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**PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E
TECNOLOGIA DE ALIMENTOS**

TESE

**DESENVOLVIMENTO E CARACTERIZAÇÃO
FÍSICO-QUÍMICA DE FARINHAS EXTRUDADAS DE
ARROZ E SORGO COLORIDO COM CASCA DE UVA**

LAÍS MARTINS FONTOURA

2023



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*Sob a Orientação do Professor Doutor
José Luis Ramírez Ascheri*

Tese submetida como requisito parcial para obtenção do grau de **Doutora em Ciência e Tecnologia de Alimentos**, no Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos, Área de Concentração em Tecnologia de Alimentos.

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RESUMO GERAL

FONTOURA, Laís Martins. Desenvolvimento e Caracterização Físico-química de Farinhas Extrudadas de Arroz e Sorgo Colorido com Casca de Uva. 2023. Tese (Doutorado em Ciência e Tecnologia de Alimentos). Instituto de Tecnologia, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ. 2023.

As indústrias processadoras de alimentos, em sua maioria, geram uma quantidade significativa de subprodutos, muitos deles, ao não contar com sistemas para seu aproveitamento, resultam em descartes ao meio ambiente, causando contaminação indesejada em diversas áreas, com consequências e danos à população. Particularmente, a cadeia produtiva de uvas, em 2020 alcançou cerca de 80 milhões de toneladas no mundo. Considerando que, em média cerca de 20-25% corresponde à casca de uva (GP), o teor de descarte é cerca de 15,6 milhões de toneladas/ano. Nesse sentido, há necessidade de se implantar políticas na qual se incluam formas de solucionar este problema e evitar seu descarte ao meio ambiente. Existe grande número de atividades, sejam estas agroindustriais, farmacêuticas, de transformação de bioativos, processadoras de alimentos, etc., que estão aproveitando as diversas propriedades, principalmente nutricionais e nutracêuticas, que este subproduto possui. Nos últimos anos, o número de trabalhos tem crescido, enfatizando a importância do uso da casca de uva (GP) como forma de agregar valor, reduzir o descarte no meio ambiente e utilizar esse recurso como fonte para a extração de muitos compostos, óleos bioativos e essenciais, entre outros. Como agente bioativo, diversas publicações destacam os resultados de grandes benefícios para a saúde humana, como por exemplo, por ser rico em antioxidantes, pode ajudar a combater os radicais livres no organismo, auxiliar no controle de doenças crônicas, como hipertensão, colesterol alto, diabetes, promovendo um envelhecimento saudável. Trabalhos científico mostraram que pode atuar como um agente anticancerígeno. Com relação às diversas formas de transformação dos subprodutos, a extrusão termoplástica tem se mostrado uma ferramenta eficaz na obtenção de diversos produtos, sejam eles insumos ou produtos acabados prontos para consumo imediato. Isso porque oferece vantagens significativas: baixo custo por peça, flexibilidade de operação na extrusão a quente, fáceis alterações pós-execução porque o produto ainda está aquecido, operação contínua, altos volumes de produção, uso de muitos tipos de matérias-primas, produtos com boa mistura (composição), e bom acabamento superficial. Os cereais quando processados por extrusão, podem ser preparados com diferentes graus de cocção, permitindo propriedades funcionais diferentes. Neste trabalho de Tese, com três capítulos, o primeiro é uma revisão que trata do bagaço de uva e sua utilização como fonte de fibra e antioxidante e sua relação na atividade industrial, econômica e social. No segundo capítulo, artigo já publicado, trata do enriquecimento da farinha de arroz com bagaço de uva, utilizando a tecnologia de extrusão termoplástica. No terceiro capítulo, um artigo já publicado, trata do impacto na atividade antioxidante, na extrusão de misturas coloridas de farinha de sorgo, com adição de casca de uva. Uma extrusora monorosca Brabender 19/20 DN, foi utilizada para os experimentos. A taxa de compressão do parafuso foi 3:1, com uma matriz circular de 3 mm de diâmetro. A velocidade rotacional da rosca, umidade e porcentagem GP foram monitorados conforme desenho experimental para cada caso, seja utilizando GP com farinha de arroz, ou GP com farinha de sorgo (SF). Os extrudados foram secos em secador com recirculação de ar forçado. Os extrudados foram então utilizados para as caracterizações físicas e químicas a fim de se verificar os efeitos dos parâmetros estabelecidos em cada desenho experimental. Os resultados referentes ao processamento de formulações com farinhas GP/Arroz (15/85,

20/80 e 25/75%, respectivamente), resultaram em que maiores percentagens de GP na formulação e velocidade do parafuso criam valores mais altos no índice de expansão longitudinal (LEI) dos extrudados. Este efeito pode ser devido a uma redução na viscosidade e provocando menos grau de conversão no amido. Aumentando a velocidade do parafuso, o índice de solubilidade em água (WSI) foi aumentado. A casca de uva demonstrou efeito negativo sobre a farinha extrudada, por melhorar a interação amido-redução e consequentemente reduzir a solubilidade. A cor é um parâmetro importante do produto para os consumidores. A farinha de casca de uva foi mais escura e o controle o mais claro pela ausência de casca de uva. Assim, aumentando o teor de casca de uva, a cor dos extrudados tornou-se mais escura, indicando que a casca de uva teve um forte efeito na coloração das farinhas extrudados. Os resultados obtidos demonstraram que a incorporação da casca de uva no arroz é viável. No entanto, é necessário fazer alguns ajustes nos parâmetros de processamento a fim de obter produtos com características tecnológicas atraentes aos consumidores. Referente ao processamento de extrusão com farinha de sorgo, o objetivo foi avaliar o efeito da combinação da farinha GP e da farinha de sorgo (SF) por extrusão e o consequente impacto sob os antioxidantes nos produtos finais. Foram utilizadas as seguintes proporções de inclusão GP/SF, (10/90, 15/85, 20/80). As misturas com conteúdo de umidades de: 15, 17, e 19%, foram processadas considerando as seguintes temperaturas na última zona de aquecimento: 120, 130 e 140 °C. Os extrudados foram avaliados quanto a propriedades físicas e químicas. De acordo com os resultados, as melhores condições de processamento foram para o tratamento com 15% de GP, a 120 °C e 17% de umidade de processamento apresentou atividade antioxidante, ORAC, de $37,889 \pm 0,32$ ($\mu\text{mol Trolox.g}^{-1}$), e o tratamento com 20% GP a 140 °C e 19% de umidade apresentou atividade antioxidante, ABTS, de $12,222 \pm 0,14$ ($\mu\text{mol Trolox.g}^{-1}$). O teor de antocianinas foi de 138,31 $\pm 0,11$ (mg cianidina-3-glicosídeo.100 g $^{-1}$) e os fenólicos totais: 307,95 $\pm 0,11$ (mg catequina.100 g $^{-1}$), indicando valores importantes de bioativos nos extrudados. O índice de absorção de água foi de $38,99 \pm 0,19$ g de gel. g $^{-1}$ matéria seca, valores suficientes para o preparo de bebidas no café da manhã ou em mingaus a fim de contribuir para a saúde do consumidor.

Palavras-chave: Subproduto, Extrusão termoplástica, Arroz, Bagaço de uva, Sorgo.

GENERAL ABSTRACT

FONTOURA, Laís Martins. **Development and Physical-chemical Characterization of Extruded Flours of Rice and Colored Sorghum with Grape Peel.** 2023. Thesis (Doctorate in Food Science and Technology). Instituto de Tecnologia, Universidade Federal Rural do Rio de Janeiro, Seropédica, RJ. 2023.

The food processing industries, for the most part, generate a significant amount of by-products, many of which, by not having systems for their use, result in disposal into the environment, causing unwanted contamination in several areas, with consequences and damage to the population. Particularly, the grape production chain, in 2020 reached around 80 million tons in the world. Considering that on average around 20-25% corresponds to grape pomace, it will be around 15.6 million tons/year and 20% corresponds to grape peel (GP). In this sense, there is a need to implement policies that include ways to solve this problem and avoid its disposal into the environment. There is a large number of activities, whether agro-industrial, pharmaceutical, bioactive transformation, food processing, etc., which are taking advantage of the different properties, mainly nutritional and nutraceuticals, that this by-product has. In recent years, the number of works has grown, emphasizing the importance of using GP as a way to add value, reduce disposal in the environment and use this resource as a source for the extraction of many bioactive compounds and essential oils, among others. As a bioactive agent, several publications highlight the results of great benefits for human health, such as, for example, being rich in antioxidants, it can help fight free radicals in the body, help control chronic diseases, such as hypertension, high cholesterol, diabetes, promoting healthy aging. Scientific work has shown that it can act as an anticancer agent. With regard to the various forms of transformation of by-products, thermoplastic extrusion has proven to be an effective tool in obtaining various products, whether inputs or finished products ready for immediate consumption. This is because it offers significant advantages: low cost per part, flexibility of operation in hot extrusion, post-run changes are easy because the product is still heated, continuous operation, high production volumes, the use of many types of raw materials, good mixing (composition), finished products with good surface. There are certain foods, when processed by extrusion, – cereals, for example – that can be prepared with different degrees of cooking, allowing different functional properties. In this thesis work, with three chapters, the first is a review that deals with grape pomace and its use as a source of fiber and antioxidant and its relationship in industrial, economic and social activity. In the second chapter, an article already published, deals with the enrichment of rice flour with grape pomace, using thermoplastic extrusion technology. In the third chapter, an article already published, deals with the impact on the antioxidant activity, in the extrusion of colored mixtures of sorghum flour, with the addition of grape skin. A Brabender 19/20 DN single screw extruder was used for the experiments. The screw configuration was a compression ratio of 3:1; with a circular matrix of 3 mm in diameter. The screw speed, humidity and GP percentage were monitored according to the experimental design for each case, either using GP with rice flour or GP with sorghum flour. The extrudates were dried in a dryer with forced air recirculation. The extrudates were then used for physical and chemical characterizations to verify the effects of the parameters established in each experimental design. The results referring to the processing of formulations with GP/Rice flours (15/85, 20/80 and 25/75%, respectively), resulted in that higher percentages of GP in the formulation and screw speed create higher values in the longitudinal expansion index (LEI). This effect may be due to a reduction in viscosity and causing less starch conversion. By increasing screw speed, the water

solubility index (WSI) was increased. Grape skin showed a negative effect on the extruded flour, by improving the starch-reduction interaction and consequently reducing solubility. Color is an important product parameter for consumers. The grape skin flour was darker and the control lighter due to the absence of grape skin. Thus, by increasing the grape skin content, the color of the extrudates became darker, indicating that the grape skin had a strong effect on the color of the extruded flours. The results obtained demonstrated that the incorporation of grape skin in rice is feasible. However, it is necessary to make some adjustments in the processing parameters to obtain a product.

Keywords: By-product, Thermoplastic extrusion, Rice, Grape pomace, Sorghum.

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LIST OF ABREVIATIONS AND SYMBOLS

ABTS	2,2'-azino-bis (3-etylbenzotiazolin) 6-ácido sulfônico
λ_{\max}	Maximum absorption wavelength
ϵ	Molar absorptivity
XX_1	Proportion of grape peel flour
XX_2	Barrel temperature
XX_3	Feed moisture
ASH	Ash content
PRO	Protein content
LIP	Lipid content
CHO	Carbohydrate content
BDV	Breakdown viscosity
SBV	Setback viscosity
BD	Bulk density
SEI	Sectional expansion index
LEI	Longitudinal expansion index
VEI	Volumetric expansion index
μL	Unit of volume: microliters (10^{-6} L)
μm	Unit of length: micrometers (10^{-6} m)
ρ_e	Extrudate density
M_o	Initial moisture
M_e	Extrudate moisture
D	Extrudate diameter
D_o	Diameter of the die
ρ_d	Melt density
M_d	Melt moisture content
SS	Screw speed
FM	Feed moisture
GS	Grape peel
SS×FM	Interaction effect of screw speed and feed moisture
SS×GS	Interaction effect of screw speed and grape peel
FM×GS	Interaction effect of feed moisture and grape peel
β_o	Regression coefficient mean
WSI	Water solubility index
WAI	Water absorption index

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INTRODUÇÃO GERAL

A produção mundial total estimada de uvas em 2020 foi de 78 034,332 toneladas, a qual teve um aumento de 1,3% em relação às 77 000,008 toneladas em 2019. A China foi o maior produtor de uvas, respondendo por 18,9% da produção global. A Itália ficou em segundo lugar com 10,5%, seguida pela Espanha com 8,7% (FAOSTAT, 2022). Considerando os diferentes processos industriais da uva, como as vitivinícolas e a indústria do suco, volumes significativos dos subprodutos resultantes também são gerados. Nem todas as indústrias que se beneficiam da uva possuem sistemas de processamento de subprodutos resultantes de seus processos de fabricação. Considerando que em média cerca de 20-25% corresponde ao bagaço de uva (GP), serão cerca de 15,6 milhões de toneladas/ano de subproduto.

O bagaço de uva, composto por resíduos da casca, semente, engaço e polpa, é o maior subproduto da indústria do vinho e suco de uva, rico em compostos bioativos. Geralmente é subutilizado na compostagem e na alimentação animal, ou descartado no meio ambiente. Adicionar casca de uva à alimentação pode ser uma forma de agregar valor ao produto, enriquecendo o produto e promovendo uma saúde melhor, contribuindo com o meio ambiente. Hoje, diversas indústrias estão utilizando o bagaço de uva como forma de aproveitar a riqueza de seus bioquímicos, principalmente antioxidantes.

Os antioxidantes têm se tornado muito populares além de enriquecimento de alimentos, estabilização, mau gosto e desodorização, nos campos tecnológicos como encapsulamento, filme comestível e embalagens, estudos in vivo em animais e plantas. Assim, os antioxidantes sempre causaram uma impressão indelével em áreas como especialmente alimentos, cosméticos, farmacologia e medicina. Como pode ser entendido pelos estudos, a ingestão diária de fontes naturais de antioxidantes é muito importante na prevenção do estresse oxidativo, pois tem muitos efeitos positivos em nossa saúde.

Os antioxidantes são grupos de compostos que neutralizam os radicais livres e as espécies reativas de oxigênio (ROS) na célula (ABUAJAH et al. 2015). A atividade antioxidante em alimentos e bebidas tornou-se uma das características mais interessantes da comunidade científica. Os antioxidantes fornecem proteção contra os danos causados pelos radicais livres e desempenham papéis importantes no desenvolvimento de muitas doenças crônicas, incluindo doenças cardiovasculares, envelhecimento, doenças cardíacas, anemia, câncer, inflamação.

Neste trabalho de tese, com três capítulos, o primeiro é uma revisão do bagaço de uva e sua utilização como fonte de fibra e antioxidante e sua relação na atividade industrial, econômica e social.

No segundo capítulo, artigo já publicado, trata do enriquecimento da farinha de arroz com bagaço de uva, utilizando a tecnologia de extrusão termoplástica.

