^{-1} \qquad \text{Equation 4.}$$

$$SI = (Wpi - Wpf) \cdot Ws^{-1} \qquad \text{Equation 5.}$$

$$SP = (Vf - Vi) \cdot Ws^{-1} \qquad \text{Equation 6.}$$

Where,

Wtw is the weight of the falcon tube after discarding the water supernatant.

Wti is the initial weight of the falcon tube.

Ws is the weight of the sample.

Wto is the weight of the falcon tube after discarding the oil supernatant.

Wpi is the initial weight of the petri dish.

Wpf is the final weight of the petri dish.

Vf is the final volume of the sample in the graduated tube and

Vi is the initial volume of the sample in the graduated tube.

2.2.3. Choice of the ideal conditions for the DHP, ACT and ENZ processes

With a view to optimizing the processes considering the industrial requirements and management of the resources, the subsequent assays were only carried out for the ideal process and reaction conditions, that is, those that guaranteed the best responses for the WHC, OHC, SI and SP. Low pressures, cycle numbers, times and reactant concentrations (acetic anhydride or cellulase) were preferred.

2.2.4. Particle size distribution

The particle size distributions of the control and modified CCP were determined using the laser diffraction technique with a Partica LA-950V2 particle size distribution analyzer (Horiba, Kyoto, Japan) and absolute ethanol as the dispersion medium. The mean particle size was expressed as the mean volume diameter (D4,3). Six readings were taken.

2.2.5. Scanning electron microscopy (SEM)

The samples (control and modified) were analyzed using a TM300 scanning electron microscope (HITACHI, Japan) and the images captured using the software HITACHI TM3000, with magnitudes of x250 and x1000.

2.2.5. Dietary fiber content

The total and insoluble dietary fiber (TDF and IDF) contents of the CCP (control and modified) were determined using the AACC enzymatic-gravimetric method nº 32-07.01 (2012). The soluble dietary fiber (SDF) was calculated by difference. The results were expressed as grams of DF per gram of CCP on a dry weight basis.

2.2.6. Extraction of phenolic compounds

The phenolic compounds were extracted from the CCP samples according to the methodology described by Magalhães et al. (2016), with modifications. Briefly, 200 mg of CCP were weighed in Falcon tubes and extracted with 40 mL of an aqueous 50% (v/v) ethanol solution. The tubes were shaken in an orbital shaker bath (Tecnal, Piracicaba, Brazil) at 30°C for 5h. The extract was stored at -20°C until analysed.

2.2.7. Chromatographic quantification of the chlorogenic and caffeic acids and caffeine contents

The chlorogenic and caffeic acids and caffeine contents of the ethanolic CCP extracts were determined using a LC-10 Shimadzu modular high performance liquid chromatograph (Shimadzu Scientific Instruments, Columbia, USA) (HPLC) coupled to a diode array detector (DAD), according to the procedure described by Magalhães et al. (2016), with some modifications. The samples were injected manually and the chromatographic separation was effected using a Symmetry C18 column (6.6 mm x 75 mm x 3.5 µm) (Waters, Milford, USA) at 30°C. Isocratic elution with a mobile phase composed of 0.01 Mol.-1 sodium acetate buffer (pH 3.9) and methanol (75:25, v/v) at 1 mL.min-1 was adopted. The peak areas of the chromatograms were calculated at 325 nm for the chlorogenic and caffeic acids and caffeine and quantification was carried out by external standardization.

2.2.8. Total reducing power (TRP) and antioxidant capacity

The total reducing power was determined using the Folin-Ciocalteau method with gallic acid as the standard. The results were expressed in milligram equivalents of gallic acid per gram of CCP (mg EqGA/ g CCP).

The oxygen-radical absorption capacity (ORAC) was determined according to Ou et al. (2013) and the ferric reducing antioxidant power (FRAP) according to Benzie and Strain (1998). The results were expressed in µM Trolox Equivalents per g of CCP (µM Eq Trolox/g CCP). Both the fluorescence and absorbance readings, respectively, were made in triplicate using a BioTek HT microplate reader (Winooski, USA) with the Gen5 ™ 2.0 data analysis software.

2.2.9. Statistical analysis

The analytical assays of each sample were mostly performed in triplicate, as described above. The results were presented as the mean ± standard deviation. The statistical analyses were carried out using the Statistica Software, applying the ANOVA and Tukey's test ($p<0.05$) to evaluate any significant differences between the means.

3. Results and discussion

3.1. Technological properties of CCP

Table 2-2 shows the results of the technological assays (WHC, SI, SP and OHC) for the control and modified CCP (DHP, CT and ENZ).

Table 2-2 Water holding capacity (WHC), solubility index (SI), swelling power (SP) and oil holding capacity (OHC) of the coffee coproducts

Process	**WHC (g water/ g CBP)**	**SI (g solubles / g CBP)**	**SP (mL water / g CBP)**	**OHC (g oil / g CBP)**
Control				
	5.8 ± 0.36^{B}	0.036 ± 0.001^{A}	6.34 ± 0.28^{B}	3.6 ± 0.1^{C}
Dynamic high pressure				
DHP501c	7.88 ± 0.26^{b}	0.034 ± 0.003^{a}	7.76 ± 0.60^{c}	5.82 ± 0.47^{bc}
DHP502c	8.56 ± 0.34^{a}	0.033 ± 0.005^{a}	10.27 ± 0.52^{ab}	5.69 ± 0.35^{c}
DHP503c	8.82 ± 0.31^{a}	0.035 ± 0.002^{a}	9.09 ± 0.77^{bc}	5.17 ± 0.31^{c}
DHP1001c	8.58 ± 0.14^{aA}	0.034 ± 0.003^{aA}	11.72 ± 0.67^{aA}	6.84 ± 0.30^{aA}
DHP1002c	8.4 ± 0.47^{ab}	0.038 ± 0.001^{a}	11.45 ± 0.53^{a}	6.71 ± 0.60^{ab}
DHP1003c	8.86 ± 0.15^{a}	0.038 ± 0.005^{a}	8.94 ± 0.91^{bc}	5.19 ± 0.63^{c}
Acetylation				
ACT1030	7.77 ± 0.16^{b}	0.035 ± 0.003^{b}	6.34 ± 0.16^{bc}	5.12 ± 0.19^{ab}
ACT1060	8.63 ± 0.21^{aA}	0.035 ± 0.002^{bA}	6.58 ± 0.41^{abcB}	5.42 ± 0.21^{aB}
ACT10120	8.69 ± 0.16^{a}	0.035 ± 0.005^{b}	7.13 ± 0.28^{a}	5.25 ± 0.15^{a}
ACT3030	7.81 ± 0.16^{b}	0.046 ± 0.002^{a}	6.26 ± 0.18^{c}	4.84 ± 0.28^{b}
ACT3060	8.39 ± 0.15^{a}	0.043 ± 0.005^{a}	6.81 ± 0.25^{ab}	5.23 ± 0.14^{a}
ACT30120	8.67 ± 0.28^{a}	0.041 ± 0.001^{ab}	7.1 ± 0.19^{ab}	5.25 ± 0.04^{a}
Enzymatic				
ENZ0530	8.23 ± 0.52^{aA}	0.04 ± 0.008^{bA}	7.04 ± 0.14^{aB}	5.37 ± 0.13^{aB}
ENZ0560	8.33 ± 0.63^{a}	0.047 ± 0.007^{b}	7.01 ± 0.12^{a}	5.56 ± 0.05^{a}
ENZ05120	8.38 ± 0.30^{a}	0.051 ± 0.005^{b}	6.93 ± 0.26^{a}	5.49 ± 0.11^{a}
ENZ1530	8.58 ± 0.44^{a}	0.057 ± 0.005^{ab}	6.81 ± 0.19^{a}	5.42 ± 0.14^{a}
ENZ1560	8.24 ± 0.24^{a}	0.067 ± 0.009^{a}	7.12 ± 0.20^{a}	5.4 ± 0.10^{a}
ENZ15120	8.08 ± 0.42^{a}	0.072 ± 0.011^{a}	6.9 ± 0.25^{a}	5.53 ± 0.13^{a}

Results are given as the mean ± the standard deviation.
Same small letter in a column means there is no significant difference ($p>0.05$) between the samples in the same process.
Same capital letter in a column means there is no significant difference ($p>0.05$) between the control and samples of different processes.

The modification methods improved the technological properties of the CCP as compared to the control sample ($p<0.05$), except for the SI of the DHP-processed sample. The WHC increased by up to about 1.5-fold for DHP, ACT and ENZ; and SI by up to 1.3-fold for ACT and by up to 2-fold for ENZ. SP increased by up to 1.8-fold for DHP and by up to 1.1-fold for ACT and ENZ. The OHC increased by up to 1.9-fold for DHP and by up to 1.5-fold for ACT and ENZ.

With respect to the DHP process, a pressure changes from 50 to 100 MPa increased ($p<0.05$) the WHC and SP after 1 pressure cycle, whereas the OHC only increased when 1 and 2 cycles were applied. At 50 MPa, the application of a second cycle resulted in a positive effect on the responses for WHC and SP but no significant difference ($p>0.05$) was observed for the OHC. The application of a third cycle did not change ($p>0.05$) any of the technological properties at 50 MPa as compared to the application of a second cycle. At 100 MPa, the application of an increasing number of cycles did not change ($p>0.05$) the WHC, but the application of 3 cycles was responsible for a slight decrease ($p<0.05$) in the SP and OHC. Previous studies also reported enhancement in the technological properties of both DF isolated from citrus (Su et al.,2019) and from rice bran Xie et al. (2019) processed by DHP at 90-160 MPa and 120 MPa, respectively, with three cycles of pressure.

