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LUCAS CANTÃO FREITAS

APLICAÇÃO DA TECNOLOGIA SUPERCRÍTICA VISANDO A VALORIZAÇÃO DA CASCA DO FRUTO DO BACURI (*Platonia insignis* Mart.)

BELÉM - PA
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Dissertação de mestrado apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos da Universidade Federal do Pará, Instituto de Tecnologia, como requisito para obtenção do título de Mestre em Ciência e Tecnologia de Alimentos.

Orientador: Prof. Dr. Raul Nunes de Carvalho Junior.

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RESUMO

O aproveitamento de subprodutos agroindustriais visando a sua agregação de valor tem gerado interesse da comunidade científica e do setor industrial. Em vista disso, esse trabalho faz uma abrangente abordagem do atual estado da arte em relação a utilização e aproveitamento de subprodutos agroindustriais, enfatizando a obtenção de produtos de alto valor agregado por meio da tecnologia supercrítica e outras tecnologias ambientalmente amigáveis. Além disso, os principais produtos gerados a partir do aproveitamento de subprodutos agroindustriais foram relatados e discutidos em termos de processo, viabilidade técnica e perspectivas futuras. Nesse contexto, trazendo para o cenário amazônico e colocando em prática o atual estado da arte, optou-se por aplicar a tecnologia supercrítica como ferramenta para a valorização do subproduto agroindustrial do fruto do bacuri, mais especificamente a sua casca, por ser a maior fração desse fruto, representando até 70% em massa. Assim, o trabalho teve como objetivo desenvolver um processo de separação e/ou minimização da resina que exsuda da casca do bacuri, uma vez que essa é a principal barreira para o aproveitamento tecnológico desse subproduto. Para isso, aplicou-se a extração consecutiva com fluido supercrítico, onde foram estudados os parâmetros de processo como tamanho de partícula, pressão e uso de cosolvente, além das etapas de pré-processamento. Os extratos obtidos foram analisados em termos de compostos fenólicos e atividade antioxidante (ABTS) por métodos espectrofotométricos. Os resultados mostraram que o processo foi capaz de separar a resina da casca do bacuri, sendo este o primeiro relato descrito na literatura. Além disso, o menor tamanho médio de partícula estudado (0,25 mm) exibiu o impacto mais proeminente na taxa de extração, proporcionando bons rendimentos de extratos lipídicos (até 10,09 ± 0,02%) e extratos etanóicos (até 13,78 ± 0,41%). Os extratos obtidos apresentaram elevados teores de compostos fenólicos, o que foi associado à sua alta atividade antioxidante. Assim, a aplicação da tecnologia supercrítica agregou valor à casca do bacuri, possibilitando novas vertentes para aproveitamento industrial desse subproduto com potencial aplicação na indústria alimentícia, farmacêutica e cosmética, incentivando a economia circular e a bioeconomia da região Amazônica.

Palavras-chave: Subproduto agroindustrial, *Eco-friendly*, Resina, Sustentabilidade, biorrefinaria, Amazônia.

ABSTRACT

The use of agro-industrial waste envisioning its valorization has generated interest from the scientific community and industries. Therefore, this work provides a comprehensive approach to the current state of the art in relation to the use of agro-industrial waste, emphasizing the obtainment of high value-added products through supercritical technology and other environmentally friendly technologies. In addition, the main products generated from the use of agro-industrial residues were reported and discussed in terms of process, feasibility and future perspectives. In this context, bringing to the Amazon scenario and putting into practice the current state of the art, it was decided to apply supercritical technology as a tool for valuing the agro-industrial residue of the bacuri fruit, more specifically its shell, as it is the largest fraction of this fruit, representing up to 70% in mass. Thus, the work aimed to develop a process for separating and/or minimizing the resin that exudes from the bacuri shell, since this is the main barrier to the technological use of this residue. For this, consecutive extraction with supercritical CO_2 was applied, where the process parameters such as particle size, pressure and use of cosolvent were studied, in addition to the pre-processing steps. The extracts obtained were analyzed in terms of phenolic compounds and antioxidant activity (ABTS) by spectrophotometric methods. The results showed that the process was able to separate the resin from the bacuri shell, which is the first report described in the literature. Furthermore, the smaller particle size (0.25 mm) exhibited the most prominent impact on extraction rate, providing good yields of lipid extracts (up to 10.09 ± 0.02 %) and ethanoic extracts (up to 13.78 ± 0.41%). The obtained extracts presented good levels of phenolic compounds, which was associated with its high antioxidant activity. Thus, the application of supercritical technology added value to the bacuri shell, enabling new strands for industrial use of this residue with potential applications in the food, pharmaceutical and cosmetic industries, encouraging the circular economy and the bioeconomy of the Amazon region.