No terceiro capítulo, um artigo já publicado, trata do impacto na atividade antioxidante após a extrusão de misturas coloridas de farinha de sorgo com adição de casca de uva.

Um grande número de artigos menciona as qualidades e usos do bagaço de uva. Alguns o utilizam como complemento de enriquecimento alimentar, outros formulam pós de bagaço de uva com outras farinhas e passam pelo processo de extrusão como forma de mesclar ambos, obtendo outro produto com determinadas propriedades tecnológicas. Nas indústrias farmacêuticas, incluem corantes, antimicrobianos, modificadores de textura e fortificantes, extratos, seja da semente da uva ou da casca da uva, com diversas utilizações (MONTEIRO et al., 2021).

De acordo com ZEHIROGLU & SARIKAYA (2019) os antioxidantes tornaram-se compostos cientificamente interessantes devido aos seus muitos benefícios, como anti-envelhecimento e anti-inflamatório. Ainda hoje, é muito utilizado em alimentos, em produtos

farmacêuticos, em cosmética etc. Na tecnologia de alimentos, os antioxidantes são adicionados para enriquecer os alimentos e eliminar os problemas de oxidação. Os antioxidantes naturais também foram incluídos nos estudos de encapsulamentos, usados para preservação e estabilização de componentes alimentares. Desta forma, estudos para determinar as atividades antioxidantes de alimentos naturais e seus componentes continuam sendo importantes.

Várias pesquisas mencionaram que o bagaço de uva é rico em compostos fenólicos, que são metabólitos secundários da planta, mas também são uma parte importante dos nutrientes das plantas. Alimentos ricos em polifenóis são amplamente estudados devido aos seus potenciais efeitos positivos. Os polifenóis mostraram várias bioatividades positivas, como propriedades anticarcinogênicas. Os mais importantes nas plantas são os flavonoides, ácidos fenólicos e estilbenos. As estruturas químicas podem variar de moléculas muito simples a moléculas muito complexas. Os ácidos fenólicos formam cerca de um terço dos fenóis dietéticos que podem ser encontrados em formas livres e ligadas em plantas e são conhecidos como potentes antioxidantes.

Por outro lado, em relação às diferentes formas de transformação dos subprodutos, a extrusão termoplástica tem se mostrado uma ferramenta eficaz na obtenção de diversos produtos, seja como insumos ou produtos acabados prontos para consumo imediato. Isso porque oferece vantagens significativas: baixo custo por unidade, flexibilidade de operação, alterações fáceis pós-extrusão dado que o produto ainda está aquecido, operação contínua com altos volumes de produção, uso de tipos diversos de matérias-primas e extrudados com bom acabamento superficial. Certos alimentos como os cereais, quando processados por extrusão, podem ser preparados com diferentes graus de cozimento. Isso gera uma gama de produtos intermediários (pellets após desidratação adequada), os quais são comercializados para uso posterior, como no caso de produtos expandidos por fritura ou cozimento em micro-ondas. Graus de transformação caracterizados pela elevada absorção de água do extrudado, podem ser usados na obtenção de farinhas pré-cozidas, multigrãos ou não, para utilização no preparo de mingaus, sopas instantâneas, ou como insumo no preparo de outros produtos alimentícios. Dentre os maiores graus de transformação do material amiláceo, sejam os cereais individuais – farinha de arroz ou de milho, por exemplo – ou as misturas, estão o preparo das farinhas solúveis, utilizadas no preparo de bebidas instantâneas.

Nesse sentido, surgiram diferentes formas de utilização do bagaço de uva, seja integralmente ou separando-a em cascas, sementes e engaços. Nos capítulos finais desta Tese foram utilizados dois cereais com a casca de uva: o arroz e o sorgo, processados por extrusão. A mistura com arroz, visou enriquecer uma farinha pré-cozida, utilizando a casca de uva, na tentativa de agregar valor, seja do ponto de vista nutricional ou comercial.

A utilização do sorgo colorido foi justificada pelo fato de ser um cereal não comercial e, praticamente, não utilizado para consumo humano no Brasil. Além disso, essa variedade também se caracteriza por possuir uma quantidade significativa de compostos fenólicos. Desta forma, a agregação de valor, pela significativa presença de compostos fenólicos nas farinhas resultantes dos tratamentos realizados, com a possibilidade destas farinhas misturadas com casca de uva pode ser utilizada de diversas formas, como já mencionado.

OBJETIVO PRINCIPAL

Elaborar farinhas mistas, utilizando casca de uva com farinhas de arroz e sorgo, através do processamento por extrusão termoplástica.

OBJETIVOS ESPECÍFICOS

Desenvolvimento e caracterização físico-química de farinhas mistas de arroz e casca de uva mediante cozimento por extrusão, e sua utilidade para possibilidades futuras.

Avaliar o efeito da combinação de farinha de casca de uva (*Vitis vinifera* L.) e da farinha colorida de sorgo BR305 mediante cozimento por extrusão, e o consequente impacto nos antioxidantes do produto final.

1 INTRODUCTION

The food processing industry generates a large amount of waste by-products and, consequently, when not properly treated, can affect the environment. To minimize this problem and value-added to new products, the use of by-products can be advantageous, due to their nutritional composition, containing high contents of antioxidants, fibers, sugars, and minerals, among other components that can improve health when consumed. One of these by-products is the waste from grape juice and wine production: grape pomace (GP) or grape flour. This is because a considerable number of works using GP, in different areas, such as technology, science, and medicine, have considered this material very promising (ABREU et al., 2019; BALDÁN et al., 2021; BOFF et al., 2022; CAETANO et al., 2022).

It is evident that the consumption of GP pure, as it is, is not feasible, given its characteristics, not only because it is a powder, but also because of its typical flavor. In this sense, there is a need to associate this ingredient with another products, such as some cereals, which it can be combined and thus be feasible to consume allowed a unique combination of antioxidants accounts for many of its health benefits. For red GP extract, for example, benefits include supporting heart health, cholesterol level management, antioxidant and anti-inflammatory support for the brain and the body's ability to manage healthy blood sugar levels (SABRA; NETTICADAN; WIJEKOON, 2021). Thermoplastic extrusion, with adequate ratios, can facilitate fusion with starchy materials. Extruded grape pomace and rice, as well as extruded grape pomace and sorghum, could be important ingredients in the food industry due to their unique functional and nutritional properties according to the proportionality between GP and cereal flour, according to the treatment intensity during the extrusion process. The use of grape pomace in food products will be able to provide various health benefits.

Grape pomace is a rich source of polyphenols, which are powerful antioxidants that have been shown to have a positive impact on human health. Extruding grape pomace with rice or sorghum can enhances the functional properties of the final product and improves its nutritional profile. Rice and sorghum are staple crops widely consumed globally. They are rich in carbohydrates and provide essential nutrients such as fiber, vitamins, and minerals.

When combined with grape pomace, these grains can be used to produce functional food products with improved nutritional value, texture, and taste (FONTOURA; ASCHERI; BAZAN-COLQUE, 2022; FONTOURA; ASCHERI; VARGAS, 2019). These authors have concluded that there is a great possibility using extruded grape pomace and, rice or sorghum could be used as a base ingredient, in the preparation of different foods that include: drinks, baby foods, elderly foods and/or special foods, in a variety of food products, including cereal-based snacks, breakfast cereals, bread, biscuit, pasta, and snacks among other alternatives. The use of extruded grape pomace and rice or sorghum in food products can help to improve the overall healthfulness of the diet and provide consumers with a nutritious and delicious alternative to traditional food products.

2 GRAPE POMACE

Currently, there are several activities that allow the use of this important by-product and are part of the circular bioeconomy, as described by CHOWDHARY et al. (2021), in Figure 1.

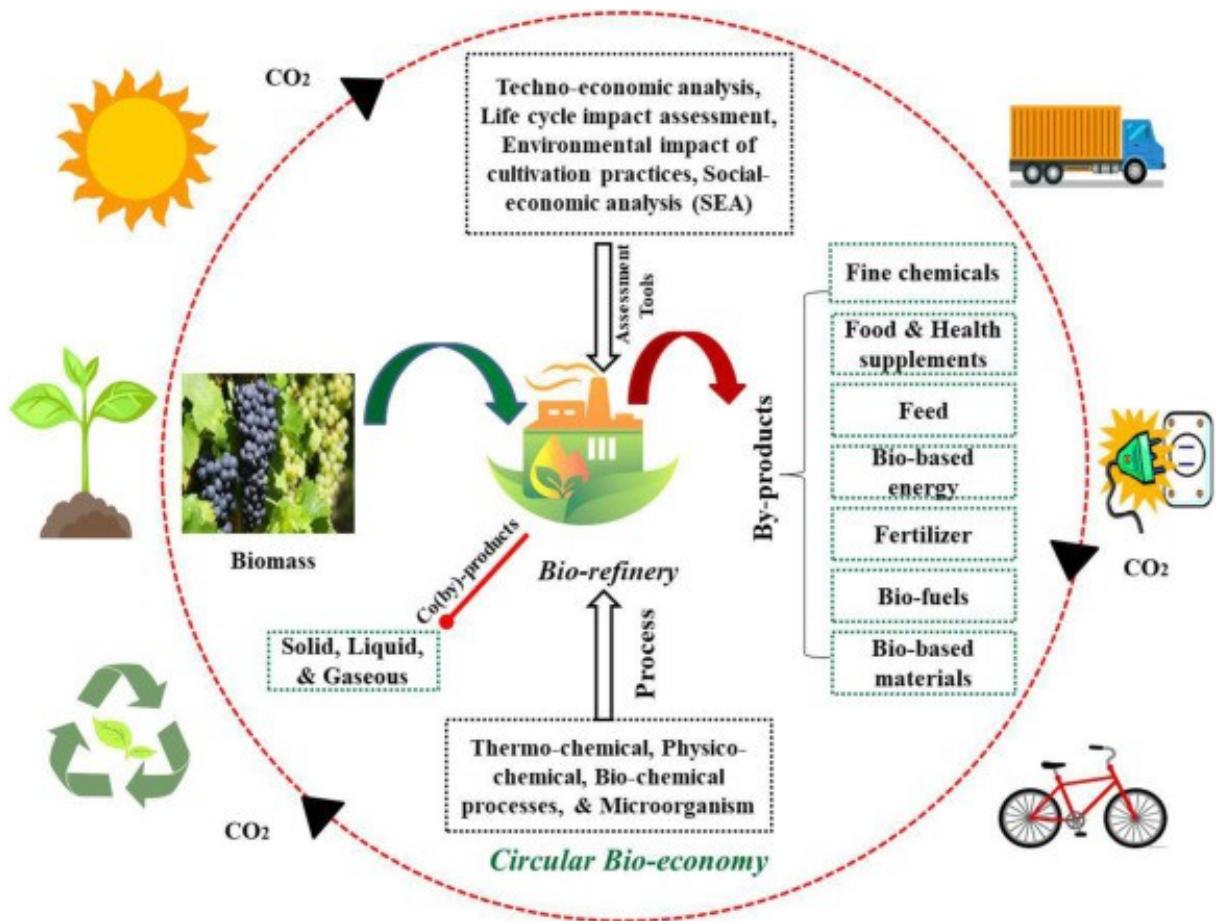


Figure 1. The role of grape pomace in the circular bioeconomy. Source: CHOWDHARY et al. (2021).

According to CHOWDHARY et al. (2021), bioeconomy is the science that studies biological systems and natural resources combined with the use of new technologies to create more sustainable products and services. It certainly applies to the large volume of grape production in the world. The estimated total world production for grapes in 2020 was 78,034,332 metric tons, up by 1.3% from 77,000,008 tons in 2019. China was the largest producer of grapes, accounting for 18.9% of global production. Italy came second at 10.5%, followed by Spain at 8.7% (FAOSTAT, 2022).

Despite higher supplies, imports are expected to ease slightly to 3.5 million tons on reduced demand from the European Union and China. According to a report by the United States Department of Agriculture (USDA), there is an important volume of GP that may have different destinations, in the various economic activities already established with the use of this important by-product. However, for the proper use of this GP material, there is a need to avoid further deterioration and/or contamination, due to several aspects intrinsic to this consequence

of the inheritance of grape juice. For example, improper processing of the material, which may cause fermentation, attack by entities from the external environment, checking the quality and validation of the by-product. This implies that there must be a strategy, in which this residue is soon transferred to the place where it will receive its transformation. In many cases, business entities that received the waste, considering that any treatment without adequate cost/benefit, dispose of it in the environment. This is because most of the by-products have high levels of moisture, which favors rapid deterioration. For storage, it would have to be dehydrated, implying high-energy costs and collective facilities, which sometimes were not considered in the company's structure. During grape processing, a whole grape is pressed to produce wine or juice. The pomace is waste, being, mainly, discarded in landward, animal feed or incineration (MONTEIRO et al., 2021). These practices are not economically viable because not all essential nutrients are present in grape pomace, being necessary repositioning. The use of animal feed is limited by antinutritional factors. Besides causing environmental problems such as water pollution, attracting disease-spreading vectors (DWYER; HOSSEINIAN; ROD, 2014).

Contributing to reducing waste discarded in landfill, an environmental concern, grape pomace is safe for use and could be added in food industrial processes, as a byproduct. Significant number of works described grape pomace as a source of dietary fiber rich in bioactive compounds, utilized in many ways (DENG; PENNER; ZHAO, 2011; MONTEIRO et al., 2021; SPIGNO; MARINONI; GARRIDO, 2017).

Around 20–25% of the total grape weight is grape pomace (DWYER; HOSSEINIAN; ROD, 2014; SPIGNO; MARINONI; GARRIDO, 2017). Major fractions of grape pomace are the seeds and seedless. Seedless is considered residual pulp, peel, and stem.

Grape pomace consists of GP and grape seeds, showing in Figure 2 different compounds from this byproduct. However, these ratios may differ according to some factors such as grape variety, edaphoclimatic environments, geographic origin, ripening time, and technology of grape processing (DENG; PENNER; ZHAO, 2011).

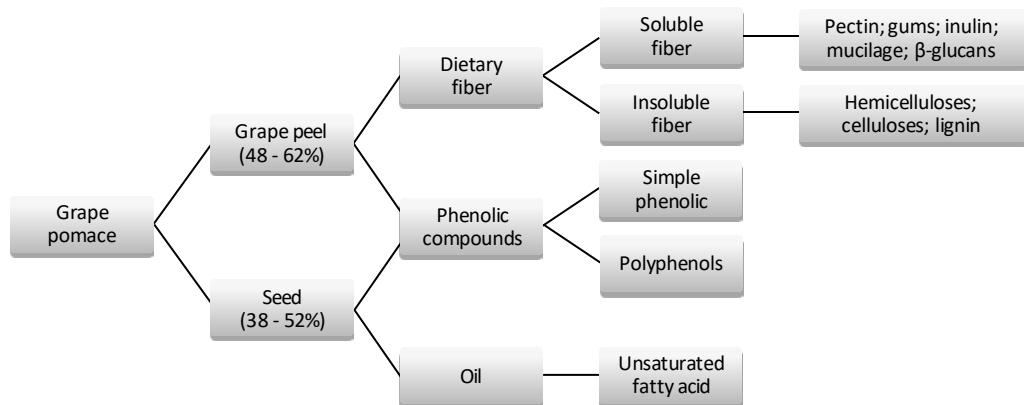


Figure 2. Main grape pomace fraction. Source: DENG; PENNER e ZHAO (2011).