As far as the acetylation reaction was concerned, the SI was the only property affected by the acetic anhydride concentration with an increase ($p<0.05$) in the reagent concentration for 30 or 60 min of reaction increasing the solubility. Extending the reaction time from 30 to 60 minutes with 30% of acetic anhydride, led to greater ($p<0.05$) WHC, SP and OHC values. Longer reaction times (120 minutes) caused no further changes and the time was not important for acetylation carried out at 10% of acetic anhydride. Teli & Valia (2013) also reported an increase in the oil absorbance of DF from banana modified by acetylation.

The impact of enzymatic hydrolysis by cellulase on the technological properties of CCP lead to an increase and was independent ($p>0.05$) of the enzymatic activity or time applied in this work. Similarly, the technological properties of DF from okara (Huang et al., 2015) and carrot pomace (Yu et al., 2018) were increased by cellulase treatment. Also, Zheng et al., (2021) reported that enzymatic treatment of DF from coconut cake caused an increase in the WHC and SP, whereas the OHC was slightly decreased.

The technological properties of food materials which are abundant sources of dietary fiber, such as CCP, are determined by the molecular size, degree of branching, intermolecular aggregation and water binding sites of this component (Belmiro et al., 2018). The dietary fibers are structured by intramolecular and intermolecular linkages. The intramolecular linkages are formed by covalent bonds (glycosidic bonds) which are less prone to disruption by processing (Van Buggenhout et al., 2015). The intermolecular hydrogen bonds (weaker bonds) are responsible for forming the so-called DF aggregates, resulting in large-sized particles (Meuser, 2000). These bonds are easily disrupted by the shear stress caused by DHP, by the esterification of the hydroxyl groups (ACT) and by the cleavage of the β-glycosidic linkages near the terminal ends of the intramolecular linkages (ENZ) (Belmiro et al., 2018; Han et al., 2012; Phillips & Willians, 2009; Santala et al., 2014). The structural changes caused by the different modification methods may be reflected in a reduction in particle size and/or increased particle porosity, as can be seen in Figures 2-1 and 2-2, respectively. In both cases, the modification results in an increased surface area of the aggregates, which can improve the permeability and diffusion of water or oil into the fiber (Chau et al., 2007; Ulbrich & Flöter, 2014; Van Buggenhout et al., 2015; Fan Xie et al., 2017; Yu et al., 2018). This explains the increased values ($p<0.05$) for WHC, SP and OHC found for all the modified CBP when compared to the control sample. The degree of modification caused by the DHP process increased with increasing pressure and was thus responsible for a progressive reduction in particle size of the fibrous material. However, the results suggest that at 100 MPa the DF of the CCP reached a maximum in structural change (breakdown of the DF), and hence no further changes (p>0.05) in the technological properties (WHC, SP and OHC) were observed with an increased number of cycles.

The damage caused to the CCP structure by ACT seemed not to be significantly dependent on the acetic anhydride concentrations studied (10 and 30%). However, an extended reaction time from 30 to 60 min maximized most of the technological properties, which could be a result of more intense depolymerization and acetylation. On the other hand, the damage caused to the fiber structure by ENZ was neither affected (p>0.05) by the cellulase activity (5 and 15U) nor by the reaction time (30, 60 or 120 min). It appears that the amount of acetic anhydride or enzyme and time applied can lead to a partial disruption of the DF structure up to a certain level, where the increase in reactant concentration, enzyme activity or time applied has no further effect on the fiber structure, probably due to steric hindrance caused by the flat structure of the DF (Phillips & Willians, 2009)

3.2. Choice of the ideal conditions

The solubility index was considered too low for all the processed samples and was therefore not considered in this screening. The conditions that guaranteed the highest values for WHC, OHC and SP, simultaneously, with the lowest pressure, nº of cycles, time and amount of reactant applied, were DHP1001c, ACT1060 and ENZ0530. Table 2-3 summarizes the values obtained for WHC, SP and OHC for the selected samples.

Table 2-3 Water holding capacity (WHC), swelling power (SP) and oil holding capacity (OHC) of the control and best conditions.

Process	WHC (g water/ g CBP)	SP (mL water / g CBP)	OHC (g oil / g CBP)
Control	5.8 ± 0.36^{B}	6.34 ± 0.28^{B}	3.6 ± 0.1^{C}
DHP1001c	8.58 ± 0.14^{A}	11.72 ± 0.67^{A}	6.84 ± 0.3^{A}
ACT1060	8.63 ± 0.21^{A}	6.58 ± 0.41^{B}	5.42 ± 0.21^{B}
ENZ0530	8.23 ± 0.52^{A}	7.04 ± 0.14^{B}	5.37 ± 0.13^{B}

Results are given as the mean ± the standard deviation.
Same capital letter in a column means there is no significant difference ($p>0.05$) between the samples for the different processes

It is believed that the ideal conditions presented in this study were achieved when the pressure intensity or number of cycles, acetic anhydride content or enzyme activity applied caused the maximum level of disruption or disordering of the fiber structure.

3.3. Particle size distribution and scanning electron microscopy (SEM)

Figure 2-1 shows de particle size distribution of the control and of the selected modified CCP samples, and the respective scanning electron micrographs are presented in Figure 2-2.

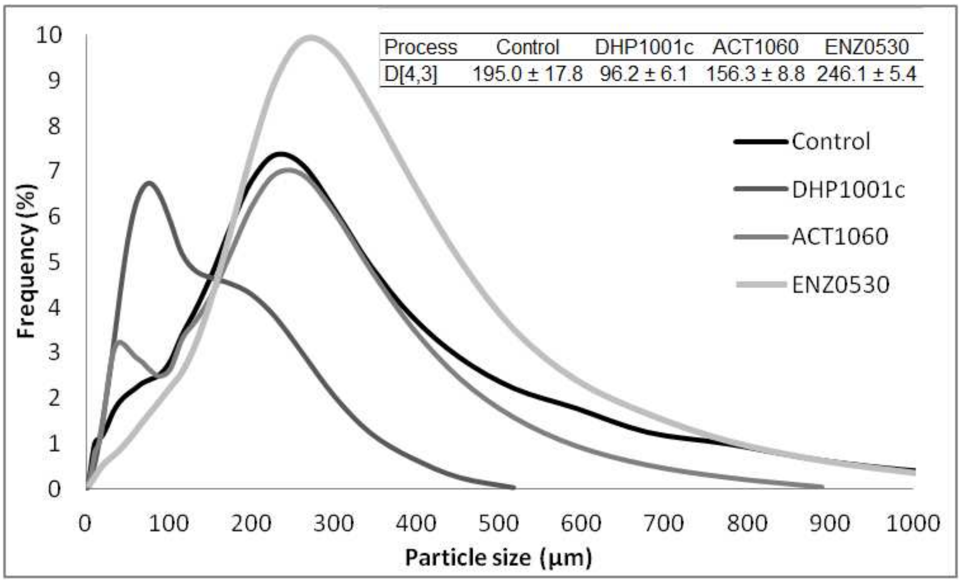

Figure 2-1 Particle size, particle dispersion and volume mean diameter (D[4,3]) of the sample processed by DHP1001c, ACT1060 and ENZ0530.

Figure 2-1 shows that the samples modified by dynamic high pressure and by cellulose hydrolysis presented monomodal distributions. Moreover, DHP caused reductions in the particle size, the particle size dispersion and the mean volume diameter (D[4,3]). However, enzymatic modification led to increases in the particle size, particle size dispersion and D[4,3]. Acetylation led to slight reductions in the particle size and D[4,3] and a second peak appeared (particles of around 50 µm). As seen in Figure 2-2, the structure of the CCP control appears to be intact, tight and ordered (Figures 2-2A and 2-2E). DHP caused severe disruption of the CCP structure (Figures 2-2B and 2-2F), especially, as seen in Figure 2-2F, the cellulose coil was partially disrupted (indicated by the arrow). The structure of the CCP was partially disrupted by ACT (Figures 2-2C and 2-2G), where both intact ordered and disrupted disordered structures can be distinguished. The SEM images of the enzymatically modified CCP shown in Figures 2-2D and 2-2H, also reveal a partial disruption of the CCP structure, making it more disordered and open, but the disruption was less pronounced than that caused by DHP and ACT. Similar reduction in the particle size and disruption in the structure of the DF due to the DHP modification were found for orange (Buggenhout et al.2015) and for potato (Xie et al., 2017). Zheng et al. (2018) reported a slight reduction in the particle size of the coconut cake DF treated with cellulase. A disruption in the structure of the IDF was observed by Yu et al. (2018) for carrot pomace modified by enzymatic hydrolysis. Zhang et al. (2013) that the acetylation of rice straw lead to the disruption of the surface and the fibrillar structure.

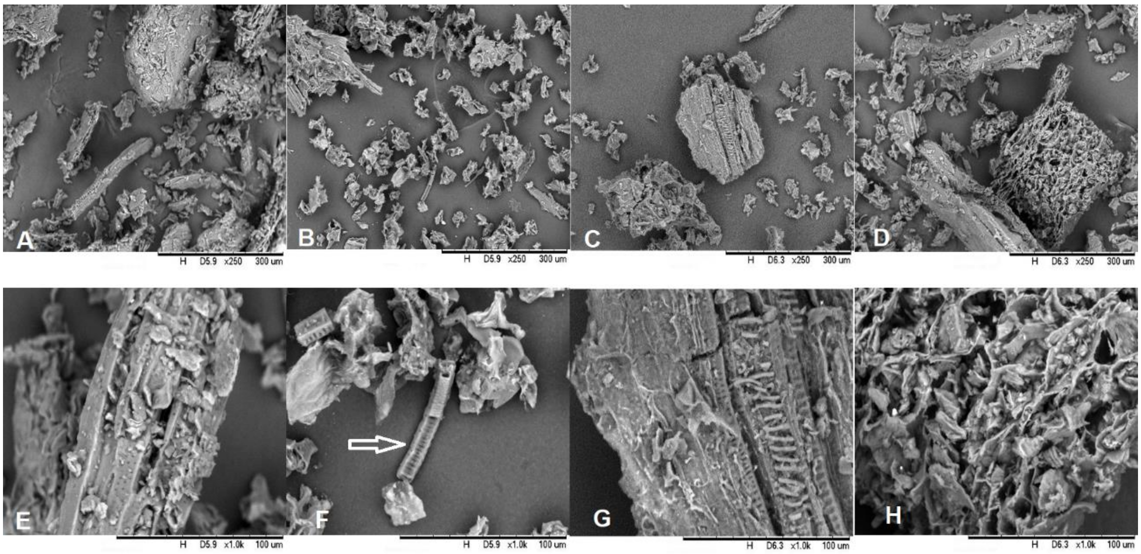

Figure 2-2 Scanning electron microscopy (SEM) of the coffee by-products at 250K: Control (A), DHP1001c (B), ACT1060 (C), ENZ0530 (D); and at 1000K: Control (E), DHP1001c (F), ACT1060 (G), ENZ0530 (H).