Keywords: By-product, Eco-friendly, Resin, Sustainability, Biorefinery, Amazon.

SUMÁRIO

From waste to sustainable industry: how can agro-industrial wastes help in the development of new products?

(Dos resíduos à indústria sustentável: como os resíduos agroindustriais podem ajudar no desenvolvimento de novos produtos?)

Supercritical fluid technology as a tool to valorize bacuri fruit (Platonia insignis Mart.) shell.

(Tecnologia de fluido supercrítico como ferramenta para a valorizarização da casca do fruto do bacuri (*Platonia insignis* Mart.)

Processo para a separação da resina da casca do fruto do bacuri (*Platonia insignis* Mart.) utilizando a tecnologia de fluido supercrítico.

1 TEXTO INTEGRADOR

Em uma era onde os conceitos de bioeconomia e economia circular têm sido amplamente discutidos e incentivados, a aplicação de tecnologias limpas visando o aproveitamento de subprodutos agroindustriais tem sido o foco de relevantes estudos em todo o mundo. Atualmente, os subprodutos agroindustriais não são mais vistos como um problema, mas sim como um grande aliado para o desenvolvimento de uma indústria mais sustentável, pois podem auxiliar no desenvolvimento de diversos produtos, promovendo novas oportunidades de investimentos que atendam tanto aos anseios econômicas quanto os ambientais, além de geração de renda e desenvolvimento regional.

A região amazônica é detentora de um grande espectro de espécies frutíferas, dentre elas a fruta do bacuri (*Platonia insignis* Mart.) que é muito consumida pela população local de forma *in natura*, na culinária regional, na fabricação de doces, geleias, sorvetes e elaboração de polpas, apresentando grande importância para o mercado regional. No entanto, a fruta é composta predominantemente pela casca (60-70%), fração que é considerada um subproduto agroindustrial, sendo geralmente descartada. Apesar de poucas pesquisas voltadas para a valorização da casca do bacuri, os estudos existentes apontam que esta fração do fruto é uma promissora fonte de compostos de valor agregado, podendo ser utilizada em diferentes setores industriais como na indústria alimentícia, farmacêutica, cosmética e de nanomateriais. No entanto, a presença de uma resina de coloração amarela que exsuda de seu mesocarpo é considerada a maior barreira que dificulta o seu aproveitamento tecnológico. Portanto, torna-se necessária a aplicação de novos processos que minimizem as barreiras existentes e possibilitem o aumento da diversificação do uso, a agregação de valor e, consequentemente, a ampliação de mercado do bacuri.

Paralelamente, o apelo mundial pelo uso de tecnologias limpas, visando o incentivo à bioeconomia e à economia circular, trouxe um novo cenário a ser explorado pela ciência, tecnologia e engenharia de alimentos, principalmente na região Amazônica. Em vista disso, a presente dissertação de mestrado intitulada “Aplicação da tecnologia supercrítica visando a valorização da casca do fruto do bacuri (*Platonia insignis* Mart.)” foi desenvolvida com a finalidade de estudar as potencialidades e possibilidades para o uso desse resíduo agroindustrial, sugerindo alternativas sustentáveis e incentivando a bioeconomia na Amazônia.