GP is composed of 5-12% protein, 2-8% ash and soluble sugars between 1% to more than 70%. Indeed, this range depends on the processing and overall, for the quantity in fiber and phenolic compounds. Insoluble dietary fiber corresponds to 98.5% of total dietary fiber (DENG; PENNER; ZHAO, 2011).

The potential use of grape pomace is wide, as an additive in food and pharmaceutical industries (MONTEIRO et al., 2021), including the use as antioxidant, colorant, antimicrobial, texture-modifying agent and fortifying products (SPIGNO; MARINONI; GARRIDO, 2017).

It is acknowledged that antioxidants have a positive correlation with antitumor, anti-aging, antimicrobial, and anti-inflammatory effects (SIES and JONES, 2020; PEIXOTO et al.,

2018). Many researches have described that grape has bioactive compounds that plays an important role in health, such as antioxidant (ANDRADE et al., 2019; LIU et al., 2018), anti-

inflammatory (BARONA et al., 2012), anticancer activity (BADR EL-DIN; ALI; ABOU-EL-MAGD, 2019; YANG; XIAO, 2013), cardioprotective (SVEZIA et al., 2020; XIA et al., 2010), antidiabetic (CISNEROS-YUPANQUI et al., 2023; IRAK et al., 2018; OLADIRAN; EMMAMBUX, 2018), and gut microbiota regulating (ABUAJAH; OGBONNA; OSUJI, 2015; HAN et al., 2020).

These bioactive compounds are, mainly, polyphenols that include: proanthocyanins, flavonols, phenolic acids and stilbenes (XIA et al., 2010; YANG; XIAO, 2013). Mainly, grape seed is constituted of proanthocyanidins, grape peels in anthocyanins (DE OLIVEIRA et al., 2019; ZHAO; SIMON; WU, 2020).

The cultivar, climate and agricultural practices are factors that can modify the chemical composition, including profile phenolic compounds and antioxidant capacity of grapes (MONTEIRO et al., 2021; SAURA-CALIXTO, 1998).

The range of bioactive compounds in dry grape pomace is about 50-75% of dietary fiber, 15-30% of non-extractable polyphenols and 1-9% of extractable polyphenols (SAURA-CALIXTO, 1998).

Figure 3 shows the antioxidant properties of polyphenolic compounds. The most important grape pomace compositions are fibers, phenolic compounds, colorants and minerals. The main grape pomace antioxidant potential comes from phenolic compounds, colorants and anthocyanins. The oily fraction has unsaturated fatty acids, colorants, and minerals (GARCÍA-LOMILLO; GONZÁLEZ-SANJOSÉ, 2017).

Dietary fiber can be described as an edible material none hydrolyzed by human enzymes. In humans, the small intestine cannot absorb fibers and the fermentation process is developed on the large intestine by gut microbiota (LATTIMER; HAUB, 2010). Dietary fiber is divided in soluble and insoluble fractions.

Soluble dietary fiber, generally count pectin, gums, inulin, mucilage, and β -glucans. Soluble dietary fiber in human gut controls satiety, promotes fermentation through colonic bacteria, modulates gut microbiota, and generates short-chain fatty acids. Also produces gel capable of decreasing blood glucose and cholesterol levels (MUDGIL, 2017).

While, insoluble dietary fibers are hemicellulose, cellulose, and lignin (AHMAD; KHAN, 2020). Insoluble dietary fiber in the human gut increases fecal bulk, catches toxins, promotes intestinal mobility, increases defecation regularity, and decreases transit time (ELLEUCH et al., 2011).

The addition of dietary fiber to a product can modify technological properties of dietary fibers such as water and oil holding capacity, viscosity, and solubility. These modifications occur due to the chemical structure of component polysaccharides, porosity, particle size, temperature, ionic form, and mechanical stresses on fibers (ELLEUCH et al., 2011).

It should be emphasized that a higher grape pomace concentration makes higher product fortification with modified textural and sensory properties (ANTONIĆ et al., 2020).

Sant'anna et al. (2014) investigated the effect of GP powder inclusion (2.5, 5, and 7.5%) in pasta. Insignificant modifications were observed on water absorption and cooking loss. Despite improving nutritional quality with total phenolic, condensed tannins, monomeric anthocyanin and antioxidant capacity, sensory properties like appearance, aroma, flavor and aftertaste were reduced.

(BENDER et al., 2017) concluded that GP flours might be used as an alternative to increasing the dietary fiber content of muffins without having a negative effect on the sensorial properties of the products. The inclusion of 5, 7.5, and 10% ratios of these flours affected the texture, mainly the hardness, which increased as the levels of addition increased, color and total dietary fiber (TDF) content, mainly soluble dietary (SDF).

Altan et al. (2008) studied texture properties in grape pomace-barley extruded and concluded that rising grape pomace addition, and raised brittleness, cause less crispy extrudates

increase in peak force. Increasing GP initially decreased sectional expansion index (SEI) of extrudates up to 6% after that SEI increased lightly with respect to the quadratic effect of pomace level.

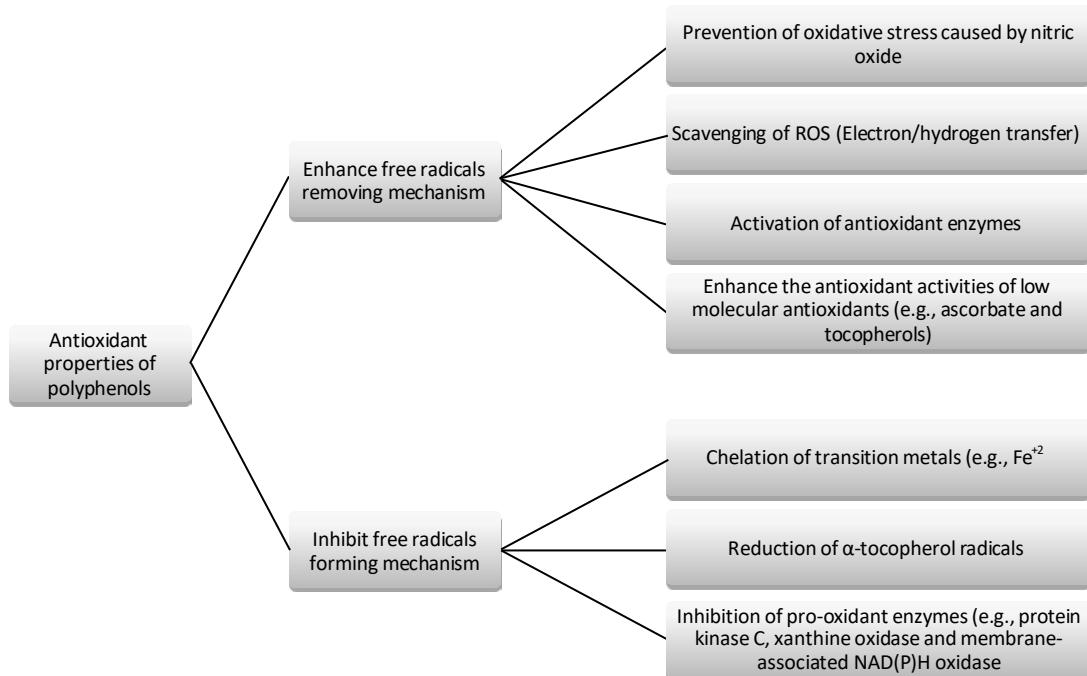


Figure 3. Antioxidant properties of polyphenolic compounds. Source: ABDEL-MONEIM et al. (2020).

3 PHENOLIC COMPOUNDS

In Table 1, the proximal composition of organic GP and corresponding phenolic compounds according with ABREU et.al, (2019).

Table 1. Centesimal composition of organic grape peel flour and Phenolic compound.

Proximal composition		Phenolic compound (mg/100g)
Moisture (g%)	8.72 ± 0.02	Resveratrol 54.27 ± 0.79
Ash content (g%)	3.46 ± 0.01	Epicatechin 43.94 ± 0.90
Total lipids (g%)	5.84 ± 0.01	Chlorogenic acid 35.70 ± 1.47
Protein (g%)	11.21 ± 0.02	Quercetin 14.40 ± 0.26
Carbohydrate (g%)	20.73 ± 0.03	Kaempferol 6.96 ± 0.18
Total dietary fiber (g%)	50.10 ± 0.01	Gallic acid 4.75 ± 0.09
Total caloric value (kcal%)	180.22 ± 0.25	Catechin 4.39 ± 0.06

Source: Adapted from ABREU et.al (2019).

In the formulation of products with GP inclusion, the components described in Table 1 will depend on the amount included, as well as the type of thermal treatment adopted. For example, the extrusion-cooking process, according to adopted parameters, especially when it comes to the melting of ingredients in order to obtain a pre-cooked mixed flour, causes these values to decrease. However, even so, there is a reasonable number of antioxidants (FONTOURA, 2022).

Among the results made in HPLC (Table 2) of several extracts of phenolic contents presented by Shrikhande (2000), procyanidins are abundant in seeds and transferred to red wine during fermentation of red must. GP extracts are likely to be relatively richer in procyanidins and anthocyanins and may have lower concentrations of cinnamic acids.

Several aspects have evolved in relation to GP exploration, in the case of GP extract, Dataintelo (2023), reported issues such as political, economic, social, technological, environmental, and legal. In the political sphere, GP extract market is affected by the political environment of the countries in which it operates. Governments of different countries have different regulations and policies that affect the market. This includes taxation, import/export regulations, health and safety regulations, and labor laws. Understanding these regulations and policies is essential for the market to operate efficiently and effectively. Referring to the economic part, the economic environment of the countries in which GP extract is produced and sold has a significant impact on the market. This includes exchange rates, inflation, consumer income, and consumer spending. Understanding the current economic conditions is important for the market to successfully launch and expand.

About social, the environment is also an important factor to consider when looking at the GP extract market. This includes consumer attitudes and beliefs, as well as trends in consumer preferences. Understanding consumer attitudes and beliefs can help the market position and market its products in the most effective way.

Technology plays an increasingly important role in the GP extract market. This includes the use of advanced machinery and processes to improve the efficiency and effectiveness of production.

Table 2. Comparison of phenolic compounds in high anthocyanin powders.

Empty Cell	High anthocyanin grape extract	Bilberry extract	Anthocyanin grape extract	Grape extract
Total phenols (g GAE/100 g)	56.2	60.3	40.2	57.1
Total anthocyanins (g/100 g)	35.3	42.1	10.5	2.9
Sulfur dioxide (ppm)	<10	ND	ND	533
Gallic acid (mg/g)	2.9	0.8	1.4	0.1
Monomeric flavan-3-ols (mg/g)	1.2	3.8	5.7	20.4
Oligo proanthocyanidins (mg/g)	81.1	91.9	130.3	292.0
Phenolic acids (mg/g)	3.1	23.1	1.5	0.2
Resveratrol (mg/g)	<0.1	<0.1	<0.1	0.2
Flavonols (mg/g)	41.4	56.9	14.4	14.4

Source: SHRIKHANDE (2000)

Technology can also be used to improve the quality and safety of the product. Understanding the latest technological advances and how to use them is essential for the market to remain competitive. Referring at environmental impact of the GP extract market is also an important consideration. This includes the impact of production on the environment, as well as the use of renewable resources and sustainable production practices. Understanding the environmental impacts of the market is essential for ensuring the market is operating in a sustainable manner.

Another important aspect is the legal environment when looking at the GP extract market. This includes laws and regulations related to the production and sale of the product. Understanding the legal environment of the countries in which the market operates is essential for the market to remain compliant.

Grape peel extract

GP extracts, known in the pharmaceutical, beverage, and cosmetic industries, provide high-added value. The global GP extract market size was projected to grow from USD 1.81 billion in 2021 to USD 2.5 billion in 2025. The growth of this market can be attributed to the rising demand for GP extract from the food and beverage industry and increasing awareness about the benefits of GP extract among consumers. GP extract is a natural ingredient that is derived from the skin of grapes. It is rich in antioxidants and has many health benefits.

Some of the health benefits of GP extract include: reducing inflammation, protecting against heart disease, improving brain function, and preventing cancer. GP extract can be taken in pill form or applied topically to the skin.

Liquid GP extract is a concentrated form of extract that is typically sold in liquid form. This type of GP extract is usually made using a process known as supercritical fluid extraction, which uses high pressure and temperature to extract the desired compounds from the grape skins. Liquid GP extract is generally considered to be safe when consumed in moderate amounts.

Solid GP extract is an ingredient made from the skin of grapes. It's a common ingredient

in supplements and cosmetics. GP extract is rich in antioxidants and other nutrients. Some people take it for its potential health benefits, including heart health, anti-inflammatory effects, and cancer prevention.

Powder GP extract is a powdered form of GP extract. It is made from the skins of red grapes and is rich in antioxidants, including resveratrol. Powder GP extract is used as a dietary supplement and in cosmetics and skincare products. Powder GP extract has numerous potential health benefits, including reducing inflammation, protecting against heart disease and cancer, and improving brain function. Additionally, powder GP extract can be used to add flavor to food or as a natural colorant.

Applications of grape peel extract

Based on application, the market is segmented into food and beverage, pharmaceutical, cosmetic and personal care.

Food and beverages: GP extract is used in food and beverages as a coloring agent in various food and beverage products such as jams, jellies, wines, juices, spirits. It is also used as an antioxidant and preservative in food products. GP extract is added to wine for its astringent taste. It is also used in the preparation of jams, jellies, and other fruit preserves. Nowadays, the application of grape pomace in the production of fortified foods has gained increasing scientific and industrial interest, owing to its considerable promise. Many studies have revealed that the addition of grape pomace to a wide range of food products, such as plant, dairy and meat products, could improve the nutritional composition of the final products and increase their values (18, 101). Plants food like muffins, biscuits, bread, cookies, pasta, noodles, pancakes and extruded cereals with inclusion of grape peel showed increased contents of dietary fiber and polyphenols, as well as improved antioxidant activity (101). Moreover, studies showed that meat of fish products fortified with grape pomace could inhibit lipid oxidation and prolong storage or shelf life (102,103).

However, the use of grape pomace in high concentrations might negatively affect the textural and sensory properties of final products.

Pharmaceutical: GP extract has a number of benefits when it comes to pharmaceuticals. For one, it is an antioxidant. This means that it can help to protect cells from damage caused by free radicals. Additionally, GP extract can help to reduce inflammation and pain. It has also been shown to have anti-cancer properties. Finally, GP extract can help to improve the appearance of skin and hair. In terms of specific pharmaceutical uses, GP extract can be used to treat a variety of conditions such as Alzheimer's disease, arthritis, diabetes, and high cholesterol.