The particle size reduction (Figure 2-1) and the porosity observed from the micrographs (Figure 2-2) for the selected DHP and ACT modified CCP corroborates the hypothesis that the increases in WHC, SP and OHC (shown in section 3.1) were due to disruption of the fiber aggregates and an increase in fiber porosity. It appears that this disruption caused the appearance of a second peak in the particle size distribution of the ACT. For the ENZ modified CCP, this disruption probably led to the increase in porosity and disordering of the particles, without decreasing their size. The increase in porosity could possibly be explained by a partial disruption in the particle structure (to a smaller extent as compared to that caused by DHP and ACT), which caused opening of the channels (cleavage of the β-glycosidic bonds of the cellulose). This opening facilitates the binding of water and oil, in agreement with the technological properties presented in section 3.1. The opening of the channels may also contribute to an increase in particle size (Ozyurt & Ötles, 2016; Phillips & Willians, 2009).

3.4. Dietary fiber, antioxidant compounds and antioxidant capacity

Table 2-4 shows the dietary fiber, chlorogenic and caffeic acids and caffeine contents and Table 2-5 shows the antioxidant capacity of the CCP.

Table 2-4 Total, insoluble and soluble dietary fiber and caffeine, chlorogenic and caffeic acid content in the ethanolic extract (50%) of the coffee coproducts

	Control	**DHP1001c**	**ACT1060**	**ENZ0530**
TDF (g of TDF / g of CBP)	0,63 ± 0,02[a]	0,61 ± 0,02[a]	0,73 ± 0,01[b]	0,75 ± 0,01[b]
IDF (g of IDF / g of CBP)	0,58 ± 0,02[a]	0,57 ± 0,01[a]	0,72 ± 0,01[b]	0,73 ± 0,02[b]
SDF* (g of SDF / g of CBP)	0,05	0,04	0,01	0,02
Chlorogenic acid**	0,88 ± 0,01	0,32 ± 0,02	0,03 ± 0	0,18 ± 0,01
Caffeic acid**	0,05 ± 0,01	0,05 ± 0,01	ND	0,02 ± 0,001
Caffeine**	1,75 ± 0,01	1,75 ± 0,03	0,61 ± 0,01	0,60 ± 0,02

Results are given as the mean ± the standard deviation.
Same letter in a row means there is no significant difference (p>0.05) between the samples.
* Calculated by the difference between the TDF and IDF.
** Unit is given as mg of gallic acid equivalent per g of CBP.

The TDF, IDF and SDF contents of the control and DHP processed samples did not differ statistically ($p > 0.05$). ACT and ENZ promoted an increase ($p<0.05$) in both TDF and IDF. Although all the samples exhibited a low SDF content, this fraction was slightly decreased by ACT and ENZ. Conversely, the effect of different processing methods on DF isolates have shown a considerable redistribution of IDF to SDF (Ozyurt & Ötles, 2016; Yang et al., 2017).

Tabela 2-5 Total reducing power (TRP), oxygen radical absorbance capacity (ORAC) and ferric reducing ant-oxidant power (FRAP) of the coffee coproducts

Sample	TRP (mg galic acid eq/ g CBP)	ORAC (mg trolox eq/ g CBP)	FRAP (mg trolox eq/ g CBP)
Control	22,77 ± 0,68[a]	328,54 ± 37,72[a]	91,67 ± 6,55[a]
DHP1001c	16,95 ± 0,95[b]	301,69 ± 31,45[a]	60,85 ± 5,37[b]
ACT1060	8,55 ± 0,44[d]	124,59 ± 11,84[b]	28,95 ± 2,9[d]
ENZ0530	9,81 ± 0,21[c]	132,74 ± 7,67[b]	43,23 ± 2,15[c]

Results are given as the mean ± the standard deviation.
Same letter in a row means there is no significant difference (p>0.05) between the samples.

The chlorogenic acid content of the CCP was reduced (p<0.05) by the DHP process by about 60%. However, no changes (p>0.05) were observed in either the caffeic acid or caffeine contents. In any case, the effects of ACT and ENZ were more pronounced with respect to reducing the phenolic acids and caffeine contents. Regarding the general effect on the retention of the phytochemicals, ACT was the most drastic modification method.

DHP decreased (p<0.05) the TRP by 25% and the antioxidant capacity by 8% (ORAC) and 34% (FRAP). ACT promoted a reduction (p<0.05) of 62% in both TRP and ORAC and of 68% in FRAP, and ENZ presented similar results to ACT. All the modification methods (DHP, ACT and ENZ) led to reductions in the TRP, ORAC and FRAC. However, DHP only caused a minor impact, leading to a smaller reduction in the antioxidant capacity of the CCP.

Dietary fibers can form aggregates with polyphenols (Jakobek, 2015a) such as chlorogenic and caffeic acids. The formation of such polyphenolic-fiber aggregates can be either beneficial or detrimental to the bioactive effects associated with the phenolic compounds. These aggregates can reduce the polyphenol bioactivity by reducing the bioaccessibility in the upper gut, but can protect the polyphenols against the pH and enzymes present in the stomach, delivering them intact to the colon, thus promoting an antioxidant environment and the growth of the natural microbiota (Jakobek, 2015b; Palafox-Carlos et al., 2011). Polyphenolic-fiber aggregates can be formed by physical trapping, by hydrogen bonds or, to a lesser extent, by covalent bonds. It is known that the more porous the fiber complex is, the more aggregates can be formed (Jakobek, 2015b; Palafox-Carlos et al., 2011). Rosa et. al. (2013) showed that the disintegration of the DF of wheat by mechanical and enzymatic methods led to an increase in the formation of polyphenolic fiber complexes. Since no degradation of the polyphenols is expected due to the DHP process (Fan Xie et al., 2017), the formation of polyphenolic fiber complexes should explain the differences observed in the antioxidant assays and in the chlorogenic and caffeic acid contents between the control and the DHP processed samples. However, a more detailed study concerning the effects of DHP on the polyphenolic fiber aggregates and on the polyphenol bioaccessibility and bioactivity is necessary for a better comprehension. On the other hand, since chlorogenic acid is stable in the pH and temperature ranges applied in the ACT and ENZ processes (Dawidowicz & Typek, 2010, 2011), it appears that the pronounced reduction in the antioxidant status of these samples occurred due to both the formation of polyphenolic fiber aggregates and leaching occurring during the post process washing.

The application of the CCP in the food and nutraceutical industries is arousing more attention due to its DF and polyphenol content and varies from production of enzymes, ethanol, mushroom, animal feed or DF and polyphenol extraction (Osorio-Arias et al., 2020; Singh & Sharma, 2020). Improving the technological properties of the CCP and preserving its antioxidant status make possible novel applications as enhancing the food stability and shelf life and improving consumers' health (Mateo & Maicas, 2015; Nunes et al., 2016). Examples of such novel application are replacement of flour and fat without impacting the texture of the product, as well as enhancing the water and oil retention or prevent them from being lost during the cooking process in products with reduced sodium content (Elleuch et al., 2011; Spotti & Campanella, 2017).

4. Conclusion

The three independent methods of modification investigated in this study (DHP, ACT and ENZ) were proven to modulate the technological properties (WHC, OHC, SI and SP) of the fiber-rich coffee coproducts (CCP). An enhancement (increase) in these properties of unmodified CCP were mainly favored by the physical effect of DHP at higher pressures (100 MPa) or by the chemical effect at a minimum concentration of acetic anhydride (10 %). Moreover, enzymatic reaction with at least 5U of cellulase for 30 min was sufficient to maximize the technological properties of CCP within conditions. Despite different principle methods of modification, the observed changes were attributed to the disruption or disordering of the DF structure and consequent forming of aggregates. Reduction of phenolic compounds and caffein contents, and antioxidant capacity of the CCP were inherent to the modification techniques, however DHP only caused a minor impact. These results imply the potential to obtain sustainable food ingredients from modified CCP, bringing about improved technological properties and significant antioxidant status, specially at optimized DHP conditions.

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Capítulo 3

Techno-functional properties of coffee by-products are modified by dynamic high pressure: a case study of clean label ingredient in cookies

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Techno-functional properties of coffee by-products are modified by dynamic high pressure: a case study of clean label ingredient in cookies

Running Title: Coffee by-products cookies

Ricardo Henrique Belmiro[1], Ludmilla de Carvalho Oliveira[1], Alline Artigiani Lima Tribst[2], Marcelo Cristianini[1]

Abstract

Coffee by-products (CBP), non-processed and modified by dynamic high-pressure technology (DHP – 100 MPa, 1 pressure cycle and 25 °C), were incorporated in 3% and 6% into formulations of cookies to replace wheat flour. Dimensions, spread ratio, density, water activity (aw), hardness, and total reducing power (TRP) in the cookies were determined. Affective and CATA (check-all-that-apply) tests were used for the sensory evaluation of samples enriched with 6% CBP. The enrichment of the cookie with *non-processed* or modified CBP contributed to the increase in TRP and did not change the spread ratio compared to the control. The density and hardness of the control cookie decreased slightly after incorporation of non-processed CBP, while they remained unchanged in cookies enriched with modified CBP. Compared to the control, the sensory acceptance of cookies enriched with CBP was quite lower, which could be explained by their association with "bitter", "burnt favor/ taste" and "dark". The incorporation of CBP, non-processed or modified, can increase the fiber content and TRP in the cookies, causing little impact on dimensions, physical properties, and sensory attributes. Therefore, this study confirms the potential for using CBP as a healthy and "clean label" ingredient in cookie formulations.