Desse modo, esta dissertação de mestrado foi desenvolvida e dividida em três capítulos. O **Capítulo I** apresenta o artigo de revisão intitulado "*From waste to sustainable industry: how can agro-industrial wastes help in the development of new products?*" publicado na revista "*Resources, Conservation & Recycling*". O artigo apresenta uma abrangente abordagem sobre as mais recentes aplicações dos subprodutos agroindustriais para a obtenção de produtos de alto valor agregado por meio de tecnologias limpas como a tecnologia de fluido supercrítico (SFE). O trabalho destaca ainda os mais recentes aspectos relacionados ao aproveitamento de subprodutos agroindustriais, inclusive em termos de biorrefinaria, geração de energia e produção de biomateriais.

Nesse contexto, a fim de trazer o atual estado da arte para a realidade Amazônica, optou-se por estudar uma matéria prima da região. Apesar de ser um subproduto agroindustrial de grande relevância no contexto amazônico, a casca do fruto do bacuri (*Platonia insignis* Mart.) ainda possui poucas informações na literatura relacionadas à sua valorização. Trabalhos envolvendo a polpa e as sementes do fruto são mais facilmente encontradas. Em vista disso, decidiu-se estudar esse subproduto a fim de trabalhá-lo em um contexto de valorização através da agregação de valor, aumentando seu espectro de utilização e minimizando suas limitações industriais.

Desse modo, os próximos capítulos tratam da etapa experimental da pesquisa, onde a casca do fruto do bacuri foi estudada através da aplicação da tecnologia supercrítica, buscando a valorização desse subproduto no cenário industrial. Para isso, foi desenvolvido o **Capítulo II** que aborda um artigo de pesquisa intitulado "*Supercritical fluid technology as a tool to valorize bacuri fruit (Platonia insignis* Mart.*) shell*". O mencionado artigo relata a aplicação da extração sequencial por fluido supercrítico à casca do fruto do bacuri, estudando seus parâmetros de processo como tamanho de partícula, pressão e uso de cosolvente, além de analisar os extratos obtidos em termos de compostos fenólicos e capacidade antioxidante. Adicionalmente, sendo um dos principais objetivos do trabalho, foi realizado o primeiro relato de separação/minimização da resina da casca do fruto do bacuri utilizando a tecnologia supercrítica, fornecendo informações que podem auxiliar na viabilidade de aplicação industrial desse subproduto agroindustrial, visando a sua valorização e incentivando o desenvolvimento da bioeconomia local.

Tendo em vista o sucesso dos resultados obtidos no trabalho referente ao capítulo II, principalmente no que concerne à separação da resina da casca do bacuri, decidiu-se por elaborar uma patente, descrita no **Capítulo III**. A mencionada patente é intitulada "*Processo para a separação da resina da casca do fruto do bacuri (Platonia insignis* Mart.*) utilizando a tecnologia de fluido supercrítico*". A decisão de patentear o processo ocorreu devido à sua inovação e ineditismo, além de ser uma potencial opção para substituir o atual estado da arte do processo de separação da resina deste resíduo agroindustrial. Como a técnica de decocção (atual estado da arte) possui algumas desvantagens evidentes, a aplicação da nova tecnologia, ambientalmente correta, é capaz de sanar algumas das limitações inerentes ao antigo método.

Ao final do desenvolvimento deste trabalho de pesquisa, foram geradas três publicações, sendo um artigo de revisão, um artigo de pesquisa e uma patente, cumprindo, portanto, a proposta inicial do projeto de mestrado. Além disso, o projeto possui grande potencial de continuidade, uma vez que os resultados obtidos abriram novas possibilidades, além da existência de apelo industrial relacionado à casca do bacuri. Desse modo, a dissertação de mestrado foi concluída e está apresentada com mais detalhes nos capítulos a seguir.