Cosmetic and personal care: The use of GP extract in cosmetic and personal care products has grown in popularity in recent years. This growth can be attributed to the many benefits that GP extract offers for the skin. These benefits include its ability to protect the skin from damage, its ability to improve the appearance of the skin, and its ability to provide antioxidant protection.

The market of derivate GP extract is segmented into North America, Latin America, Europe, Asia Pacific, and Middle East & Africa. North America and Europe can be the key revenue-generating regions in the global GP extract market during the forecast period. Probably, due to the growing demand for functional food & beverage and dietary supplements in these regions. The Asia Pacific is anticipated to grow at a rapid pace during the forecast period, owing to increasing disposable income, changing lifestyles, and urbanization in this region. (Dataintelo published report: <https://dataintelo.com/report/grape-skin-extract-industry/17/04/2023>).

4 CONCLUSION AND FUTURE PROSPECTS

GP can currently be considered an excellent by-product, useful in several areas, in order to add value and improve the properties of the products that make it up. Whether as an antioxidant, as a complement to treatments to improve health and various symptoms, proven by medical sciences, technological processes, among other various applications currently practiced in the exploitation of GP. When used as a fiber supplier, it fulfills two roles, including both dietary fiber and insoluble fiber, as well as providing antioxidants, providing greater nutritional value. Certainly, the direct consumption of GP flour is not palatable due to its characteristic, in addition to being astringent. It is also necessary to consider, according to the origin of the GP, the sanitary condition of the material, as it may have a certain microbial load, fungi, or molds, so that it has to undergo heat treatment, for safe consumption. For this reason, one of the ways adopted by some processors is appropriately mixed, depending on the destination of use, with cereal flour or other starchy source, and pre-cooked by extrusion, or its application in the formulation of some foods. On the other hand, it has to be considered that GP when separated from the seed, it also has several uses, after extracting the compounds in isolation and their application in pharmacopoeia, or important industrial uses. For food processors, whose objective is to add significant amounts of fiber to a given product, GP is undoubtedly an important alternative, as it can provide important values of antioxidants, minerals and peculiar sensory characteristics to the final product.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CHAPTER II

ENRICHMENT OF RICE WITH GRAPE PEEL POWDER BY EXTRUSION

Enrichment of Rice with Grape Peel Powder by Extrusion

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ABSTRACT

Following the tendency to reduce food loss and contributing with environment sustainability, generating value-added utilizing food industry residues, this research aims the technological characterization of grape by-product and rice extruded flour. The physical behavior of rice (*Oryza sativa L.*) and grape peel (*Vitis vinifera L.*) extruded flours were investigated. A range of grape peel (15 - 25%), screw speed (100 - 150 rpm) and moisture content (18 - 26%) were studied. The aim of this study was to evaluate the effect of extrusion cooking process in a grape peel powder and the white rice flour addition. The results of bulk density were between 270 and 566 kg/m³; sectional expansion ratio was 2.42 to 6.51; longitudinal expansion ratio was 0.58 to 0.96; volumetric expansion ratio was 2.15 to 4.64; water solubility index was 7.60 to 15.57; water absorption index was 4.35 to 6.82. Results of instrumental color was measured and the range of L* was 26.38 to 37.68; a* was 11.70 to 14.56 and b* was 3.78 to 7.42. The grape peel addiction on extrudates increased the bulk density and longitudinal expansion index. However, decreased on sectional expansion index, volumetric expansion index, water solubility index, water absorption index and luminosity. Results obtained with conditions processing demonstrated the incorporation of grape peel in rice is viable.

Keywords: Extruded, Byproduct, Characterization.

1 INTRODUCTION

The primary source of human foods consumed in many countries are cereal and their derivates. Rice (*Oryza sativa L.*) is one of the global staple foods most important for more than two-thirds world population with a huge cultivation worldwide (GONG et al., 2017; NDJIONDJOP et al., 2010; XU et al., 2016). Therefore, rice issued in many glutens free products and has a large acceptability and a neutral taste and color (DI CAIRANO et al., 2018; MATEJOVÁ et al., 2016).

Grapes (*Vitis spp.*) are one of the most consumed fruits in the world. The winemaking industry generates a lot of waste like peels, seeds and stems. This waste is considerate grape pomace and has an economic and environment impact (FONTANA et al., 2013). It has many bioactive compounds and can be used as a by-product, with added-value products (SÁNCHEZ-TENA et al., 2013).

Mixtures of ingredients are advantageous and each ingredient can contribute to improve the dough or the final product, making the product appealing (DI CAIRANO et al., 2018).

There is a tendency to reduce food loss and waste with environmental sustainability, one way is enrichment food using agro-industrial by-product. It's possible to use pomace and others by-products to enhance nutritional quality, being a good source of fibers, micronutrients and others bioactive compounds (DI CAIRANO et al., 2018; MATEJOVÁ et al., 2016).

Extrusion cooking process is a high-temperature short time (HTST) technology, using mechanic forces and pressure, changing the molecular structure of the starch and protein (SÁNCHEZ-TENA et al., 2013). This technology is also used to improve food by-products (ROMÁN et al., 2017) and develop dietary fiber enriched foods (STOJCESKA et al., 2009).

After the extrusion cooking, the extrudates digestibility is increased and this could be explained by the own process (BRENNAN et al., 2008). The extrusion cooking process may gelatinize and disintegrate the starch, being more accessible to amylolytic hydrolysis and then, rising the starch digestibility (SHRESTHA et al., 2012).

Extrusion cooking was chosen a favorite technology over the conventional techniques because is possible to promote versatile products with different textural properties, like expansion, crispiness and mouthfeel. The technology has high productivity, a short period of cooking process and low costs with operation and energy. In addition, makes better the nutrients bioavailability and digestibility (BRENNAN et al., 2011).

Many studies of fruit by-products were done to create new possibilities using extrusion cooking. MATEJOVÁ et al. (2016) added grape pomace in gluten free biscuits. ALVES et al. (2018) extruded passion fruit shell and rice flour. Extruded rice flour and apple pomace (MEHRAJ et al., 2018). Cereal breakfast extrudates with rice and pomelo rind (SHI et al., 2017). Sugar replacement using citrus fiber extracted from orange pulp on wheat-corn extrudates (PITTS et al., 2016). Cherry pomace and direct expanded corn starch (WANG et al., 2017). OLADIRAN e EMMAMBUX (2018) studied the nutritional and functional properties of extruded cassava-soy composite with grape pomace and concluded that it is possible to develop instant products with health promoting properties, based in starch-rich foods added with grape pomace, using extrusion cooking process.

Follow the tendency of healthier products and sustainable development and also a gluten-free food, the combination of rice and grape peel using extrusion cooking process is a good alternative to formulate new products based in these extrudates flours. The aim of this work was the development of mixed flours of rice and grape peel by extrusion cooking and the usefulness to future possibilities.

2 MATERIALS AND METHODS

2.1 Raw Material

White rice (*Oryza sativa L.*) was purchased in local shops (Rio de Janeiro, Brazil). Grape pomace (Alicante Bouschet) from the production of grape wine was donated by Embrapa (Petrolina – PE, Brazil) and was manually separated and the peels were used in this study. Rice and grape peel were ground, separately, in a Laboratory Mill 3600 disc mill (Perten Instruments, model 2600, Kungens Kurva, Sweden).

2.2 Sample Preparation

The moisture content of the raw materials was calculated and was added water to equalize the moisture, according to the experimental design, shown in Table 1. The blends were stored under refrigeration conditions to balance the moisture, overnight.

2.3 Extrusion Cooking Process

The process was in a single-screw extruder Brabender 20 DN DSE. A feed rate of 3.0 kg/h and the zones of temperatures were 60 °C, 80 °C and 150 °C were constant throughout the process at a pressure of 9-11 MPa. The screw configuration was L/D 1:3 (compression ratio) and included a circular die 3 mm diameter. The screw speed, moisture and percentage of grape peel were not constant and could be verified with the experimental design in the Table 1. After extrusion cooking, the extrudates were dried in a forced-air drier (WTB Binder, Tuttlingen, Germany) at 60 °C for 4 h up to obtain the range of 4 – 7 g/100g moisture. The extrudates were milled in a disc mill, with a particle size of less than 400 µm. The extruded flours were maintained under refrigeration (5 – 8 °C) until further analysis.

2.4 Experimental Design

The experiments were conducted using factorial design 2^3 with four central points. Independent variables were: X1 screw speed (SS, rpm), X2 feed moisture (FM, %) and X3 grape peel proportions (GP, %) and the code levels studied are presented in Table 1.

Table 1. Code levels to independent variables.

Variable	Code Level		
	-1	0	+1
Screw speed (SS, rpm)	100	125	150
Feed moisture (FM, %)	18	22	26
Grape peel (GP, %)	15	20	25

2.5 Bulk Density

Bulk density is measurement of mass and volume. The diameter was measured with a digital caliper (Vonder, Curitiba, Brazil) and the length per unit weight (g) of the extrudates

was determined. Density was calculated by the Equation (1). The methodology was described by ALVAREZ-MARTINEZ; KONDURY e HARPER (1988).

$$\text{Density } (\rho_e) = \frac{4m}{\pi D^2 L} \quad (1)$$

2.6 Expansion Ratio

To determine the expansion ratio, mean a digital caliper was used on 15 samples. Expansion indices: sectional (SEI), longitudinal (LEI) and volumetric (VEI) was calculated by measuring, according with the Equations (2), (3) and (4), respectively

$$SEI = \left(\frac{D}{D_0} \right)^2 \quad (2)$$

$$LEI = \left(\frac{\rho_d}{BD} \right) \left(\frac{1}{REI} \right) \left(\frac{1 - M_d}{1 - M_e} \right) \quad (3)$$

$$VEI = SEI \times LEI \quad (4)$$

where D is the extrudate diameter and D_0 is the diameter of the die. ρ_d was defined to be 1400 g.cm⁻³, the bulk density of the melt. BD is the extrudates density. M_e is the extrudate moisture content and M_d is the melt moisture content. The triplicate measurement was done with 2 g samples in an oven drier at 105°C for 2 hours (ALVAREZ-MARTINEZ; KONDURY; HARPER, 1988).

2.7 Water Absorption and Water Solubility Indexes

The $WWSI$ and $WWAI$ of the samples were determined in quadruplicate as described by ANDERSON (1969). $WWSI$ is the sample mass in supernatant divided by sample mass. Moreover, $WWAI$ is the sample mass with absorbed water divided by sample mass. The results were obtained by the Equations (5) and (6).

$$WWAI = \frac{WWRC}{WW_S - WWRE} \quad (5)$$

$$WWSI = \frac{WWRE}{WW_S} \quad (6)$$

where $WWRC$ is the weight of the centrifuge residue, in g; W_S is the sample weight, in g; and WRE is the weight of the evaporation residue, in g.

2.8 Instrumental Color

A colorimeter CR 400 (Konica Minolta, Osaka, Japan) was used to measure the color of the extruded flours and grape peel powder. The measurements were done in three replications in the CIE-Lab parameters as L^* (whiteness/darkness), a^* (redness/greenness) and b^* (yellowness/blueness).

2.9 Statistical Analysis

Linear model was used and includes means effects and interactions (Eq. 7, 8) to present the values of response based on independent variables function studied.

$$Y = \beta_0 + \beta_1(SS) + \beta_2(FM) + \beta_3(GS) + \beta_{12}(SS \times FM) + \beta_{13}(SS \times GS) + \beta_{23}(FM \times GP) \quad (7)$$

$$\hat{Y} = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \sum_{j \neq i}^2 \beta_{ij} X_i X_j \quad (8)$$

where predict responses; SS : main effect of screw speed (rpm); FM : main effect of feed moisture (%); GP : main effect of grape peel (%); $SS \times FM$, $SS \times GP$ and $FM \times GP$: interactions effects; β_0 : regression coefficient means.

Analysis of variance (ANOVA) test was carried out using the Statistic software version 12.0 (StatSoft, Tulsa, USA) with 5% of significance.

3 RESULTS AND DISCUSSION

The data with regard to rice extrudates with distinct parameters: screw speed, feed moisture and grape peel flour content. For the characterization purpose, bulk density, expansion ratio, WSI, WAI and color analysis were done and responses and real levels were presented in the Table 2.

Table 2. Real levels of extrusion parameters and responses of rice and grape peel extrudates

Run	Real levels			Responses								
	SS rpm	FM %	GP %	BD kg/m ³	SEI	LEI	VEI	WSI %	WAI g/g	L*	A	b
1	100	18	15	373.0±12.0	5.05±0.18	0.67±0.00	3.40±0.11	11.22±0.23	4.55±0.02	34.71±0.19	13.16±0.0	5.65±0.02
2	150	18	15	270.6±10.4	6.51±0.30	0.72±0.01	4.64±0.18	15.53±0.31	5.09±0.02	37.68±0.30	14.56±0.03	7.42±0.02
3	100	26	15	444.5±91.8	4.78±0.96	0.58±0.03	2.77±0.56	13.5±0.25	6.06±0.01	28.96±0.11	12.04±0.81	4.29±0.47
4	150	26	15	513.4±15.6	3.72±0.09	0.64±0.01	2.39±0.07	15.57±0.14	6.82±0.05	27.29±0.65	13.64±0.45	5.16±0.36
5	100	18	25	370.0±10.0	4.68±0.14	0.72±0.01	3.41±0.09	11.57±0.45	4.35±0.04	31.57±0.41	13.71±0.17	5.57±0.05
6	150	18	25	352.1±32.4	4.59±0.19	0.83±0.04	3.73±0.32	12.43±0.09	4.56±0.09	31.04±0.03	14.03±0.08	5.81±0.00
7	100	26	25	566.5±17.9	3.46±0.17	0.62±0.01	2.15±0.08	7.60±0.04	5.64±0.00	26.38±0.46	12.41±0.09	4.14±0.23
8	150	26	25	538.5±9.4	2.42±0.04	0.96±0.01	2.34±0.04	9.04±0.05	4.91±0.01	28.46±0.79	11.70±0.46	3.78±0.21
9	125	22	20	455.1±7.0	4.15±0.07	0.65±0.01	2.72±0.04	10.71±0.01	4.84±0.00	29.73±0.62	12.40±0.07	5.77±0.10
10	125	22	20	494.7±53.0	3.86±0.40	0.70±0.01	2.46±0.25	8.88±0.10	4.79±0.01	29.79±0.18	12.30±0.01	5.41±0.10
11	125	22	20	447.6±23.2	4.06±0.25	0.69±0.02	2.79±0.14	9.22±0.02	4.82±0.00	27.92±0.34	12.89±0.09	5.68±0.02
12	125	22	20	437.9±19.4	4.29±0.20	0.70±0.01	2.84±0.12	9.96±0.10	5.13±0.08	29.24±0.34	12.68±0.35	5.81±0.36

SS: Screw speed; FM: Feed moisture; GP: Grape peel; BD: Bulk density (kg/m³); SEI: Sectional expansion index; LEI: Longitudinal expansion index; VEI: volumetric expansion index; WSI: Water solubility index; WAI: water absorption index. Results are mean standard deviation, n= 15 observations.