Keywords: High pressure homogenization, emerging technology, dietary fiber, phenolic compounds, bakery product

1. Introduction

Consumer demand for healthier food and environmental concerns has grown and this scenario has led the food industry to seek, among others, new sources of bioactive compounds, such as dietary fibers and phenolic compounds (Galanakis, 2015, 2020). The use of agro-industrial by-products as food ingredients has great potential, since they are usually rich in dietary fibers and sources of antioxidant compounds. If these insights are properly addressed, it is possible to predict contributions to reduce the negative impacts of the disposal of by-products in the environment and at the same time to improve the nutritional and functional quality of processed foods (Lai et al., 2017; Mudgil et al., 2017; Yang et al., 2017).

Coffee by-products (husk, mucilage, parchment, and silver skin – CBP) are significant sources of dietary fibers (DF), which are mainly insoluble. CBP is also a source of antioxidant compounds (AC), mainly chlorogenic and caffeic acids and tannins (Belmiro et al., 2021; Esquivel & Jiménez, 2012). Despite its nutritional and functional value, CBP is still not used by the food industry, being used mainly as a fertilizer (Belitz et al., 2009) and as a fuel in the roasting process of the coffee bean (Braham & Bressani, 1979). Since the techno-functional properties of the fiber in the CBP, such as the water and oil retention capacity, are relatively limited (Belmiro et al., 2021), the use of modification techniques (such as dynamic high-pressure) to modulate such properties can be an alternative to overcome these technological limitations and extend the application range of this residue (Belmiro et al., 2021). Although losses in the content of phenolic compounds and antioxidant activity are inherent to the techniques and conditions of fiber modification in CBP, it is desirable for them to be minimized.

Dynamic high-pressure (DHP) is a non-conventional technology that, due to the physical principles/phenomena of high cavitation, pressure, turbulence, and shear stress, is capable of modifying the DF of the agro-industrial by-products (Kleinig & Middelberg, 1997; Yang et al., 2017). The changes caused in the fibrous material by DHP are a result of the rupture of the DF structure and compartments of plant cells, which may be responsible for the redistribution of IDF to SDF and increased water and oil holding capacity (Belmiro et al., 2018; Ozyurt & Ötles, 2016). Since this technology is applied in mild temperature conditions and does not use organic reagents, it has the potential to modify dietary fiber and at the same time prevents or minimizes the loss of nutrients and phenolic compounds (Belmiro et al., 2021; Ozyurt & Ötles, 2016). Therefore, DHP technology can be an alternative for the modification of coffee by-products, to improve its techno-functional properties and enable new applications. This could add to the food industry and market the development of “clean label” ingredients, sources of DF and with retention of natural AC.

Among the possibilities of using DF-rich ingredients in food products, as a way of attributing a healthier (Galanakis, 2015, 2020) and functional appeal to them, bakery products, such as cookies, stand out (Blanco Canalis et al., 2019; Milićević et al., 2020; Turksoy & Özkaya, 2011; Varastegani et al., 2015). Bakery products are consumed in large quantities by the population on a daily basis, thus constituting an appropriate means for the delivery of DF to consumers (Ktenioudaki & Gallagher, 2012). However, the incorporation of ingredients rich in DF in bakery products can lead to undesirable techno-functional and sensory changes (Milićević et al., 2020; Moro et al., 2018; Mudgil & Barak, 2013), and can impact the properties of the dough as well (Paciulli et al., 2018). In this context, modified fibers may appear as an alternative to avoid or to minimize such negative effects.

In this study, CBP were modified by dynamic high-pressure technology and applied to the nutritional and functional enrichment of cookie formulations. The impact of replacing wheat flour with CBP was evaluated, at two different levels (3 and 6%), on the dimensions, physical and antioxidant properties, and sensory parameters of the cookies.

2. Material and methods

2.1. **Material**

Coffee cherries, *Coffea arabica* var *ruby* (Anexo A), ripe and dried in the sun, were kindly donated by a local producer (22°11'39.4" S 46°53'54.4" W). The fruits were peeled using a manual peeler and then the epicarp (husk), mesocarp (pulp or mucilage), endocarp (parchment), and silver skin, which compose the CBP, were separated from the endosperm (coffee bean) and stored in polyethylene bags. The CBP was washed in a chlorinated solution at 200 ppm, rinsed with distilled water, drained to remove excess water, frozen at −18 °C, lyophilized at −40 °C for 48 hours, ground in a plate mill followed by an analytical mill bench top (IKA model-A11, Germany) and sieved through a 0.250 mm sieve (60 mesh – Anexo B). The sample was vacuum-packed and stored in a dry place, protected from light. The proximate composition of the CBP was determined, on a dry basis (d.b.), being: 63% of total dietary fiber, 12% of protein, 4% of lipids, 5% of ash, and 16% of non-complex carbohydrates (calculated by difference). All raw materials for the production of cookies were purchased in a local market in the city of Campinas, São Paulo, Brazil.

2.2. **Methods**

2.2.1. Dynamic high-pressure processing

CBP (400.0 g – d.b.) was suspended in 1000 mL of distilled water and stirred for 30 min. The suspension was processed using a high-pressure homogenizer (Panda GEA Niro Soave, Italy) at 100 MPa for 1 pressure cycle and with an inlet temperature of 25 °C. These process parameters were determined according to the optimal condition found in a previous study by Belmiro et al. (2021). The control sample was defined as the CBP not processed by DHP. After processing, the samples were lyophilized and packed under vacuum in polyethylene bags. The composition of the CBP was 63% of DF (being 58% of insoluble and 5% of soluble dietary fibers), 21% of non-complex carbohydrates (calculated by difference), 12% of proteins and 4% of lipids, on a dry weight basis (d.w.b.). No differences were observed between de composition of the modified and non-modified samples.

2.2.2. Formulation of cookies

Non-modified control cookies, denominated as traditional (TCO), were prepared based on a formulation described by Silva & Conti-Silva, 2016. For each 100g of formulation, 50.0 g refined wheat flour, 22.3 g of sugar, 13.0 g of butter, 13.0 g of eggs, 1.6 g of baking powder, and 0.4 g of sodium bicarbonate were added. As a proposal to enrich traditional cookies, control CBP and CBP modified by DHP were incorporated into the base formulation in the proportions of 3% and 6%, in partial replacement for wheat flour. Thus, besides control cookie, four different cookie formulations were prepared, as described: TN3 - cookies with 3% of non-processed CBP; TN6 - cookies with 6% of non-processed CBP; TM3 - cookies with 3% of DHP-processed CBP; TM6 - cookies with 6% of DHP-processed CBP. These replacement levels were determined from preliminary tests, where 6% of CBP was the highest possible replacement without changing the moisture of the dough. The ingredients were mixed in a semi-industrial planetary mixer (first the liquid ingredients and then the dry ones) until they formed a homogeneous mass, which was left to stand for 30 min, molded with circular molds (40 mm in diameter and 4 mm high), resulting in cookies with about 14 g each. The molded cookies were baked in a convection oven at 150 °C for 12 min, left to stand for 30 min at room temperature for stabilization, and then packed in polyethylene bags and stored until the next day for the analysis.

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2.2.2.3. Analysis of the dimensions and techno-functional properties of cookies

The cookies were weighed and measured regarding diameter and height (using a digital caliper), spread ratio (defined as the relationship between diameter and height), density (determined by the displacement of millet seeds), and water activity (aw) (determined by infrared using the equipment AquaLab 4Tev – Meter – Brazil), according to Rai et al. (2014). The hardness was determined to be the peak force required to promote the cracking of the biscuit in half, using a texturometer (TA XT2 Texture Analyzer, USA) coupled with a 3-point probe (Gerzhova et al., 2016), loaded with a load of 50N, descent speed of 1mm/s, and initial distance of 5 cm. A total of 14 cookies were used in each analysis, except for aw, whose measurements were performed in triplicate.

2.2.2.4. Total reducing power

Prior to the analysis of total reducing power (TRP), the cookies were ground in a bench analytical mill. Exactly 1.0g of ground biscuit was placed in a falcon tube with 20mL of 50% (v/v) aqueous ethanol solution, homogenized in ultra turrax (T 25 digital, IKA, Germany) at 1000 RPM for 10 seconds, left to rest for 5 minutes; the supernatant was carefully recovered. TRP was estimated using the Folin-Ciocalteau method, with gallic acid as the standard. The analysis was performed in triplicate and the results were expressed as mg equivalent of gallic acid per g of CBP (mg Eq GA/g CBP).

2.2.2.5. Sensory analysis

A total of 110 panelists were recruited at the University of Campinas (Campinas, SP, Brazil). Screening criteria included declared habits of cookies consumption and interest to participate in the test. The study was approved by the Ethics Committee at the University of Campinas, Brazil (CAAE 16556019.3.0000.5404 – Anexo C). Participants signed an informed consent form before beginning the test. TCO and cookies added with 6% of native CBP (TN6) or modified CBP (TM6) were produced according section 2.2.2. Sensory analysis was carried out after one day of production.