2 OBJETIVOS

2.1 GERAL

Estudar a aplicação da tecnologia supercrítica ao subproduto agroindustrial do fruto do bacuri, mais especificamente a sua casca, visando a sua valorização e minimizando as limitações existentes para a sua aplicabilidade industrial.

2.2 ESPECÍFICOS

- ✓ Desenvolver um processo para reduzir a concentração de resina na casca de bacuri desidratada;
- ✓ Caracterizar a matéria prima e determinar parâmetros de rendimento global da extração, enfatizando os diferentes tamanhos de partícula;
- ✓ Determinar o conteúdo de compostos fenólicos totais (TPC) do extrato resultante da extração;
- ✓ Estudar a potencial atividade antioxidante *in vitro* pelo método ABTS e correlacioná-lo com o resultado de TPC e com a sua composição química disponível na literatura;
- ✓ Sugerir potenciais aplicações industriais para a casca do fruto do bacuri, ampliando o seu espectro de possibilidades.

CAPÍTULO I

From waste to sustainable industry: how can agro-industrial wastes help in the development of new products?

(Dos resíduos à indústria sustentável: como os resíduos agroindustriais podem ajudar no desenvolvimento de novos produtos?)

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Review

From waste to sustainable industry: How can agro-industrial wastes help in the development of new products?

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ABSTRACT

Demand for food production has been promoting an increase in the generation of agro-industrial wastes. Although in the past these wastes were mainly seen as a big issue, in the current scenario they are seen as the key strategy for the development of sustainable industrial processes. In this context, several new environmentally friendly technologies such as supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) have been studied and applied to obtain products with high added value in order to supply the chemical, pharmaceutical and food industries. Similarly, the energy generation from biomass and production of new biomaterials such as bionanofilms, bioaerogels, hydrogels and nanocomposites have been intensely studied in order to cross the barriers of the laboratory scale. Therefore, this review aims to update the scientific community, industries, governments and society on the sustainable applications, latest advances and trends in the valorization of agro-industrial wastes for new product development, highlighting the new possibilities for the progress of sustainable production.

1. Introduction

The sustainable reuse of biomass from agro-industrial wastes envisioning the production of food, drugs, biologically active compounds, biomaterials and sustainable energy generation is, undoubtedly, one of the biggest challenges of the 21st century. Agricultural and food sectors generate a substantial amount of waste, which can be used as raw materials to obtain high added-value products, promoting a range of possibilities for a sustainable production (Ng et al., 2020). The Organization of the United Nations (FAO, 2011) estimates that approximately one-third of all food produced for human nutrition in the world is lost or wasted, which is approximately 1.6 billion tons per year. Moreover, fruits, vegetables, roots and tubers represent about 40–50% of the total quantity of food wasted (Ravindran et al., 2018). In such a framework, the valorization of these wastes has emerged as a key strategy for an environmentally-friendly production.

Agro-industrial wastes such as peels, seeds, pits, pulps, press cakes and leaves are the focus of numerous investigations. These residues are source of a huge spectrum of secondary plant metabolites (Alexandre, 2017), such as phenolic compounds, known as the most significant class of bioactive compounds with antioxidant activity found in fruit tissues (Rossetto et al., 2020). Various studies show that these components have many health benefits, as anti-inflammatory, antidiabetic, antioxidant, anticancer, antimicrobial and antiproliferative activities (Peanparkdee and Iwamoto, 2019; Ballesteros-Vivas et al., 2019; Santos et al.,2019; Tunna et al., 2017).

Agro-industrial wastes from various processing sectors contribute to the increase in biomass, and the vast majority of which are deposited in landfills or simply discarded in inadequate places. The main problems associated with the increase in biomass production are the fuel and microbiological potentials, attributed to the bioavailability of highly energetic organic material such as carbohydrate and fat polymers. The biomass accumulation contributes to fires in regions with a drier climate, leading to large losses of forests and biomes. Also, these wastes serve as food for the proliferation of microorganisms, which although important for decomposition, on a large scale they become a major problem, mainly associated with the production of greenhouse gases, toxic degradation products, and proliferation of pathogenic bacteria and

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fungi (Ng et al., 2020). Due to the abundance of agro-industrial waste, developing countries suffer from the permanent lack of viable alternatives for the recovery and reuse of these precious inputs, which is normally incinerated, increasing the production of greenhouse gases, contributing to the loss of energy potential, worsening health crises and affecting the population's quality of life (Ravindran et al., 2018).