Bulk density is related with mass and volume, being inversely proportional to volume expansion index. In the experiment, run 7 and run 2 had the higher and the lower values, suggesting that increasing feed moisture and grape peel content, resulted bulk density increased. Bulk density, feed moisture and grape peel interactions are shown on the Figure 1.

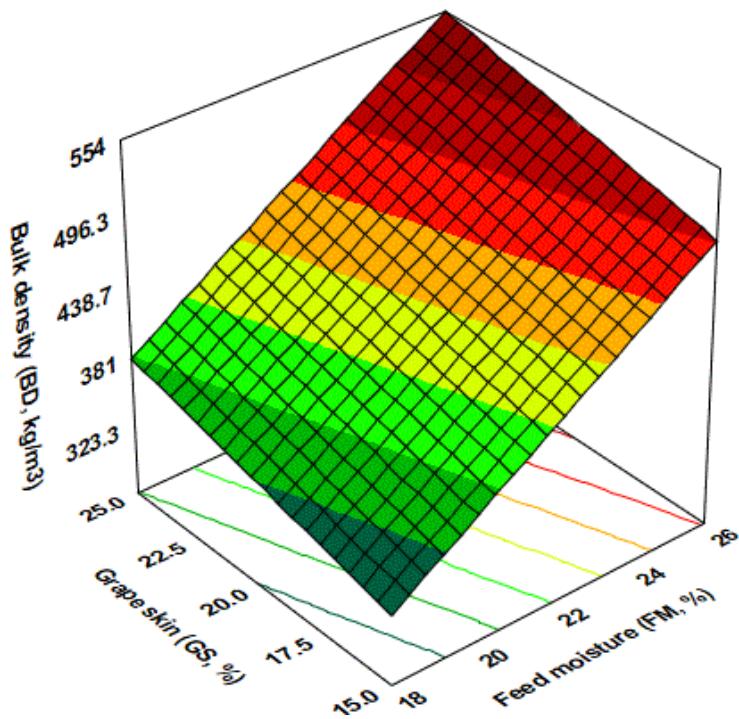


Figure 1. Interaction between bulk density, feed moisture and grape peel on extrudates.

Others extrudates studies with carrot pomace and corn (KAISANGSRI et al., 2016), passion fruit shell with rice (ALVES et al., 2018), citrus fiber with wheat-corn (PITTS et al., 2016) described similar results.

Moisture loss is the comparison between the final product and the mixture before extrusion. Increasing the addition of grape peel flour, the moisture content increased. Probably, the higher amount of dietary fiber presents on grape peel flour absorbed and confined more moisture than white rice extrudates. SHI et al. (2017) reported similar result with brown rice and pomelo rind.

Expansion ratio analysis can be correlated with others analysis to have a product overview characteristic. The samples had a lower expansion ratio in comparison with rice samples, without grape peel addition.

Others studies had the same conclusion, demonstrating association among extrudates and fibers quantity. The products had water retention and the expansion ratio was reduced with increased in density product (BECK et al., 2018; MEHRAJ et al., 2018; SHI et al., 2017; WANG et al., 2017).

Sectional expansion index is the ratio between cross- sectional area of the extrudates and the cross- sectional area of the die (ALVAREZ-MARTINEZ; KONDURY; HARPER, 1988). Both feed moisture and grape peel affected the SEI at all extrusion conditions. The influence of feed moisture and grape peel on sectional expansion index is shown in Figure 2.

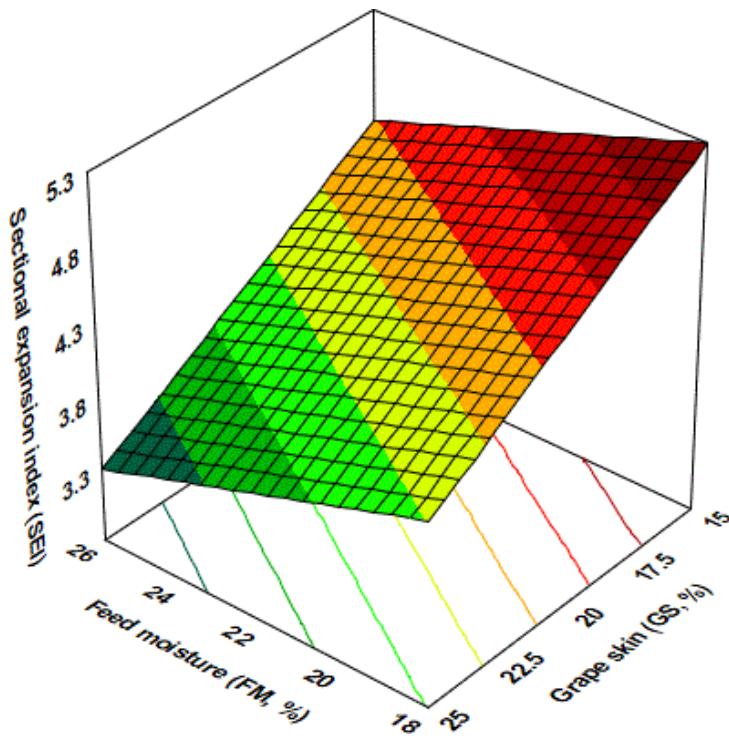


Figure 2. Interaction between sectional expansion index, feed moisture and grape peel.

In the current study, the higher SEI was negative interaction with feed moisture and grape peel. Thus, with the addition of grape peel and the increase the feed moisture made the sectional expansion index decreased. Mainly, extruded blends of pea protein, pea fiber and rice starch had reduced the SEI with the increase of moisture content (BECK et al., 2018).

The effect of screw speed and grape peel on longitudinal expansion index was presented in Figure 3.

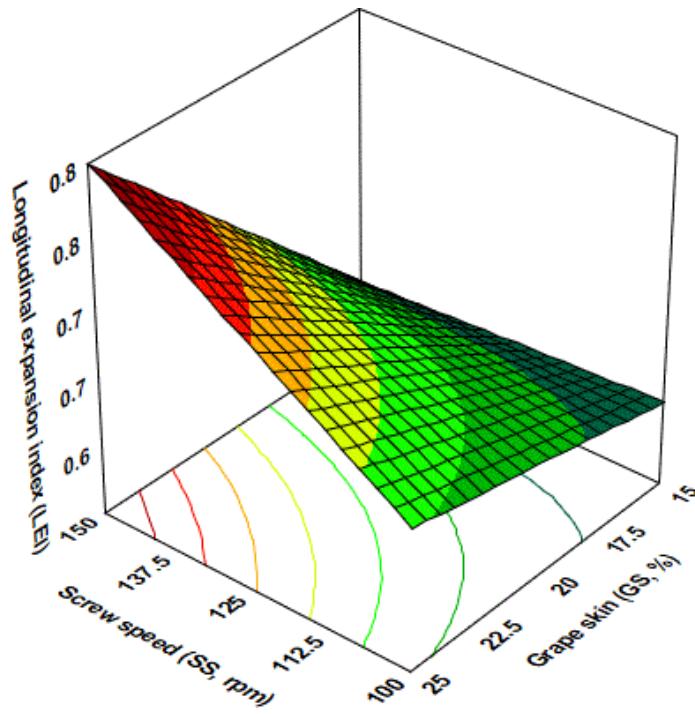


Figure 3. Interaction between longitudinal expansion index, screw speed and grape peel.

Higher values of grape peel and screw speed create higher values on LEI. This effect may be due to a reduction in viscosity and starch with less damage. Thus, the dough possibly expanded more and faster. Similar studies were reported by AČKAR et al. (2018), BECK et al. (2018) and BASEDIYA et al. (2013).

It is believed that the addition of materials with high fiber content, such as grape peel, has a negative influence on the expansion. Whereas during the melting of the ingredients, the amylose structures contained do not achieve sufficient elution bonds between the amylose/amyllopectin chains. Making the final product have a lower degree of expansion. Although this is a finding, the product according to the added percentile allows the fusion between the rice and the grape peel. In this way, it becomes feasible its use in the preparation of other foods.

The influence of feed moisture and grape peel on volumetric expansion index was presented in Figure 4.

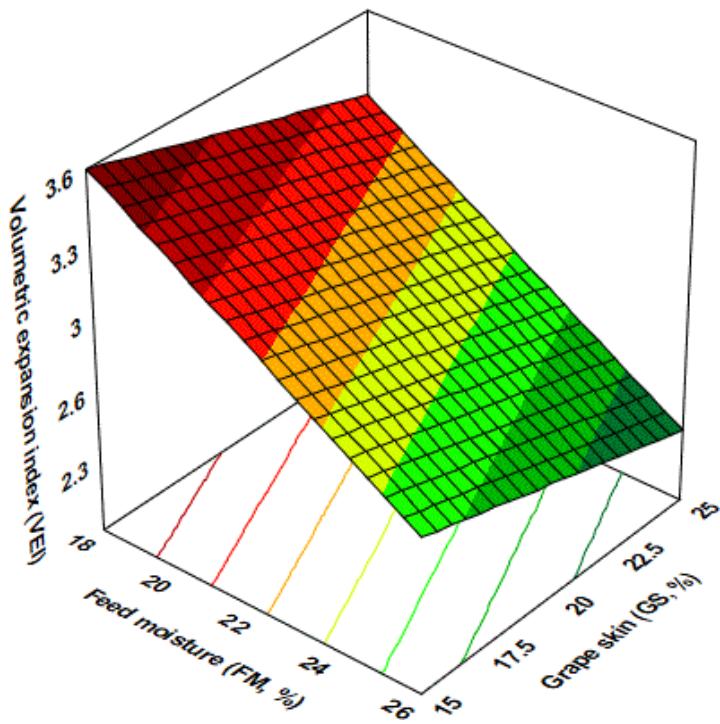


Figure 4. Interaction between volumetric expansion index, feed moisture and grape peel.

Increasing feed moisture and grape peel content generates extrudates with low VEI values.

Feed moisture has been found to be the essential factor affecting bulk density and expansion (MEHRAJ et al., 2018), (BECK et al., 2018) which is agreement with our findings. There is a huge relation between bulk density and expansion on the feed moisture of starch-based materials, which indicates the importance on elasticity characteristics of extrudates. During extrusion, increasing feed moisture amylopectin molecular structure changes, reducing the melt elasticity, decreasing the expansion and increasing the density of extrudates. AČKAR et al. (2018) studied and solved the problem of poor expansion in corn extrudates enriched with brewer's spent grain, sugar beet pulp and apple pomace adding pectin.

Usually, the WAI and WSI indexes show the hydrophobic and hydrophilic characterizations of the samples that could be the affected by degree of starch degradation, hydration of fiber, protein denaturation (BROWN et al., 2015).

The effect of screw speed and grape peel on water solubility index was presented in Figure 5.

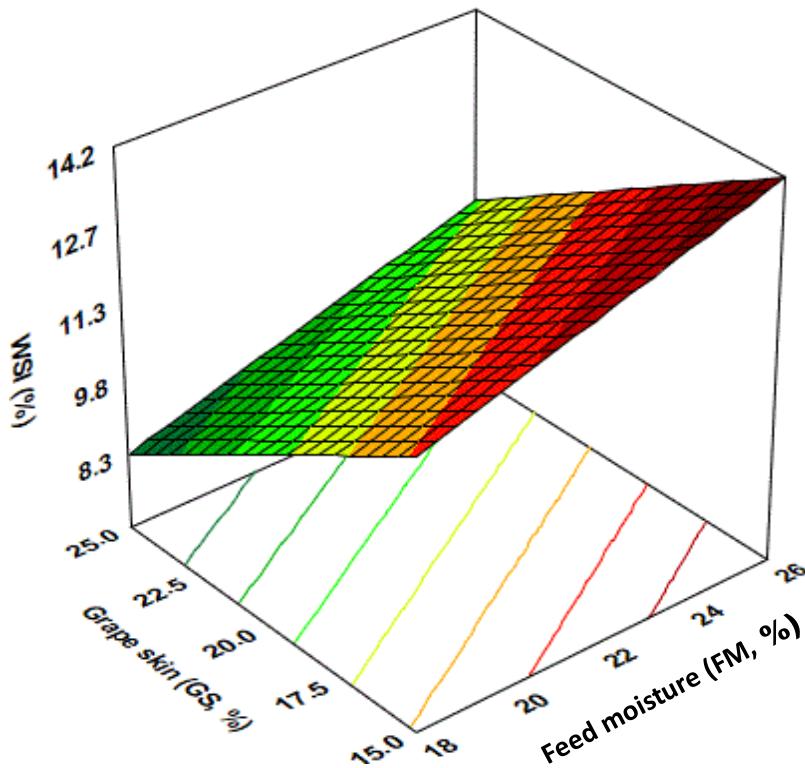


Figure 5. Interaction between water solubility index, grape peel and feed moisture.

Increasing the screw speed, the WSI was increased. The grape peel demonstrated negative effect on extruded flour, due to improve the starch-interaction and consequently, reducing the solubility. Others researches reported similar conclusions (ALVES et al., 2018).

Low screw speed collaborates to reducing WSI values. High screw speed breaks up the long into shorter starch chain and this structure is more soluble than long chain, increasing the degradation ratio of starch granules.

The WSI analysis with extruded rice had enhanced from 9.16 to 50.13 g.g⁻¹. These results were caused by thermal and mechanical effect (HAGENIMANA; DING; FANG). However, in a study with rice and oat extrudates have a reduction of WSI. It could be explained by the lipophilic characteristic of the mixture, protecting the starch granules in high screw speed (SANDRIN et al., 2018).

The influence of screw speed and grape peel on water absorption index was presented in Fig. 6.

Considering the statistical analysis obtained and using the principle of hierarchy the SS effect was removed, as a result of the effect of screw speed x feed moisture interaction was significant.

According to the study of the effect of extrusion temperature and screw speed on properties of oat and rice flour extrudates by SANDRIN et al. (2018), the WAI have a significant positive linear effect by screw speed.