Participants were asked to try the samples and indicate their acceptance to appearance, flavor, taste, texture and overall liking using a structured 9-point hedonic score (from “1-extremely bad” to “9=extremely good”) (Pereira et al., 2019). The check-all-that-apply (CATA) test was used to obtain a sample description from the participants (Pereira et al., 2019). The 29 CATA attributes were selected from a flesh profile test preliminary applied for 12 untrained panelists (data not shown). Purchase intention was also assessed using the five-point hedonic score (from “1- certainly would not buy” to “5- certainly would buy”). The Ideal sample was determined by participants answering the CATA test about characteristics expected for an ideal cookie.

2.2.6. Statistical analyses

The results of the dimensions and techno-functional assays of the cookies were presented as mean ± standard deviation. Differences among the samples were evaluated through analysis of variance (ANOVA) and Tukey test ($p<0.05$).

For affective and purchase intention tests, ANOVA and Tukey tests ($p<0.05$) were also used to verify differences among different samples. The frequency citation of each CATA term was determined for each sample. Cochran Q test was used to identify significant differences in the frequency usage of terms to describe samples and Marascuilo test was used compare each pair of products to identify significant differences among samples in each CATA term at 5% of significance level (Tribst et al., 2020). Principal component analysis (PCA) was used to obtain a two-dimensional representation of the samples and attributes distribution and confidence ellipses around the samples were constructed using bootstrapping (95% confidence level), considering the first two dimensions of the configurations (Pereira et al., 2019).

3. Results and discussion

3.1. Dimensions and physical properties of cookies

As can be seen in Figure 3-1, the addition of coffee by-products promoted a darker color in the cookies. Table 3-1 shows that the addition of CBP (non-modified or modified) to cookies, in general, did not promote significant changes ($p>0.05$) in the diameter, height, spread ratio, and water activity of the cookies compared to the control. Concerning the density of cookies, TM6 did not showed a significant difference ($p>0.05$) compared to the control, while the other samples promoted a reduction in this parameter, possibly due to a lower volume of these samples.

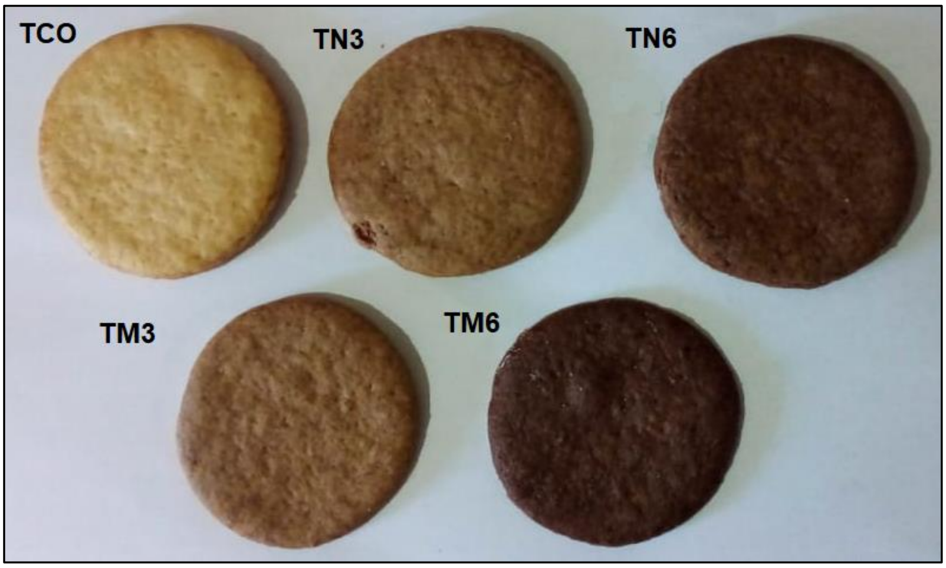


Figure 3-1 Picture of the cookies: Traditional cookie without CBP (TCO); Traditional cookies with 3% of natural CBP (TN3); Traditional cookies with 6% of natural CBP (TN6); Traditional cookies with 3% of modified CBP (TM3); Traditional cookies with 6% of modified CBP (TM6)

Changes in the texture of cookies enriched with coffee by-products were observed, these changes being dependent on the type of CBP (modified or non-modified) and the level of replacement (Figure 3-2). TN6 showed a reduction in hardness ($p<0.05$), while TM3 led to an increase in the strength needed to break the cookies. The hardness of the other samples (TN3 and TM6) did not differ significantly ($p>0.05$) from that of the control. No changes in the distance at rupture of the cookies were observed for all samples (from 1.60 to 1.69 mm).

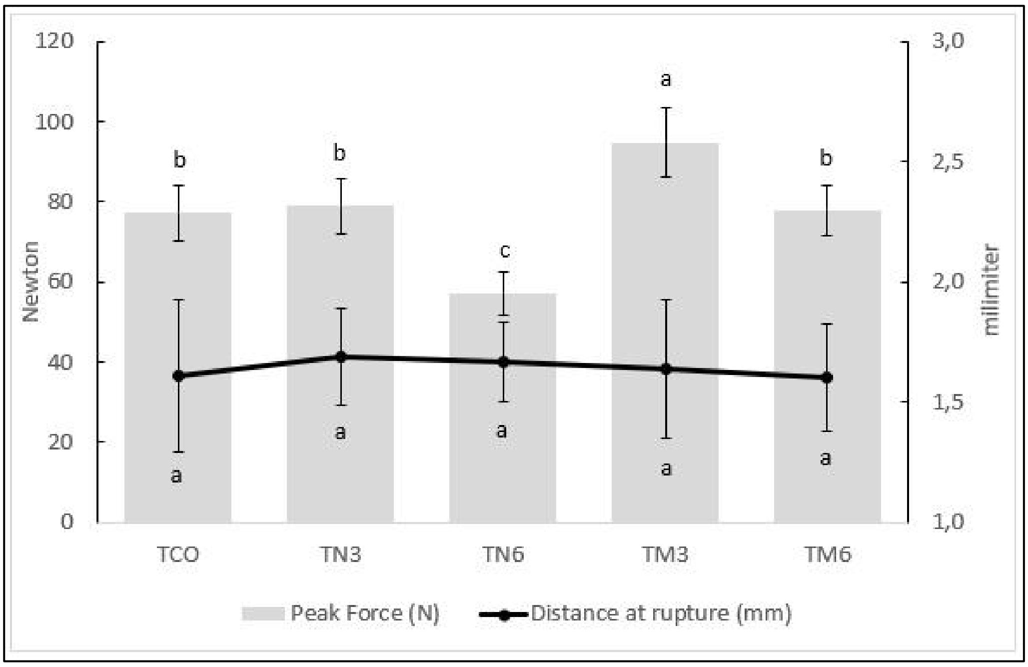
Table 3-1 Diameter (D), height (h), spread ratio, density (d) and water activity (aw) of the cookies

Sample	D (mm)	h (mm)	Ratio (D/h)	d (g/mL)	aw
TCO	53.05 ± 0.86^{a}	10.44 ± 1^{ab}	5.12 ± 0.43^{ab}	0.58 ± 0.05^{a}	0.544 ± 0.002^{a}
TN3	52.63 ± 0.85^{a}	11.04 ± 0.1^{a}	4.77 ± 0.11^{b}	0.47 ± 0.04^{c}	0.525 ± 0.001^{a}
TN6	52.21 ± 0.88^{ab}	10.86 ± 0.67^{a}	4.83 ± 0.36^{b}	0.47 ± 0.03^{c}	0.553 ± 0.001^{a}
TM3	52.38 ± 0.96^{ab}	10.58 ± 0.7^{ab}	4.97 ± 0.3^{ab}	0.50 ± 0.02^{bc}	0.527 ± 0.001^{a}
TM6	49.22 ± 0.98^{b}	9.4 ± 0.8^{b}	5.27 ± 0.43^{a}	0.54 ± 0.02^{ab}	0.544 ± 0.001^{a}

Results are given as the mean ± the standard deviation.
Same small letter in a column means there is no significant difference ($p>0.05$) between the samples.
TCO - Traditional cookie without CBP; TN3 - traditional cookies with 3% of non-processed CBP; TN6 -

traditional cookies with 6% of non-processed CBP; TM3 - traditional cookies with 3% of modified CBP; TM6 - traditional cookies with 6% of modified CBP.

Since there was no significant difference between TN6 and TM3 samples in terms of the ratio and density, it is supposed that the discrepancy in hardness induced by incorporating CBP (non-modified and modified) could be mainly attributed to the changes in the gluten content and structure porosity. The dilution of the gluten content and formation of more porous structure due to the addition of CBP in the cookie formulation may be responsible for softer cookies of the TN6 sample. In addition, fiber structure is normally more porous than that of wheat flour, and this leads to cookies with increased moisture content, which is another factor that is responsible for lower hardness (Naknaen et al., 2016). In the case of the TM3 sample, the break in the DF structure of CBP caused by DHP (Belmiro et al., 2021) may have produced a less porous structure in the cookies, causing an increase in the hardness. In any case, further studies on the effect of DHP-modified fibers on the gluten network and on the porosity of the cookies are advisable.



Figur3 3-2 Hardness (N) and distance at rupture (mm) of the cookies

Vertical bars mean the standard deviation. Same letter means there is no significant difference (p>0.05) between the samples.