Although the organic matter present in agro-industrial waste is a source of valuable components, few technologies are able to offer security regarding the process of recovery, purification and concentration of these chemical compounds. It is also important to highlight that few technologies in development offer the advantages of operational data that can be applied to scale-up. In this framework, the potential application of innovative technologies has been the focus of the discussions in the context of sustainable reuse of waste, as well as the challenges of consolidating these technologies on industrial environment through the generation of opportunities for research and technological development.

In this scenario, green extraction technologies have been standing out as an excellent alternative to extract high-added value compounds from agro-industrial wastes, since these techniques produce a final extract with high quality and purity (Soquetta et al., 2018). In addition, these technologies are environmentally friendly due to the lower energetic consumption, reduction of organic solvents and short operation times (Sik et al., 2020). Several emerging technologies have been applied to theses matrices, such as supercritical fluid extraction (SFE), ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), among others (Angoy et al., 2020; García-Pérez et al., 2019; Oliveira et al., 2019; Alexandre et al., 2017).

Agro-industrial wastes also paves the way for some other important research fields, such as the production of new fuels and energy generation. Moreover, cellulose polymers obtained from agro-industrial wastes can help developing new biomaterials such as bionanocomposities, biofilms, bioaerogels, hydrogels, as well as specific biomaterials that can be applied on tissue engineering (Fortunati and Balestra, 2019; Soorbaghi et al., 2019).

Hence, this review aims to update the scientific community, industries, governments and society on the sustainable applications, latest advances and trends in the valorization of agro-industrial wastes for new product development, highlighting the new possibilities for the progress of sustainable production. Therefore, a general approach will be made about the main green technologies applied to agro-industrial wastes, as well as, their recent uses in some industrial fields such as the food, pharmaceutical and chemical sectors. In addition, it will highlight the energy generation and the production of new biomaterials from agro-industrial waste biomass.

2. Current scenario in the use of agro-industrial wastes

A comparative approach from previous works shows that the use of agro-industrial wastes for the development of new products has evolved significantly. For instance, in a distant past, agro-industrial waste was seen as a big problem to the food production chain due to its removal costs, in addition to the environmental impact generated by the disposal of these wastes (Cattaneo et al., 2020; Cakar et al., 2019; Read et al., 2019). In a recent past, agro-industrial waste was considered neither a cost nor a benefit, since it was used mostly for composting or in the production of animal feed (Nazzaro et al., 2018). However, nowadays this concept has been changing due to the emergence of several new technologies to reuse agro-industrial waste by adding value to it. Therefore, in the current state of the art, the recovery of added-value resources from waste can improve the overall sustainability of the food production chain from both economic and environmental points of view (Udugama et al., 2019; Lai et al., 2017).

Fig. 1 shows the chronological evolution from different works involving agro-industrial waste usage from the last years, where it can be made a comparative approach from the prior works in terms of waste valorization advancement. From animal feed to fine chemicals and biomaterials, the valorization of agro-industrial wastes have reached significant changes and prospects. The introduction of new technologies has led to a very different scenario than we had thirty years ago. The current state of the art offers many possibilities for the application of agro-industrial waste for the development of new products, which will be further discussed in the next sections.

In the food industry sector, the concept of resource recovery has already been explored, both in terms of separating the valuable material from agro-industrial waste to create a food ingredient, and in using this waste as inputs to develop new products (Udugama et al., 2019; Ravindran et al., 2016). For instance, catalytic biomass transformation into furfurals, polysaccharides, alkyl glucosides, polyols, and aromatic compounds have been substantially studied (Rosero-Chasoy et al., 2020; Wang et al., 2015).