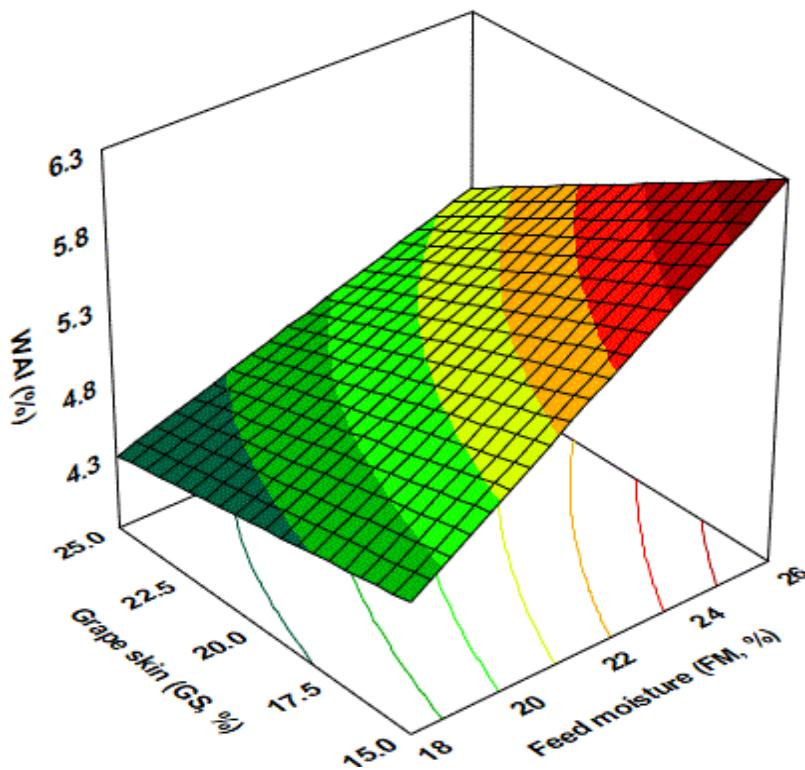


Figure 6. Interaction between water absorption index, grape peel and feed moisture.

Color is an important product parameter for consumers. The extrudates were milled and the flours were analyzed. Higher values luminosity (L^*) was observed in run 2, which has lower grape peel. Similarly, the higher grape peel content has the lower luminosity value.

The grape peel flour was the darker and the control was the lighter by the absence of grape peel. Thus, increasing grape peel content, the extrudates color became darker, indicating that the grape peel had a strong effect on the color of the extrudates flours. Oppositely, redness (a^*) samples were similar to each other. No trend was observed in yellowness (b^*).

In view of the expose the use of by-products is rising with added-value new products and increasing the number of bioactive compounds in extrudates (BRENNAN et al., 2011).

4 CONCLUSION

Extrusion cooking plays an important role as alternative to the developing by-products. Results obtained with conditions processing demonstrated the incorporation of grape peel in rice is viable. However, is necessary to do some adjusts in parameters of processing to purpose to obtain products with technologic characteristics to be attractive to the consumers. For future studies, new products using this extruded flour with nutritional analysis and sensory evaluation are the goal.

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CHAPTER III

IMPACT ON ANTIOXIDANT ACTIVITY OF INCLUDING GRAPE PEEL FLOUR IN A NOVEL SORGHUM-BASED EXTRUDED FOOD

Impact on Antioxidant Activity of Including Grape Peel Flour in a Novel Sorghum-based Extruded Food

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ABSTRACT

The aim of this study was to evaluate the effect of combining grape (*Vitis vinifera* L.) peel flour (GPF) and the colored sorghum (brown) BR305 flour (CSF) by extrusion and the consequent impact on antioxidants in the final product. The physical properties and bioactive compounds of both raw GPF and blended GPF/CSF extruded materials were investigated. The results before extrusion of raw materials, the antioxidants by ORAC the CSF was 89.111 ± 0.25 ; GPF before drying 321.033 ± 0.21 ; GPF flour after drying was $311.022 \pm 0.30 \text{ } \mu\text{mol Trolox.g}^{-1}$, respectively. Considering the different treatments (10, 15 and 20% of GPF), the highest values of the compounds obtained: Antioxidant activity, ORAC, was $37.889 \pm 0.32 \text{ } (\mu\text{mol Trolox.g}^{-1})$; with 15% of GPF, at $120 \text{ } ^\circ\text{C}$ and 17% moisture processing. ABTS, $12.222 \pm 0.14 \text{ } (\mu\text{mol Trolox.g}^{-1})$; with 20% GPF at $140 \text{ } ^\circ\text{C}$ and 19% moisture processing as best processing conditions. Anthocyanins $138.31 \pm 0.11 \text{ (mg cyanidin-3-glucoside } 100 \text{ g}^{-1})$; Total phenolic $307.95 \pm 0.11 \text{ (mg catechin. } 100 \text{ g}^{-1})$. The water absorption index was $38.99 \pm 0.19 \text{, g of gel (g dry matter)}^{-1}$ perhaps are sufficient for the preparation of beverages for breakfast or in porridge in order to contribute to the health of the consumer.

Keywords: Colored sorghum, Grape peel flour, Extrusion cooking process; Antioxidants, Pre-cooked flours.

1 INTRODUCTION

Sorghum is a versatile grain generally consumed in Asian and African countries but which is gaining interest in the United States due to its gluten-free and bioactive compound-enriched health benefits (DAVIS et al., 2019). In Brazil, the predicted production in 2021 is nearly 2.85 million tons (Companhia Nacional de Abastecimento, 2022). Therefore, colored sorghum is utilized in many gluten-free products, as it has good acceptability and an attractive neutral taste and color (DI CAIRANO et al., 2018).

Mixing ingredients can not only be an advantage but also a unique way to make feasible the consumption of certain powder products such as grape peel flour; each ingredient can contribute to improving the sensory characteristics of the final product, making the product appealing (DI CAIRANO et al., 2018).

There are several reasons why the use of agro-industrial by-products is interesting. First, due to the conditions of use, it can contribute to a reduction in environmental pollution; second, many by-products contain significant amounts of nutrients, some having a good protein content, or being a good source of fiber, bioactive compounds, other mineral profiles, etc. The third point is that value is added, not only from an economic point of view but also as a health aggregator, which in some cases is greater than the raw material itself (DI CAIRANO et al., 2018; MATEJOVÁ et al., 2016).

Grapes (*Vitis spp.*) are one of the most consumed fruits in the world. The winemaking industry generates a lot of waste like peel, seeds, and stems. This waste is called grape pomace and has an economic and environmental impact (FONTANA et al., 2013). It contains many bioactive compounds and can be used in added-value products (SÁNCHEZ-TENA et al., 2013).

Today, food extrusion technology is one of the most important ways of transforming a wide variety of food types into ready-to-eat foods, whether for human consumption or as animal feed. This is because in the formulation of these foods it is possible to incorporate different raw materials, of animal, vegetable, or mineral origin. All of this is to satisfy the specific needs of a specific consumer. In addition, according to the characteristics imposed in the process, it is possible to incorporate higher levels of dietary fiber or significant percentages of protein, or simply to improve the characteristics of acceptability and sensorial preferences (ROMÁN et al., 2017). This technology is also used to improve food by-products (OFFIAH et al., 2019) and to develop dietary fiber-enriched foods (LEONARD et al., 2020).

A large number of products have been developed using food extrusion technology, mainly due to the possibility of using different raw materials, creating texture properties that are highly acceptable to consumers. The technology also has high productivity, low operating costs, and minimal energy costs. From a nutritional point of view, foods produced by this type of processing have greater bioavailability and digestibility. For these reasons, it has become one of the most used tools in the formulation of new products derived from agro-industrial by-products (BRENNAN et al., 2011).

It is very important to note that it is not feasible to consume many inputs derived from agro-industrial by-products due to their own characteristics, for example grape skin powder, shrimp powder, etc. In this sense, there is a need to associate these raw materials with starchy sources, such as flours from rice, corn, wheat, cassava, potatoes, etc., to be processed later by extrusion. MATEJOVÁ et al. (2016) added grape pomace to gluten-free biscuits. ALVES et al. (2018) extruded passion fruit shell and colored sorghum flour. Other combinations explored are extruded colored sorghum flour and apple pomace (MEHRAJ et al., 2018); cereal breakfast extrudates with colored sorghum and pomelo rind (SHI et al., 2017); sugar replacement using

citrus fiber extracted from orange pulp in wheat-corn extrudates (PITTS et al., 2016); cherry pomace and direct expanded corn (WANG et al., 2017); and cassava-soy composite with grape pomace (OLADIRAN; EMMAMBUX).

Following the tendency for healthier products, sustainable development, and gluten-free foods, the combination of colored sorghum and grape peel by extrusion cooking is a good alternative to formulate new products based on these extruded flours. The aim of this work was to develop mixed colored sorghum and grape peel flours by extrusion cooking, evaluate the corresponding impact on antioxidant content, and consider the usefulness of the mixture for future possibilities.

2 MATERIALS AND METHODS

2.1 Raw material

A sorghum genotype with varied pericarp color, BR30, brown variety, was produced by Embrapa Milho e Sorgo (Sete Lagoas, Brazil) at the agricultural experimental field. The grape pomace (Alicante Bouschet) from the production of grape wine was supplied by Embrapa Semiárido, Petrolina, PE- Brazil. The pomace was submitted to drying oven with air circulation SL 102 (SOLAB, São Paulo, Brazil) at $45^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and 1.0 m/s of air velocity until reaching constant weight, using stainless steel mesh trays, containing layers of bagasse 0,6 cm high for 48 consecutive hours, reaching constant weigh, with a moisture near of 8.00%.

Decorticated colored sorghum and grape peel were ground, separately, in a Lab Mill 3600 disc mill (Perten Instruments, model 3600, Kungens Kurva, Sweden). Colored sorghum flour (CSF) and grape peel flour (GPF) with a particle size of less than 400 μm were used.

2.2 Extrusion Cooking Process

A single-screw Brabender 20DN DSE extruder coupled to a module 330 torque rheometer (Duisburg, Germany) was used. The screw speed of 150 rpm and feed rate of 2.5 kg.h^{-1} were constant throughout the process at a pressure of $8.5 \pm 10 \text{ MPa}$. The screw configuration was L/D 1:3 (compression ratio, Figure 1) and included a circular die 3 mm in diameter. The proportion of grape peel flour, barrel temperature, and moisture content were the independent variables described in the experimental design. The percentage of sorghum is complementary to grape peel flour. After extrusion cooking, the extrudates were dried in a forced-air drier (Fabble-Primar, São Paulo, Brazil) at 60°C for 4 h to obtain a moisture range of 4-7 g.100 g $^{-1}$. In the extrusion assays, flours were ground in a disc mill with a 0.8 mm sieve size. The extruded flours were maintained under refrigeration ($5-8^{\circ}\text{C}$) until further analysis.

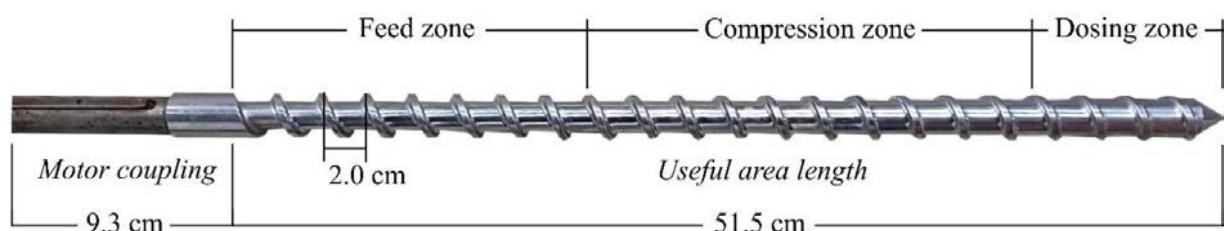


Figure 1. Brabender® extruder screw with 3:1 compression ratio.

2.3 Experimental Design

The experimental design was based on a central composite rotatable design (CCRD) for two levels and three independent variables. The experiment was conducted with 19 runs with 8 factorial points, 6 axial points, and 5 central points. Independent variables were X1: proportion of grape peel flour, X2: barrel temperature and X3: moisture content; the coded and decoded levels studied are shown in Tables 1 and 2, respectively.

Table 1. Real values used in experimental design for the production of products extruded from mixtures of colored sorghum and grape peel flours.

Independent variable	Coded level				
	-1.682	-1	0	+1	+1.682
X1: Proportion of grape peel flour (%)	6.6	10	15	20	26.4
X2: Barrel temperature (°C)	113.2	120	130	140	146.8
X3: Moisture content (%)	13.6	15	17	19	20.4

The moisture content of the mixed raw materials was calculated in order to equalize the moisture (X3) according to the real values used in the experimental design (Table 1 and 2) using Equation 1.

$$Moisture = \left(\frac{M_f - M_0}{100 - M_f} \right) \times G \quad (1)$$

Where W is the amount of water to be added, M0 is the initial moisture (%) of the mixture determined by the method of the Association of Official Analytical Chemistry (2010), Mf is the feed moisture (X3, %), fixed according to the levels of Table 1 and 2, G is the mass of mixture to be moistened.

2.4 Determination of Proximate Composition

Analysis of moisture, lipids, and ash was based on Association of Official Analytical Chemistry (2010) methods.

The total carbohydrates were obtained by difference, subtracting from 100 the values obtained for moisture, proteins, lipids, and ash (LUTZ, 2008). The results of the proximate composition were expressed in g.100 g⁻¹.

The total crude fiber content of pre-cooked mixed colored sorghum and grape peel flour was determined according to the enzymatic-gravimetric method (Association of Official Analytical Chemistry, 2010), using a Sigma enzyme kit. This method is based on the non-hydrolyzed portion of the food that resists sequential enzymatic digestion with α -amylase, protease, and amyloglucosidase.

2.5 Pasting Properties

Pasting properties were analyzed using a Rapid Visco Analyser (RVA Super-4 model, Newport Scientific Pvt. Ltd, Australia). The particle sizes of the samples used were between 125 and 250 μ m. The samples (3.0 g in 25 g of water) were corrected for moisture (14%), adding water to achieve a total weight of 28 g. The pasting profile was held at 25 °C for 2 min and heated to 95 °C. It was stabilized at this temperature for 3 min and then cooled to 25 °C. The test was performed in 20 min. The initial viscosity, maximum viscosity, final viscosity, and setback viscosity were used to evaluate the cooking degree of each sample and were expressed in Pascal-seconds (Pa.s).

2.6 Expansion Properties

The sectional expansion index (SEI), longitudinal expansion index (LEI) and volumetric expansion index (VEI) of the extruded snack products were determined for each treatment with the aid of a digital caliper (ZAAS Precision, Curitiba, Brazil). To determine the SEI (Equation 2), the diameter at the beginning, middle, and end of each extrudate was measured, to obtain the average diameter (D).

LEI and VEI were calculated using Equations 3 and 4, respectively.

$$SEI = \left(\frac{D}{D_0} \right)^2 \quad (2)$$

$$LEI = \left(\frac{\rho_d}{BD} \right) \left(\frac{1}{REI} \right) \left(\frac{1 - M_d}{1 - M_e} \right) \quad (3)$$

$$VEI = SEI \times LEI \quad (4)$$

where ρ_d is the density of the molten product inside the extruder before it leaves the die, considered to be 1400 kg.m^{-3} (density of starch); BD is the density of the extruded product; M_d is the moisture content of the wet mass of the molten product inside the extruder; and M_e is the moisture content of the extruded product, as described by ALVAREZ-MARTINEZ; KONDURY e HARPER (1988).