Cookies are formulated from three main ingredients (flour, sugar, and fat). Although water is only present in a small amount (usually < 20% on a dry basis), it takes part in the formation of the gluten network and, thus, affects the dimensions and techno-functional properties, such as the hardness and humidity, of these cookies (Chevallier et al., 2002). The addition of dietary fibers to replace wheat flour in this type of formulation leads to a reduction in the concentration of starch, in the content of proteins forming the gluten network (gliadin and glutenin), and in the amount of free water during the process, the latter being due to the hygroscopic characteristic of dietary fibers, which may result in changes in the dimensions of the cookies, due to a lower formation of the gluten network (Xiao et al., 2021). In a previous study with coffee by-products, Belmiro et al. (2021) reported that this residue has about 63% (on a dry basis) of dietary fibers, with insoluble fibers being the majority (58% of the total CBP), and that the modification by DHP did not change this proportion. Although CBP is a

DF-rich source, the partial replacement of flour by it did not cause major changes in the dimensions and techno-functional properties of cookies, possibly due to the low level of incorporation (3% and 6% in replacement of the weight of the flour). Also, the modification of coffee by-products allowed for a greater incorporation without affecting the hardness and density of the cookies and with minor changes in the diameter, height and spread ratio, thus showing that the use of DHP can be a good strategy for the production of cookies with a higher fiber content. Uysal et al. (2007) reported that the substitution of flour for up to 15% of apple, lemon, wheat, and wheat husk fiber in cookie formulations also did not promote major changes in the spread ratio and the hardness of the cookies. Similar results have also been reported by Varastegani et al. (2015) on cookies replaced with papaya flour (up to 50%) and by Moro et al. (2018) on cookies replaced with burdock root flour. On the other hand, the substitution of flour of pumpkin and carrot bagasse led to a more significant reduction in diameter and spread ratio and an increase in the height and hardness of cookies (Turksoy & Özkaya, 2011).

3.2. Total reducing power

Figure 3-3 shows that the incorporation of CBP in cookies positively affected ($p<0.05$) the total reducing power (TRP), promoting it for both the formulations with non-processed and modified CBP. The unmodified samples (TN3 and TN6) presented the highest TRP. In addition, the incorporation of modified CBP at 6% tended to increase the TRP in the cookie, compared to the respective formulation at 3% (with non-processed or modified CBP).

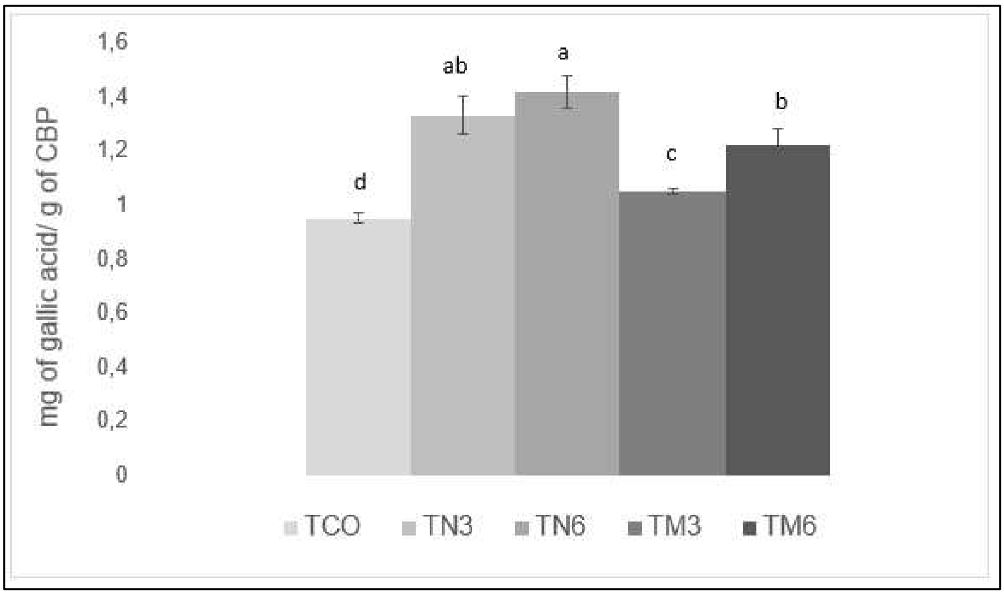


Figure 3-3 Total reduction power of the cookies.

Vertical bars mean the standard deviation. Same letter means there is no significant difference (p>0.05) between the samples. TCO - Traditional cookie without CBP; TN6 - traditional cookies with 6% of non-processed CBP; TM6 - traditional cookies with 6% of modified CBP.

CBP has a TRP of about 23 mg of gallic acid per gram/g, with chlorogenic acid being its main phenolic compound (Belmiro et al., 2021); the presence of this phenolic compound can be responsible for the increase in the TRP of the cookies replaced with coffee by-products. Milićević et al. (2020) replaced 30% fat with wheat or oat-shell flour and also reported an increase in the TRP of cookies. On the other hand, Chauhan et al. (2015) and Bilgiçli et al. (2007) assessed that the replacement of wheat flour with purified fibers from apple, lemon, wheat, or wheat skin (from 10 to 30%) reduced the TRP of cookies, thus evidencing the importance of using agro-industrial by-products as a whole, without prior purification. Although the application of DHP in agro-industrial by-products is related to the release of phenolic compounds from the structure of DF and a consequent increase in antioxidant activity, Belmiro et al. (2021) found that the use of this technology resulted in a decrease in the TRP of CBP. This effect was probably due to the formation of complexes between these phenolic compounds and the fiber caused by the rupture of the DF structure (Rosa et al., 2013), which would explain the lower increase in the reducing power of the samples replaced with the modified coffee by-products. Temperature increase during homogenization is also believed to play a role on TRP. A more detailed study is needed to better understand this effect.

3.3. Sensory analysis

The results of the affective test and purchase intention are showed in Table 3-2. Panelist did not observe differences (p>0.05) in the appearance and flavor of cookies enriched with CBP (non-modified or modified). Regarding taste, only the sample with modified CBP had a similar evaluation of the traditional cookies. On the other hand, scores for texture and overall acceptance of samples added by CBP was 17 – 28% lower than those for traditional cookies, probably explaining the purchase intention (22% lower) of samples added with coffee by-product.

Tabela 3-1 Sensorial attributes of the traditional cookies enriched with coffee by-products (CBP)

	Appearance	Flavor	Taste	Texture	Overall acceptance	Purchase intent
TCO	6.3 ± 1.9^{a}	6.3 ± 1.5^{a}	6.4 ± 1.8^{a}	6.7 ± 1.6^{a}	6.6 ± 1.5^{a}	3.3 ± 1.1^{a}
TN6	6.6 ± 1.3^{a}	6.4 ± 1.4^{a}	5.5 ± 1.7^{b}	5.3 ± 1.8^{b}	5.6 ± 1.7^{b}	2.6 ± 1.0^{b}
TM6	6.4 ± 1.6^{a}	6.7 ± 1.3^{a}	5.7 ± 1.8^{ab}	4.8 ± 2.1^{b}	5.5 ± 1.7^{b}	2.8 ± 1.1^{b}

Results are given as the mean ± the standard deviation.
Same small letter in a column means there is no significant difference (p>0.05) between the samples.
TCO - Traditional cookie without CBP; TN6 - traditional cookies with 6% of non-processed CBP; TM6 - traditional cookies with 6% of modified CBP.

The results of the texture perceived by the panelist and the texture measured by the texture analyzer are in disagreement for the TM6 sample. Although the calculated texture of this sample was the same as the control (p>0.05), the panelist rated this sample as softer and less crunchy. It is assumed that for this type of product, crunchiness has a greater impact on texture than the structure of the cookies as a whole.

Turksoy & Özkaya (2011) noted that replacing 10% wheat flour with carrot and pumpkin bagasse flour in cookies led to small reductions in the sensory scores given by untrained assessors. Uysal et al. (2007) reported that the substitution of wheat flour for 15% by-product flour from apple, lemon, and wheat skin also negatively impacted the assessment of the sensory attributes of cookies. This probably can be explained by the low adaptation of most people with products substituted with dietary fibers, instead of only white flour, which leads to strong flavor/color and texture changes in the product.

The overall evaluation of cookies acceptance suggests that the addition of CBP in cookies is feasible from a sensory point of view due to the relatively small differences between the samples scores. Moreover, information regarding expected healthy benefits of cookies added by CBP may could improve the sensory perception of these products (Tarrega et al., 2017).

Table 3-3 shows the frequency citation of attributes in CATA test. The terms “granulated”, “irregular shape”, “uniform appearance”, “soft flavor”, “roasted taste”, “compact”, “rough texture”, “hard” and “dry” had no differences in the citation among the different products ($P>0.05$). In addition, “strong flavor” and “honey taste” was cited by less than 15% of participants for all samples, being considered unimportant to describe the cookies samples. For the other 20 attributes, differences in the frequency citation were observed between TCO and TN6 and TM6. The exceptions were “flour taste/ flavor”, with sample TM6 similar to TCO and “aerated”, with similarity between TCO and TN6.

Table 3-2 Frequency of citation of the CATA attributes

Atributes	p-values	TCO	TM6	TN6
Bright	0.000	0.935 (b)	0 (a)	0.019 (a)
Traditional cookie appearence	0.020	0.222 (b)	0.120 (a)	0.120 (a)
Dark	0.000	0 (a)	0.889 (b)	0.861 (b)
Whole cookie appearence	0.000	0.019 (a)	0.185 (b)	0.306 (b)
Burnt flavor	0.000	0 (a)	0.167 (b)	0.213 (b)
Butter flavor	0.000	0.546 (b)	0.231 (a)	0.139 (a)
Roasted flavor	0.037	0.333 (a)	0.472 (b)	0.472 (b)
Flour flavor	0.000	0.454 (b)	0.315 (ab)	0.213 (a)
Coffee flavor	0.000	0 (a)	0.194 (b)	0.269 (b)
Coffee taste	0.000	0.009 (a)	0.250 (b)	0.361 (b)
Flour taste	0.000	0.611 (b)	0.500 (b)	0.296 (a)
Burnt taste	0.000	0.009 (a)	0.176 (b)	0.306 (b)
Butter taste	0.000	0.676 (b)	0.213 (a)	0.148 (a)
sweet	0.000	0.537 (b)	0.343 (a)	0.315 (a)
Whole cookie taste	0.000	0.028 (a)	0.185 (b)	0.241 (b)
Bitter	0.000	0 (a)	0.213 (b)	0.259 (b)
Aerated	0.016	0.269 (b)	0.130 (a)	0.204 (ab)
Humid	0.000	0.269 (a)	0.583 (b)	0.472 (b)
Crunch	0.000	0.472 (b)	0.009 (a)	0.009 (a)
Soft	0.000	0.583 (a)	0.870 (b)	0.870 (b)

Same small letter in a row means there is no significant difference ($p>0.05$) between the samples. TCO - Traditional cookie without CBP; TN6 - traditional cookies with 6% of non-processed CBP; TM6 - traditional cookies with 6% of modified CBP.