Regarding the furfural, it can be produced via hydrodistillation, under acidic conditions, with subsequent process of liquid-liquid extraction and purification. Furfural can be applied in the synthesis of organic solvents such as furfuryl alcohol, tetrahydrofuran alcohol and furfurilamine, the latter applied in the production of substances with pharmacological and pesticidal activities, in addition to the production of fibers (Zang et al., 2020). Another example of biomass processing includes the transformation of lignocellulosic residues into aromatic compounds through pyrolysis. This thermochemical process occurs in

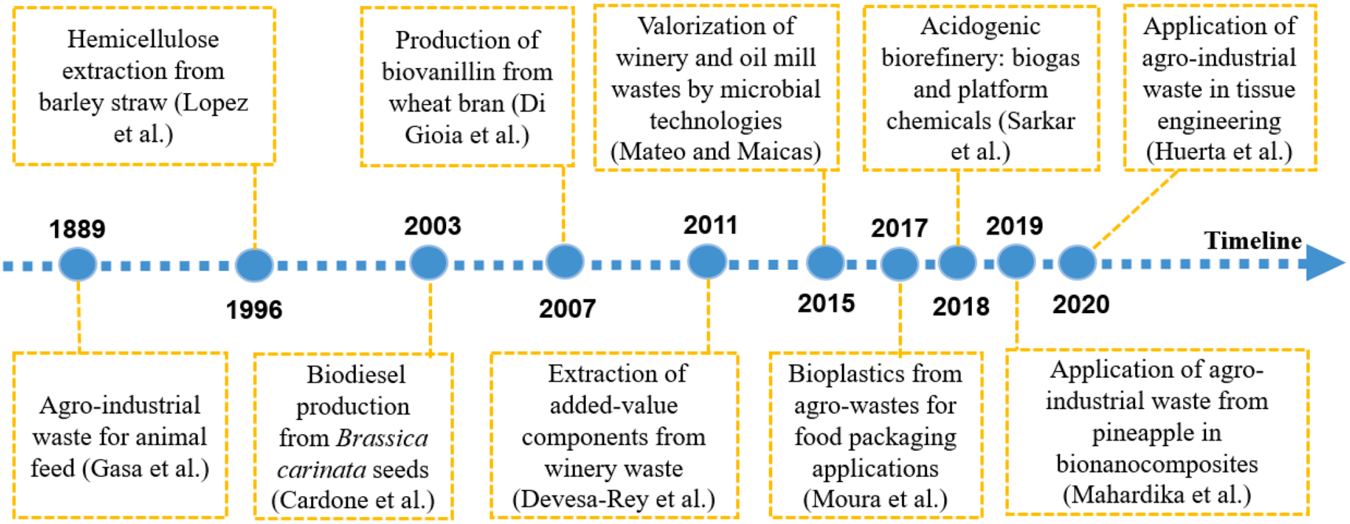

Fig. 1. Chronological evolution based on different works involving agro-industrial waste usage from the last years.

the absence of oxygen, at high temperatures (400-650°C), allowing the formation of bio-oil (liquid fraction), biochar (solids) and CO, CO_2, H_2 and CH_4 (pyrolysis gases), regardless of the biomass used (Dai et al., 2020).

The current perspective for the development of sustainable industries is linked to the gradual replacement of non-renewable sources by renewable sources of energy. Applying an illustrative comparison with the petroleum industry, a new concept emerges based on the premises of exploration, refining and generation of chemical derivatives from organic biomass (Dragone et al., 2020). As in the petroleum industries, the integrated process model that joins the transformation chain for the production of gasoline, diesel oil and other products such as plastics, motivated the emergence of a new process approach aimed at stages similar to those already consolidated in the oil refining industries, however, now applied to the exploitation of organic biomass. The term biorefinery, as the prefix (bio) suggests, consolidates a dynamic approach of several processes integrated in chains and technological routes capable of converting organic matter (or waste) into value-added products such as biofuels, inputs for the chemical industry, production of heat, electricity and specific chemicals with high pharmacological potentials (Ahmad et al., 2020).