The bulk density (AHMAD; AL-SHABIB), in kg.m^{-3} , was calculated according to FAN et al. (1996), using Equation 5.

$$BD = \frac{4m}{\pi D^2 L} \quad (5)$$

where M is the mass, in g; L is the length of extrudate, in m; and D is the extruder diameter, in m. The analysis was performed with 15 replicates of each treatment.

2.7 Water solubility and Water Absorption Indices

The water solubility index (WSI) and water absorption index (WAI) of the samples were determined in quadruplicate as described by ANDERSON (1969). WSI is the sample mass in the supernatant divided by sample mass, and WAI is the sample mass with absorbed water divided by the sample mass. The WAI was calculated using Equation 6, while the WSI was calculated using Equation 7, modified by DOĞAN; KARWE e INTERNATIONAL (2003). The results are expressed in g of gel.(g dry matter) $^{-1}$ and percentage, respectively.

$$WAI = \frac{WRC}{W_S - WRE} \quad (6)$$

$$WSI = \frac{WRE}{W_S} \quad (7)$$

where WRC is the weight of the centrifuge residue, in g; W_S is the sample weight, in g; and WRE is the weight of the evaporation residue, in g.

2.8 Determination of antioxidant capacity and phenolic compounds in grape skin flour and extruded products

Antioxidant capacity was determined using removal of the peroxy radical ORAC (Oxygen Radical Absorbance Capacity) and the ability to remove the organic radical ABTS (2,2'-azino- bis (3-ethylbenzothiazoline-6-sulfonic acid). The total phenolic compounds were determined using the Folin-Ciocalteu assay, which is the most widely used rapid reaction procedure for the quantification of phenolic compounds in plants. The complete analytical procedure was performed as previously described by GEORGÉ et al. (2011).

Extract Preparation: To determine the antioxidant capacity, an extract was used for the ABTS and ORAC analysis. For grape skin flour, 0.1 g was weighed, and for extruded mixed flours, 0.5 g was put, in triplicate, into centrifuge tubes; 10 mL of 50% methanol was added to the tubes, the mixture was homogenized in a vortex mixer (Genie 2 Scientific Industries, Bohemia, NY, USA) and left to stand for 60 min at room temperature and protected from light. The tubes were then centrifuged in a Universal 320R centrifuge (Hettich, Tuttingen, Germany) at 2000 rpm for 15 min and the supernatant content was transferred to 25 mL amber volumetric flasks; 10 mL of 70% acetone was added to the residues from the first extraction, homogenized, and left to stand for 60 min at room temperature and protect from light. The tubes were centrifuge again (under the same conditions) and the supernatant content was collected and next to the supernatant from the first centrifugation. The balloons were filled with distilled water.

The extracts were then transferred to Eppendorf tubes, frozen at -10 °C, and kept away from light to be used to analyze antioxidant capacity.

2.8.1 ABTS method

The antioxidant capacity equivalent to Trolox was estimated according to the procedure proposed by RE et al. (1999), with some modifications. The ABTS•+ radical was prepared from the reaction of 7 mM ABTS aqueous solution with 140 mM potassium persulfate, leaving the mixture at room temperature for 16 h, in the absence of light. Soon the ABTS solution was diluted with ethanol, in order to obtain a level of absorbance of 0.70 ± 0.05 at 734 nm. Aliquots of 30 μ L of the samples were added to 3 mL of the diluted ABTS solution, and the absorbance of the mixture was recorded after 6 min. The antioxidant capacity was calculated using a standard Trolox curve (100 to 2000 μ M) and respective percentage inhibition, and the test results were expressed in μ mol of equivalent Trolox per gram of fresh weight (μ mol TE.g⁻¹ PF).

2.8.2 ORAC method

ORAC was analyzed proposed by DÁVALOS et al. (2004). In microplates, aliquots of 25 μ L of the extracts were mixed with 150 μ L of the fluorescein solution (40 nM) and incubated at 37 °C for 30 min, before adding 25 μ L of the AAPH solution (153 nM). All reagents were prepared in phosphate buffer (75 nM, pH 7.1). The fluorescence intensity (excitation at 485 nm and emission at 525 nm) was monitored every minute, for 60 min, in a Synergy Mx microplate reader (BioTek, Winooski, VT, USA). The standard curve was prepared with Trolox solution (6.25 to 100 mM), and the results were expressed in μ mol equivalent of Trolox per gram of fresh weight (μ mol Trolox.g⁻¹ PF).

2.8.3 Determination of total phenolic compounds

Quantification of the total phenolic content of the extracts and products was carried out as recommended by GEORGÉ et al. (2005). The reading was performed at 720 nm, after

reduction of the reagent by the phenolic compounds. The results were expressed in mg of catechin per 100 g of grape skin flour and in the extruded product, in order to evaluate the effect of extrusion on the content of total phenolic compounds.

2.9 Determination of Total Anthocyanins

pH difference methodology was used to determine total anthocyanins in the extracts, according to LEE et al. (2005). Two buffer solutions were made, one of potassium chloride/hydrochloric acid of pH 1.0 (0.025 M), another of sodium acetate/hydrochloric acid of pH 4.5 (0.4 M). The samples were diluted in these buffer solutions, and the concentration of the sample at pH 1.0 showed a reading between 0.2 and 1.4 AU, as it is the linearity range of the spectrophotometer. Readings were taken at 520 nm and 700 nm, in both pH 1.0 and pH 4.5 buffer. The 700 nm reading was performed to discount the sample turbidity. The final absorbance (A) value was calculated using Equation 8.

$$A = (A_{520\text{nm}} - A_{700\text{nm}}) \text{pH 1.0} - (A_{520\text{nm}} - A_{700\text{nm}}) \text{pH 4.5} \quad (8)$$

The total concentration of monomeric anthocyanins was expressed in terms of cyanidin-3-glucoside, according to Equation 9.

$$MA = A \times MW \times DF \times \left(\frac{100}{\varepsilon - 1} \right) \quad (9)$$

where MA corresponds to monomeric anthocyanins, in mg.100 g⁻¹; A corresponds to absorbance; MW is the molecular weight; DF is the dilution factor; and ε corresponds to molar absorptivity.

The determination was carried out on the grape skin flour sample and on the extruded flours, in order to evaluate the effect of extrusion on the total anthocyanin content.

2.10 Statistical Analysis

The responses of the extrudates (Table 2) obtained as results of the rotating central composite design 23 were subjected to a second order polynomial regression analysis shown in the Equation 10:

$$\hat{Y} = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \sum_{j \neq i}^2 \beta_{ij} X_i X_j \quad (10)$$

where \hat{Y} is the predict response (proximal composition, paste properties, and expansion properties); X_i , X_i^2 , and $X_i X_j$ are the linear, quadratic, and interaction effects, respectively, of the factors that influence the response γ and β_0 , β_i , and β_{ij} are the coefficients of the model to be determined. Analysis of variance (ANOVA) test was carried out using the Statistic software version 12.0 (StatSoft, Tulsa, USA) with 5% of significance.

3 RESULTS AND DISCUSSION

3.1 Proximate Composition

The proximate composition (in g.100 g⁻¹ on a dry matter basis) of colored sorghum flour (CSF) and grape peel flour (GPF) and the different tests provided for in the experimental design are shown in Table 2. GPF showed a high fiber content and ash content although the physical and chemical properties of grapes vary according to the climate, soil, variety, and cultivar (OSORIO; SILVEIRA JUNIOR). As an example, the mineral composition may vary according to edaphological conditions, climatic factors, and the use of fertilizers and herbicides among other factors (BAMPI et al., 2010). The protein content of the grape depends on the cultivar and its proteins are present mainly in the grape pulp. Crushing of grapes by applying pressure, depending on the intensity can lead to a decrease in the content of soluble proteins in the GPF. At the end of the fermentation process, many proteins precipitate with tannins, mainly in the making of red wine (JACKSON, 2020). The data according to the experimental design, with regard to mixed colored sorghum extrudates containing 15%, 20%, and 25% GPF, are presented in Table 2.

The protein content varied between the different treatments from 4.89 to 7.52 g.100 g⁻¹ of sample (d.b). These values are reasonable considering the composition of the mixtures. The lipid content varied from 1.43 to 2.59 g.100 g⁻¹. This component is mainly associated with the seeds and, as the flour is made from the grape skin, there may be some remaining seed, presenting a value closer to that for the skin fraction. The lipid content of the grape skin fraction in this study is included among the values found by ROMERO et al. (2013), which was 4.76 g.100 g⁻¹.

Carbohydrates were the most abundant components in pre-cooked mixed CSF and GPF. Although the protein and lipid content are close to that of cereals in general, the mixture has an interesting contribution of nutrients in its consumption.

3.2 Physical Properties

The pasting properties determined in the RVA indicate significant degrees of conversion after extrusion. Table 3 shows the results of the different treatments for pasting properties, bulk density, SEI, LEI, and VEI for the different tests described in the experimental design.

Table 2. Regression coefficients (in coded levels) of adjusted models for proximate composition, pasting properties, and expansion properties of colored sorghum-grape peel extrudates using independent variables: proportion of grape peel flour (X1), barrel temperature (X2), and moisture content (X3).

Coeff.	Proximate composition				Pasting properties			Expansion properties		
	ASH	PRO	LIP	CHO	BDV	STV	BD	SEI	LEI	VEI
β_0	2.65**	5.39**	2.85**	89.11**	452.71**	262.37**	286.95**	5.48**	0.84**	4.52**
β_1	0.3**	-0.46**	0.34**	-	-49.08*	-75.12**	-	-0.6**	0.05*	-0.23 ^{ns}
β_{11}	-0.41**	0.42**	-0.24**	-	-	-	-	-	-	-
β_2	-	-0.18*	0.13*	-	20.08 ^{ns}	-	-12.6 ^{ns}	-	0.04*	-
β_{22}	-0.33**	-	-	0.39*	-	-	-	-	-0.02 ^{ns}	-
β_3	0.09*	-0.11 ^{ns}	-	-	43.11*	45.1**	82**	-1.2**	-0.03*	-1.18**
β_{33}	-0.34**	0.11 ^{ns}	-	0.29*	-	-	15.28*	-	-	-
β_{12}	-	-	-	-	-51.56*	-	-	-	-	-
β_{13}	-	-	-	-	-	-	-	-	-	-
β_{23}	-	0.22 ^{ns}	-	-	-	-	-	-	-	-
<i>LoF</i>	0.052 ^{ns}	0.053 ^{ns}	0.108 ^{ns}	0.174 ^{ns}	0.077 ^{ns}	0.067 ^{ns}	0.163 ^{ns}	0.581 ^{ns}	0.415 ^{ns}	0.525
<i>R</i> ²	0.931	0.7	0.711	0.614	0.446	0.808	0.902	0.925	0.718	0.903

ASH: ash content; *PRO*: protein content; *LIP*: lipid content; *CHO*: carbohydrate content; *BDV*: breakdown viscosity; *STV*: setback viscosity; *BD*: bulk density; *SEI*: radial expansion index; *LEI*: longitudinal expansion index; *VEI*: volumetric expansion index; **significant at $p < 0.01$. *significant at $p < 0.05$; ^{ns}: not significant.

In general, the addition of material containing a significant amount of fiber to the formulations causes lower expansion values. Significant number of train jobs demonstrated this effect; consequently, as GPF is added, lower expansion values are observed. This is because the links are increasingly smaller, due to the blocking of cellulose structures in the formation of hydrogen bonds. Figure 2 shows the response surface plots for expansion properties: (a) BD ($\text{kg} \cdot \text{m}^{-3}$); (b) SEI; (c) LEI; and (d) VEI. All three of the independent variables had a significant effect on the expansion properties at $p < 0.01$ (Table 3); this can be seen in Figure 2a in which the apparent density is plotted with the process temperature and moisture content. It is evident that as the moisture content increases, there is an increase in pellet density. The reverse phenomenon occurs with a decrease in temperature, but with less impact.

On the other hand, as shown in Figure 2b, the plot of SEI plot versus the proportion of GPF and moisture content, both variables have a significant effect on radial expansion. Figure 2c, the plot of LEI versus the proportion of GPF and moisture content, shows a linear inverse behavior, that is, the lower the moisture content, the higher the value of LEI and the lower the content of GPF more than LEI. An equivalent phenomenon is shown in Figure 2d, with VEI plotted against the proportion of GPF and moisture content. The starch content of sorghum flour is sufficient to cause high expansion values when extruded without any other ingredient. Thus, the levels of GPF substitution used (10%, 15%, and 20%) were sufficient to observe how, as the levels of expansion increase, they also decrease significantly.

Due to the interaction of GPF, mainly with sorghum starch carbohydrates, in the melting and expanded formation of a single product, it is understandable that there is a decrease in the level of expansion, considering the high levels of fiber that grape peel contains. A similar work

by DIEZ-SANCHEZ et al. (2019), used blackcurrant pomace rich in polyphenols and dietary fiber, the extrusion treatment of the flour caused the disruption of the starch granules, and affected starch characteristics such as water binding capacity and swelling, this causes the expansion properties in general to be affected due to the fiber content contained in the study material.

In extruded mixed flours, there was a considerable reduction in viscosity values throughout the profile. In the first phase of the viscosity test, a certain water absorption capacity was observed, being characteristic of starch processed by thermoplastic extrusion and which has undergone shearing. The mixture with the highest moisture content, 20.4%, showed a sharp viscosity peak in the temperature increase phase, which may indicate the presence of starch with a certain molecular integrity capable of swelling with the temperature increase, typical of crude starch. According to KHANAL; HOWARD e PRIOR (2009), extrusion processing can be used to increase the procyanidin monomer and dimer content in grape seeds and pomace. Table 3 shows the regression coefficients of adjusted models for the proximate composition, pasting properties, and expansion properties of colored sorghum-grape peel extrudates using the independent variables proportion of GPF (X1), barrel temperature (X2), and moisture content (X3), showing that in most events they had a significant effect on the physical properties (pasting and expansion properties).

It is important to emphasize that, the data recorded in Table 3, referring to expansion and density values, pasting properties allow the possibility of use for a given product, for example, tests with a high degree of expansion, can be used for beverage formulation, that of low expansion, can be used to compose porridge formulations, or use them in pastes or bakery products.