Figure 3-4 shows the principal component analysis (PCA) with the significant terms of CATA and the data obtained are explained by two main dimensions at 97.7% (Dim1 explains 70.4% and Dim2 explains 27.3% of the total variability), showing an excellent representation of the sample's distribution. Therefore, Figure 4 and Table 3 highlights the main terms used to describe each sample and helps to understand the differences in their acceptance and purchase intention.

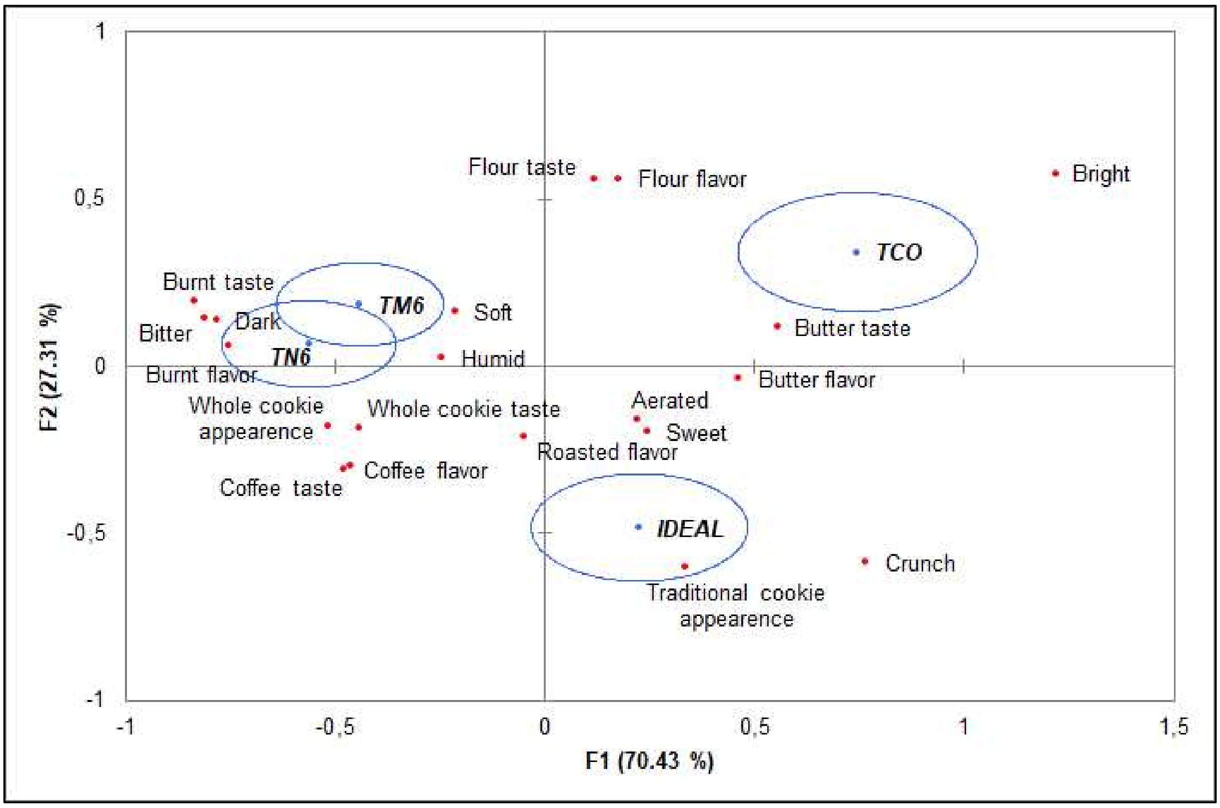


Figure 3-4 Correspondence analysis with the significant terms of the CATA test. TCO - Traditional cookie without CBP; TN6 - traditional cookies with 6% of non-processed CBP; TM6 - traditional cookies with 6% of modified CBP.

TCO was described as bright, butter taste, butter flavor, flour flavor and flour taste. TN6 and TM6 were very similar (great ellipsis overlapping) and mainly described by attributes that explicit consequences of CBP addition, such as dark, bitter, burnt taste, whole cookies taste/ appearance, soft and humid. In addition, interestingly, hypothetical ideal sample was described by some other attributes (does not used to describe the traditional sample) such as roasted flavor, sweet, traditional cookie appearance, aerated and crunch. The differences between our formulation of traditional cookie and ideal sample, and consequent low acceptance and purchase intent of all samples, might be explained by the great variety of cookies sold in Brazilian market (from artisanal to processed, with different concentrations of fat, aroma and sugar) and the common preference of Brazilians by over sweetened products (Tribst et al., 2021, Pereira et al., 2019).

Thus, the observed distance between ideal cookie, traditional cookies and those added by coffee by-products explain the relative low scores in acceptance and purchase intention that the developed cookies received by consumers.

4. Conclusion

The substitution of wheat flour for coffee by-products (3 and 6% of CBP) had great contribution for the dietary fiber enrichment and TRP in cookie formulations. Considering the challenges in minimizing the impacts of adding ingredients DF-rich ingredients in cookie formulations, the modification of CBP by DHP made possible the incorporation of up 6% with minor losses of the product dimensions, physical properties, and sensory attributes. Thus, this study confirmed the potential of DHP to offer fiber-rich ingredient from CBP (for modification), which is technologically feasible to produce cookies with nutritional and functional added values (source of dietary fiber and antioxidant compounds).

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Conflict of interest:

Authors declare there is none commercial or non-commercial conflicts of interest.

Ethical Guidelines

Ethics approval was accordingly provided by the Ethics Committee at the University of Campinas, Brazil (CAAE 16556019.3.0000.5404).

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Discussão geral

A demanda dos consumidores por alimentos saudáveis e a preocupação com a preservação do meio ambiente tem feito com que a indústria de alimentos busque novas fontes de compostos bioativos, como as fibras alimentares e os compostos fenólicos. A conversão de resíduos formados pelas indústrias de alimentos em ingredientes alimentares tem grande potencial, contribuindo, por um lado, para reduzir os efeitos negativos da sua eliminação no meio ambiente e, por outro lado, para melhorar a qualidade nutricional e funcional dos alimentos industrializados. (Galanakis, 2015, Galanakis 2020). Somado a tudo isso, a adição de valor agregado para resíduos alimentares que antes seriam descartados ou subutilizados pode gerar uma nova fonte de renda, gerando um impacto social positivo na sociedade. Assim, o aproveitamento de resíduos agroindustriais para o desenvolvimento de uma produção sustentável é uma prioridade.

Apesar de toda a importância nutricional, ambiental e social, a utilização destes resíduos pelas indústrias, como as de alimentos, precisa ser viável tecnologicamente, sendo que disto dependem as propriedades tecnológicas, como a capacidade de retenção de água, capacidade de retenção de óleo e o índice de solubilidade, dentre outras, das fibras alimentares presentes no resíduo.

Em alimentos, a interação água e óleo com ingredientes alimentícios desempenha um papel importante na textura e no sabor dos alimentos, enquanto a capacidade de um ingrediente de reter água e óleo melhora a sensação na boca e ajuda a reduzir as perdas de gordura e umidade. A sinérese em produtos alimentícios é controlada pela adição de ingredientes com alta capacidade de retenção de água. Em alimentos formulados com alto teor de gordura, ingredientes com alta capacidade de retenção de óleo são adicionados para atuarem como emulsificantes. Um bom controle sobre a atividade de água dos alimentos é necessário para manter sua textura, estabilidade microbiológica e conter mudanças químicas e enzimáticas indesejáveis.

Essas propriedades estão relacionadas ao tipo de fibra (solúvel ou insolúvel) e sua concentração presente no subproduto (Mudgil; Barak, 2013; Ozyurt; Ötles, 2016). Em geral, os subprodutos agroindustriais ricos em fibras alimentares insolúveis possuem uma baixa retenção de água e óleo, quando comparados aos ricos em fibras solúveis, limitando assim a sua aplicação. Modificações nestes resíduos ricos em fibras insolúveis poderão causar mudanças na interação das fibras alimentares com a água e o óleo podendo assim promover uma maior capacidade de retenção de água e óleo (Ozyurt; Ötles, 2016), mesmo que o resíduo tenha uma maior concentração de fibra insolúvel, ampliando assim a gama de aplicações destes ingredientes "*clean label*". Neste contexto, a modificação dos subprodutos do café, que são ricos em fibras insolúveis e fonte de compostos antioxidantes, se mostram como uma oportunidade para atender a essas demandas nutricionais, ambiental, social e tecnológica.

Desta forma, o propósito deste estudo foi avaliar a aplicação da tecnologia de alta pressão dinâmica, da acetilação e da hidrólise enzimáticas nos resíduos da limpeza do café e seus efeitos nas propriedades tecnológicas e na capacidade antioxidante do resíduo agroindustrial do beneficiamento do café. Também se realizou a incorporação destes resíduos em biscoitos tipo *cookie* para se avaliar seu efeito nas dimensões, propriedades físicas e aceitação sensorial de biscoitos.

Os três métodos de modificação aplicados nestes estudos foram capazes de melhorar a capacidade da retenção de água, capacidade de retenção de óleo e o poder de hidratação dos resíduos da limpeza do café . A alta pressão dinâmica foi capaz de romper a estrutura ligno-celulósica da fibra alimentar, causando uma abertura da estrutura e uma diminuição no tamanho das partículas. Uma abertura da estrutura da fibra alimentar também foi observada para a reação de acetilação e a hidrólise enzimática sem, contudo, promover a quebra da fibra alimentar. Em nenhum dos métodos utilizados houve uma mudança considerável na concentração de fibra insolúvel.