Biorefineries have been a reality in several countries around the world, especially countries with high agricultural productivity such as Brazil. It is worth mentioning that the productivity dynamics from Brazilian agroenergetic agriculture has been diversifying, mainly due to the expansion of agricultural crops associated with favorable cultivation conditions, territorial extension and broad investment in research and development (Fonseca et al., 2020). In this scenario, some crops such as cotton, soy, wheat, rice, bananas, coffee, potatoes, sugar cane, eucalyptus, corn and others, have grown a lot throughout the country, as well as the generation of associated lignocellulosic waste. Thus, some industries have already applied the biorefinery model to industrial processes in order to take advantage of the vegetable fiber composition and possible other valuable products from serial technologies (Longati et al., 2020). **Fig. 2** summarizes the main stages already consolidated in traditional models of biorefinery from lignocellulosic biomass of agricultural products.

Biorefineries can be applied in numerous industrial processes, being able to be linked in an integrated way to industries that are already consolidated or simply be autonomous, designed to operate independently of a specific industry. In each case, we have associated advantages and disadvantages, thus the best proposal must be evaluated in terms of operating conditions and economic advantages. On the other hand, three pillars support the idea of an industrial process based on the concept of biorefinery: the treatment, the breakdown of components into biomass, and the conversion into value-added products (Pachón et al., 2020). In general, these steps can be summarized in smaller and more specific processes such as obtaining and logistics for the transport of raw materials, pre-treatment steps, and initial separation to obtain primary products such as starch, cellulose, sugar and vegetable oil. There is also the secondary refining stage, with the conversion of primary products into new products. Finally, the by-products of the refining stages are used in new chains for the production of inputs for the food, pharmaceutical, feed and other industries. At each stage of the process, there are sub-stages associated with quality control, equipment maintenance, storage logistics, transportation and product marketing