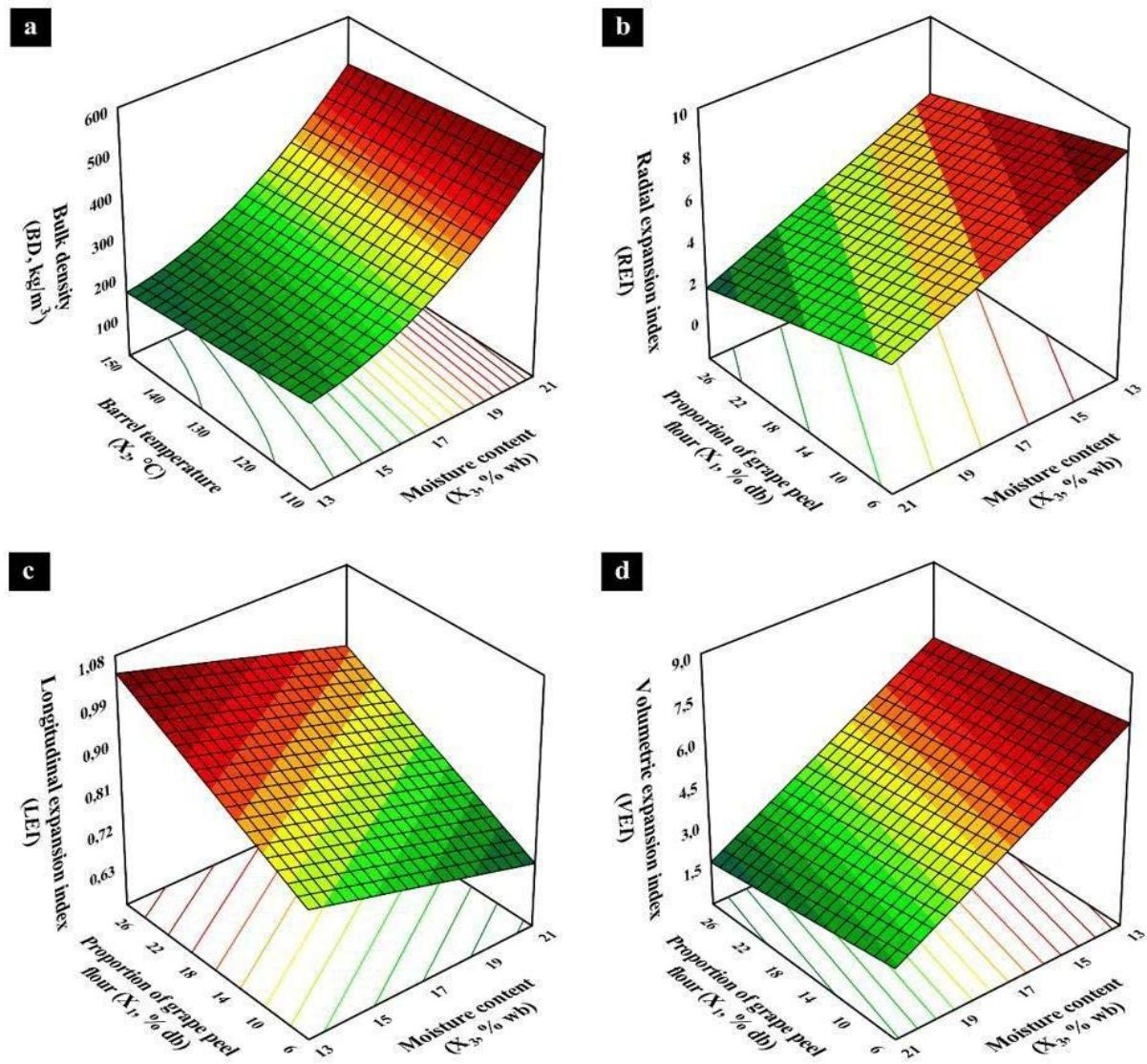


Figure 2. Response surface plots for expansion properties: (a) bulk density (BD, kg.m^{-3}); (b) sectional expansion index; (c) longitudinal expansion index; (d) volumetric expansion index.

3.3 Antioxidant capacity and phenolics in grape skin flour and extruded products

Table 4 shows the results for antioxidant capacity determined by the ORAC and ABTS methods, anthocyanin content, and total phenolic content of pre-cooked mixtures of CSF and GPF, water absorption, and solubility index.

Table 3. Antioxidant capacity determined by ORAC and ABTS methods, anthocyanin content, total phenolic content, water absorption, and solubility indices of pre-cooked blended colored sorghum and grape peel flours.

Runs	Real levels			Antioxidant activity		Phenolics		Water absorption and solubility indices	
	Grape Pomace (%)	Temperature (°C)	Moisture (%)	ORAC	ABTS	Anthocyanins	Total phenolics	WAI	WSI
1	10	120	15	16.040 ± 0.10	4.501 ± 0.11	108.23 ± 0.07	287.66 ± 0.11	18.94 ± 0.12	13.58 ± 0.11
2	10	120	19	28.633 ± 0.12	2.005 ± 0.10	112.43 ± 0.17	297.16 ± 0.16	10.49 ± 0.22	10.41 ± 0.16
3	10	140	15	16.312 ± 0.11	6.991 ± 0.13	109.13 ± 0.03	285.22 ± 0.26	18.45 ± 0.31	12.78 ± 0.21
4	10	140	19	10.715 ± 0.13	5.005 ± 0.10	111.03 ± 0.44	288.19 ± 0.33	15.22 ± 0.05	8.77 ± 0.31
5	20	120	15	29.351 ± 0.21	6.109 ± 0.14	118.53 ± 0.06	298.17 ± 0.13	12.13 ± 0.19	15.16 ± 0.24
6	20	120	19	37.627 ± 0.11	8.990 ± 0.10	122.01 ± 0.12	295.28 ± 0.91	12.15 ± 0.32	10.11 ± 0.21
7	20	140	15	34.570 ± 0.15	11.661 ± 0.11	126.21 ± 0.21	288.19 ± 0.33	20.12 ± 0.51	11.77 ± 0.33
8	20	140	19	32.263 ± 0.10	12.222 ± 0.14	125.90 ± 0.05	281.08 ± 0.72	17.05 ± 0.32	10.05 ± 0.19
9	6.6	130	17	09.324 ± 0.11	10.433 ± 0.12	95.05 ± 0.03	101.18 ± 0.12	21.56 ± 0.14	13.11 ± 0.25
10	23.4	130	17	37.122 ± 0.12	10.987 ± 0.10	138.31 ± 0.11	307.95 ± 0.11	19.41 ± 0.24	11.76 ± 0.28
11	15	113.2	17	24.311 ± 0.15	4.669 ± 0.10	101.27 ± 0.08	277.61 ± 0.22	14.55 ± 0.16	11.94 ± 0.41
12	15	146.8	17	25.541 ± 0.30	4.644 ± 0.12	112.23 ± 0.11	267.26 ± 0.07	39.89 ± 0.22	11.15 ± 0.42
13	15	130	13.6	32.335 ± 0.35	6.298 ± 0.10	100.32 ± 0.22	259.61 ± 0.22	38.99 ± 0.19	15.11 ± 0.33
14	15	130	20.4	18.777 ± 0.32	6.666 ± 0.14	128.21 ± 0.44	285.11 ± 0.04	38.72 ± 0.13	10.14 ± 0.21
15	15	130	17	31.776 ± 0.31	9.276 ± 0.12	110.11 ± 0.22	280.17 ± 0.04	17.88 ± 0.28	11.09 ± 0.41
16	15	130	17	37.889 ± 0.32	10.601 ± 0.16	109.93 ± 0.06	283.99 ± 0.55	16.91 ± 0.13	12.54 ± 0.51
17	15	130	17	33.679 ± 0.28	10.006 ± 0.12	111.88 ± 0.11	281.16 ± 0.07	19.89 ± 0.08	11.33 ± 0.13
18	15	130	17	33.666 ± 0.30	11.127 ± 0.11	112.25 ± 0.05	284.22 ± 0.66	12.93 ± 0.09	10.17 ± 0.41
19	15	130	17	33.176 ± 0.19	9.267 ± 0.16	111.66 ± 0.27	281.99 ± 0.19	16.77 ± 0.14	11.59 ± 0.14

Table 4. Antioxidant capacity determined by ORAC and ABTS methods, anthocyanin content and total phenolic content of pre-cooked mixtures of colored sorghum flour and grape peel flour

Raw materials	ORAC	ABTS	Anthocyanins	Total phenolics
Colored sorghum flour	89.111 ± 0.25	32.147 ± 0.19	71.66 ± 0.27	4.09 ± 0.19
Grape peel flour ^a	321.033 ± 0.21	49.567 ± 0.15	2098.7 ± 0.12	1821.3 ± 0.13
Grape peel flour ^b	311.022 ± 0.30	44.666 ± 0.10	1822.2 ± 0.02	1669.3 ± 0.03

ORAC: oxygen radical absorbance capacity ($\mu\text{mol Trolox.g}^{-1}$); ABTS: 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) ($\mu\text{mol Trolox.g}^{-1}$); anthocyanins (mg cyanidin-3-glucoside 100 g^{-1}); total phenolic compounds (mg catechin. 100 g^{-1}). ^abefore drying; ^bafter drying.

The antioxidant values for GPF are considered high so that when fused by the extrusion process with CSF, the product obtained has sufficient quality of antioxidants compared to the available food supplement flours (SHI et al., 2017). Procyanidins in grape by-products have many health benefits, but most are present as large molecular weight compounds, which are poorly absorbed. Extrusion processing appears to be a promising technology to increase the levels of bioactive low molecular weight procyanidins (KHANAL; HOWARD; PRIOR). According to this premise, it is considered that during the extrusion process, mainly during melt rather formation in the fusion of the two ingredients, CSF and GPF, part of the molecular structure could be exposed, so that in the determinations appear. On the other hand, considering

that extrusion is an HTSH type thermal process, its effect on the content of antioxidants is not so drastic, mainly because it takes a very short period, that is, approximately 20 to 30 s, in this sense, POKORNÝ e SCHMIDT (2010) commented that extrusion usually occurs at temperatures above 100 °C, but the residence time is very short, therefore the decomposition of antioxidants is relatively small, these authors cited an experiment with wheat flour Saracen, where they were extruded at 120 ± 200 °C. in which they observed that the content of phenolic acids increased by the release of their binding to proteins and the sum of polyphenols decreased. Considering GPF as a raw material before the mixing procedure for the extrusion procedure, at the end of Table 4, the values of antioxidants (ORAC, ABTS, total anthocyanins, and phenolic) were added, to verify the influence of the exposed time the drying of the grape skin at a temperature of 45 °C before and after drying. In which there was a decrease in the values of antioxidants, ORAC, and ABTS, of 3.2%, and 10%, respectively, in the case of Total anthocyanins and phenolics, 13.18%, and 8.35%, respectively. As an example of losses in cooking activities, during steaming cabbage cooking losses are about $21 \pm 23\%$ in ascorbic acid and total phenols about 10%. The antioxidant activity of Trolox decreased by $5 \pm 20\%$ and the phenolic compounds increased the pea antioxidant capacity, due to the phenol ± protein interaction. Hydroxycinnamic acids (such as ferulic, coumaric, and caffeic acids) were the most active ingredients (POKORNÝ; SCHMIDT). Considering the work of NAYAK et al. (2011) who used the extrusion process for a mixture of purple potato and yellow pea flour the losses in the total phenolic (TP) content of the formulations under extrusion are expected to occur, due to breaking down of complex polyphenols to other phenolic or non-phenolic compounds, because of high-temperature conditions. However, the effect of the extrusion die at temperatures, 130 and 140 °C, was not significant ($p > 0.05$) on the TP content of the extrudates. On the other hand, MORENO et al. (2018) corroborate what was described above, in which several studies have shown that extrusion and process conditions affect the phytochemical content and antioxidant activity of cereal grains, showing that important losses can occur in the Bioactive compounds due to thermal effect and chemical changes can occur during extrusion since phenolic compounds are highly dependent on the parameters, moisture content, temperature and residence time in the extrusion system.

In another work, researchers (NEDER-SUÁREZ et al., 2021) used a blend of blue corn, black beans and sweet chard by extrusion in the production of a type of third-generation snacks, considering that these ingredients contain phytochemical and polyphenols compounds. They concluded that despite thermal processes, anthocyanin retention was high (29.08 mg of cyanidin- 3-glucoside equivalents/100 g) under the optimal process conditions of 122 °C, 133 rpm, and 25% of moisture content. Screw speed and moisture content had the largest effects on the physical responses, while moisture content had the largest effects on total anthocyanin. The highest expansion index, water absorption and water solubility indexes, and hardness were obtained at high screw speed and low extrusion temperature. At low extrusion temperature and moisture content, the highest total anthocyanin was generated.

Among the possibilities of using GPF, BALDÁN et al. (2021) used this flour; processed at 75 °C (15 and 25%) improved the nutritional composition of the muffins as their content increases, highlighting protein and rude fiber content. Likewise, these had a good level of acceptability by consumers. Taking into account grape pomace is a by-product discarded by wineries, it has a potential benefit and is feasible to use as an ingredient for gluten-free muffins. It should be considered that these authors used GPF without mixing, and not processed by extrusion. In the case of the present study, however, we have the mixture, in the percentages established in the experimental design (10, 15 and 20% of GPF) with the difference of colored sorghum flour. This condition, with the starch material fused to GPF, can contribute to better performance in the elaboration of products, as the functional characteristics like absorption and water solubility can be modified only with variations in the extruder process parameters and meet specific functional properties.

4 CONCLUSION

These results indicated that extrusion of sorghum colored and grape peel flours produces acceptable extrudates. Changing process conditions affected the physical and functional properties of produced expanded products. However, this impact is not very drastic, making the products resulting from the CSF/GPF mixture have significant values of antioxidants and phenolic compounds. Under these conditions, this resulting mixture with considerable amounts of antioxidants and phenolic compounds can be used as porridge, food formulations among other alternatives. In any case, the resulting products can contribute to the health of the consumer.

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CONCLUSÃO GERAL

O uso da casca de uva extrudada e arroz ou extrudado de casca de uva e sorgo nos produtos alimentícios pode trazer diversos benefícios, incluindo o aumento nutricional. Bagaço de uva é uma fonte rica em antioxidantes, compostos fenólicos e fibra. Combinando-o com arroz ou sorgo, o valor nutricional geral do produto alimentício pode ser melhorado.

Extrusão é um processo que pode mudar a textura e as propriedades funcionais dos ingredientes alimentares. Isto pode resultar em uma textura mais apelativa ao produto alimentar final, tanto nas misturas de cereais como no bagaço de uva. Consequentemente, é possível que a utilização de resíduos de bagaço de uva como subproduto da produção de vinho seja frequentemente descartada, levando a preocupações ambientais e econômicas. Ao utilizá-lo como ingrediente em produtos alimentícios, os resíduos podem ser aproveitados e o impacto ambiental seja reduzido.

Além disso, o uso desses ingredientes é uma opção sem glúten. Sorgo e arroz são grãos sem glúten e podem ser usados em combinação com o bagaço de uva para criar produtos alimentícios sem glúten com valores mais elevados de compostos fenólicos. Isto é particularmente útil para indivíduos portadores de doença celíaca ou intolerância ao glúten. Ainda, o uso da extrusão pode aumentar a vida útil dos produtos alimentícios, porque normalmente o produto seco após o cozimento por extrusão tem cerca de 4 – 6 % de umidade. Isto se deve a mudanças na estrutura física dos ingredientes que reduzem a migração de umidade e a oxidação.