A interação da fibra alimentar com a água e o óleo está ligada à facilidade com a qual estes fluidos penetram e são retidos nas cadeias glicosídicas das fibras, e são afetadas pelas ligações inter e intra-moleculares que formam a estrutura molecular. Além de afetar as propriedades tecnológicas das fibras alimentares, essas interações entre a fibra e a água ou o óleo podem ser cruciais na definição da textura e sabor dos alimentos, enquanto a capacidade de um ingrediente de reter água e óleo melhora a sensação na boca e ajuda a reduzir as perdas de gordura e umidade. Portanto, modificações nestas ligações levarão a mudanças na interação das fibras alimentares com os componentes fluidos da formulação, podendo aumentar assim as propriedades tecnológicas das fibras alimentares como a capacidade de retenção de água e óleo (Ozyurt & Ötles, 2016), o que poderá acarretar em uma melhoria na mastigabilidade de produtos enriquecidos com fibras e ajudará a reduzir a perda de óleo e umidade durante o seu preparo, sem, contudo, afetarem de forma significativa a sua textura (Ozyurt; Ötles, 2016; Abdul-Hamid, A.; Luan, Y. S, 2000).

Além da água e o óleo, as fibras alimentares também interagem com os compostos fenólicos presentes nos subprodutos agroindustriais (Jakobek, 2015) sendo que a quebra e a abertura da estrutura destas fibras poderá liberar estes compostos para o meio (Rosa et al., 2013). Os três métodos avaliados nestes estudos ocasionaram perda no poder antioxidante dos subprodutos do café, porém a reação de acetilação e a hidrólise enzimática causaram uma perda drástica, provavelmente devido à lixiviação causada durante a etapa de pós lavagem destes métodos. Desta forma, somente a amostra modificada pela APD foi substituída nos biscoitos tipo *cookie*.

A substituição da farinha de trigo por 3% e 6% de subprodutos do café (não modificado e modificado) em biscoitos tipo *cookie* não resultou em grandes alterações nas dimensões, nas propriedades físicas e sensoriais sendo que a amostra substituída com os resíduos da limpeza do café modificados (6% de substituição) foi capaz de manter a dureza, medida em texturômetro, e o sabor, avaliado em teste afetivo, do biscoito controle. Os principais critérios para aceitação de alimentos enriquecidos com fibras alimentares são: bom comportamento no processamento, boa estabilidade e aparência, e aprovação quanto ao aroma, a cor e a textura (Mudgil; Barak, 2013). Desta forma, a aplicação dos resíduos da limpeza do café em cookies se mostra viável, do ponto de vista sensorial, uma vez que obteve uma avaliação satisfatória por parte dos consumidores.

Os estudos aqui apresentados trazem dados recentes e inéditos à literatura sobre os efeitos da modificação dos subprodutos do café pelos processos de alta pressão dinâmica, de reação de acetilação e de hidrólise enzimática nas propriedades tecnológicas e na atividade antioxidante deste resíduo, bem como na sua incorporação em biscoitos tipo *cookie*. Também contribuem para a aplicação dos subprodutos agroindustriais como ingredientes alimentares, promovendo assim desenvolvimento sustentável e a responsabilidade social.

Conclusão Geral

Os métodos de modificação das fibras alimentares dos resíduos do descascamento do grão de café levaram, de uma forma geral, ao rompimento ou desordenamento da estrutura destas fibras, o que resultou em uma melhora nas propriedades tecno-funcionais tais como capacidade de retenção de água, de óleo e a capacidade de hidratação. A redução dos compostos fenólicos e dos teores de cafeína e da capacidade antioxidante dos resíduos da limpeza do café foram inerentes às técnicas de modificação, porém a alta pressão dinâmica causou apenas um impacto mínimo. Ao ser aplicado em biscoitos tipo *cookie*, a substituição parcial da farinha de trigo pelos subprodutos do café contribuiu positivamente para a altura, densidade e sabor dos biscoitos, além de proporcionar novos atributos sensoriais como uma aparência uniforme e maciez. Desta forma, os resíduos da limpeza do café modificados se mostraram, do ponto de vista tecnológico, como um ingrediente funcional, em especial para aplicação em produtos de panificação, gerando assim valor agregado a um resíduo subutilizado e promovendo um maior desenvolvimento sustentável ao diminuir o impacto que estes resíduos causam ao serem descartados no meio ambiente. Se por um lado a alta pressão dinâmica foi capaz de reter melhor as propriedades antioxidantes do resíduo, por outro, ele é um processo mais dispendioso. A acetilação e a hidrólise enzimática são métodos relativamente mais simples e baratos, porém com menor retenção dos compostos fenólicos. Desta forma, a escolha do método vai depender do produto desejado e dos recursos disponíveis.

Trabalhos futuros

- Estudar os efeitos dos métodos de modificação pela alta pressão dinâmica, da acetilação e celulase em diferentes subprodutos agroindustriais.
- Investigar os possíveis efeitos das modificações sobre os complexos formados entre as fibras alimentares e os compostos fenólicos.
- Avaliar a aplicação dos subprodutos agroindustriais modificados em diferentes matrizes alimentares, tais como produtos de confeitaria, sopas, cremes e embutidos cárneos.
- Investigar o efeito da modificação das fibras alimentares no potencial de prevenir o surgimento de doenças do sistema gastrointestinal.

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Anexos

Anexo A

Subprodutos do café – Casca, mucilagem e pergaminho

Anexo B

Subprodutos do café (Casca, mucilagem e pergaminho) moídos e tamisados

Anexo C

Folha de rosto e folha de aprovação do parecer consubstanciado do CEP

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Plataforma Brasil

PARECER CONSUBSTANCIADO DO CEP

DADOS DO PROJETO DE PESQUISA

Título da Pesquisa: Aproveitamento e modificação dos subprodutos do café (coffea arabica) para aplicação em alimentos: teste sensorial em biscoitos tipo cookie.

Pesquisador: RICARDO HENRIQUE BELMIRO

Área Temática:

Versão: 2

CAAE: 16556019.3.0000.5404

Instituição Proponente: Faculdade de Engenharia de Alimentos

Patrocinador Principal: Capes Coordenação Aperf Pessoal Nivel Superior

DADOS DO PARECER

Número do Parecer: 3.600.837

Apresentação do Projeto:

As informações contidas nos campos "Apresentação do Projeto", "Objetivo da Pesquisa" e "Avaliação dos Riscos e Benefícios" foram obtidas dos documentos apresentados para apreciação ética e das informações inseridas pelo Pesquisador Responsável do estudo na Plataforma Brasil.

O café é um importante alimento tanto do ponto de vista comercial quanto nutricional, sendo a segunda commodity mais comercializada no mundo e tendo o Brasil como maior produtor e exportador (Belitz, Grosch, & Schieberle, 2009; FAO, 2019). A casca, a polpa e o pergaminho constituem os subprodutos do café (SC) gerados durante o processo de secagem e limpeza dos grãos, os quais são fontes expressivas em fibras alimentares e compostos antioxidantes (Bresciani, Calani, Bruni, Brighenti, & Del Rio, 2014; BRESSANI, R.; ESTRADA, E.; JARQUIN, 1972). Apesar do seu valor nutricional, tais partes são basicamente empregadas na torra do café (combustão) ou como adubo, antes mesmo de serem direcionadas à aplicação em produtos alimentícios (Vale, Gentil, Goncalez, & da Costa, 2007). O melhor aproveitamento de tais subprodutos pela indústria de alimentos está atrelado, dentre outros, às propriedades tecnológicas das fibras que majoritariamente os compõem. Sugere-se, pois, que a modificação de tais macromoléculas possa alterar propriedades tais como a capacidade de retenção de água, capacidade de retenção de óleo e a solubilidade e, consequentemente, torná-las mais apropriadas aos requerimentos de produtos do setor alimentício (Elleuch et al., 2011; Spotti & Campanella, 2017). Já se sabe que alguns processos de natureza química, mecânica,

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- Relatórios parciais e final devem ser apresentados ao CEP, inicialmente seis meses após a data deste parecer de aprovação e ao término do estudo.

-Lembramos que segundo a Resolução 466/2012 , item XI.2 letra e, "cabe ao pesquisador apresentar dados solicitados pelo CEP ou pela CONEP a qualquer momento".

-O pesquisador deve manter os dados da pesquisa em arquivo, físico ou digital, sob sua guarda e responsabilidade, por um período de 5 anos após o término da pesquisa.

Este parecer foi elaborado baseado nos documentos abaixo relacionados:

Tipo Documento	Arquivo	Postagem	Autor	Situação
Informações Básicas do Projeto	PB_INFORMAÇÕES_BÁSICAS_DO_PROJETO_1376342.pdf	20/09/2019 14:06:36		Aceito
Orçamento	Orcamento.pdf	20/09/2019 14:06:01	RICARDO HENRIQUE	Aceito
Outros	CartaRespostaParecerConsubstanciadoCEP.docx	20/09/2019 14:05:01	RICARDO HENRIQUE	Aceito
Projeto Detalhado / Brochura Investigador	ProjetoSubprodutosDoCafeREV01.docx	20/09/2019 14:03:43	RICARDO HENRIQUE BELMIRO	Aceito
TCLE / Termos de Assentimento / Justificativa de Ausência	TCLEREV01.docx	20/09/2019 14:02:32	RICARDO HENRIQUE BELMIRO	Aceito
Declaração de Pesquisadores	funcionalcristianini.jpeg	21/08/2019 07:38:09	RICARDO HENRIQUE	Aceito
Folha de Rosto	FolhaDeRosto.pdf	24/06/2019 14:05:53	RICARDO HENRIQUE	Aceito

Situação do Parecer:

Aprovado

Necessita Apreciação da CONEP:

Não