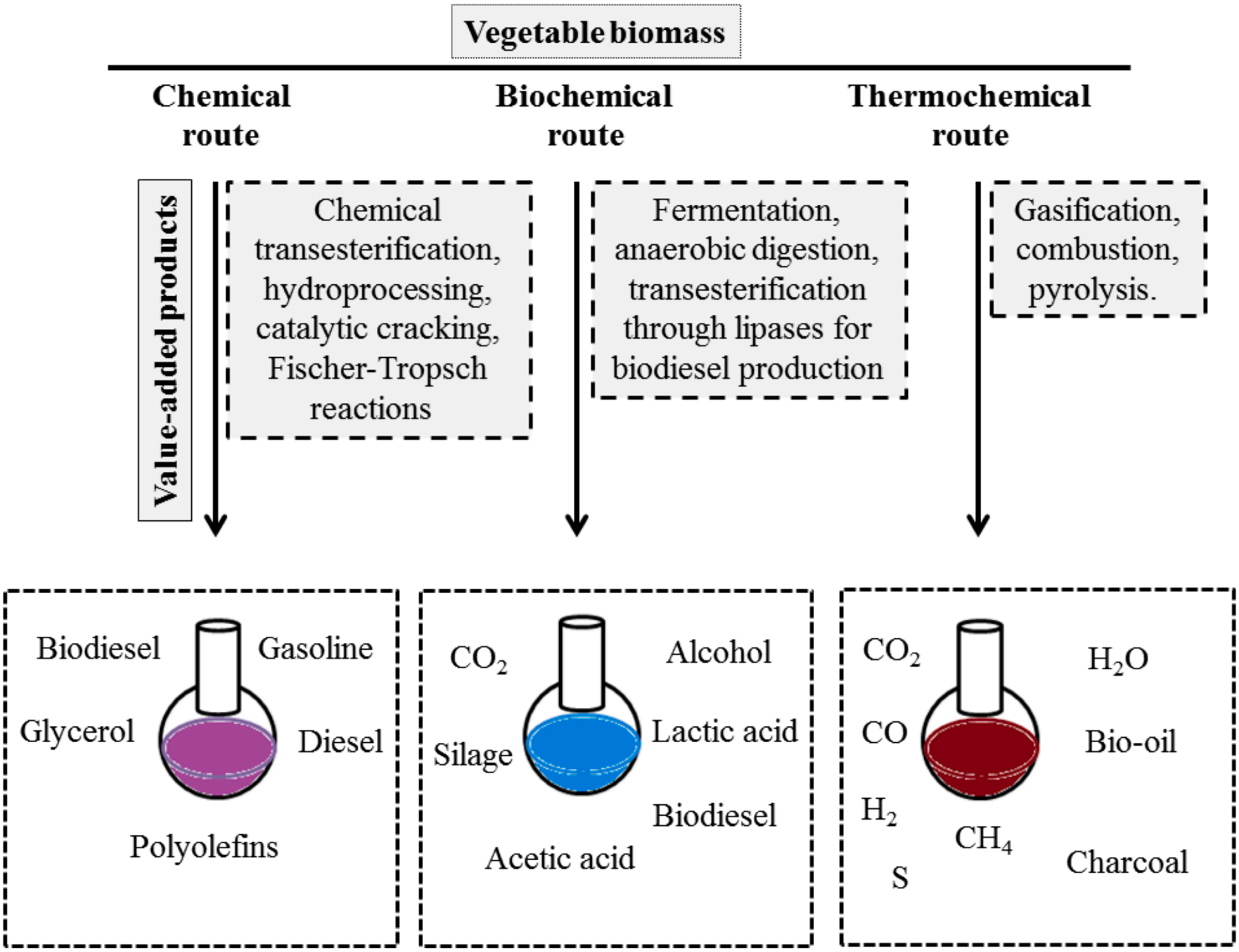

Fig. 2. Summary of the main stages already consolidated in traditional models of biorefinery from lignocellulosic biomass of agricultural products.

(Papadaskalopoulou et al., 2019). In **Figure 3**, a summary of the entire chain is described in basic process terms, associating the main steps together with the secondary steps.

Although biorefinery concept is seen today as key to implement a sustainable biobased economy (Dragone et al., 2020), the use of food waste as feedstock in biorefineries is still at an initial stage of development and studies evaluating its economic viability at large scale are rare. The study by Cristóbal et al. (2018) presents a techno-economic and profitability analysis of four food waste biorefineries that use wastes from orange, tomato, potato and olive processing as feedstock. This study revealed positive and negatives points of view, in addition to the cautions that should be taken. According to the study, the screening analysis performed at European level showed that not all the waste feedstock take the same potential and that the most profitable options are those linked to implementing fewer plants, namely concentrating the production and capitalizing on economies of scale.

Furthermore, it is also important to highlight that the usage spectrum of agro-industrial waste is quite diversified and it is not limited to the uses mentioned previously. Recently, researchers published a study in which agro-industrial waste is used as a new economical adsorbent in wastewater purification. In the study conducted by Meseldzija et al. (2019) it was used unmodified lemon peel, as agro-industrial waste, to investigate removal efficiency of copper ions from aqueous solutions and mining wastewater. This study revealed that the lemon peel was capable to remove up to 89% of copper from multicomponent mining wastewater, proving that this agro-industrial waste could be a promising adsorbent for the removal of copper ions from aqueous solutions and mining-wastewater.

Biomass can also represent a tool in the synthesis of materials in the civil construction segment by replacing conventional materials, which can reduce energy costs in the process and contribute to an effective management of agro-industrial waste (Jannat et al., 2020). The authors highlight physical-mechanical properties such as density, water absorption, resistance to compression, strength and thermal conductivity of agro-industrial waste materials, highlighting the application of these raw materials as novel construction material design.

The current scenario of the use of agro-industrial waste is closely linked to the development of new technologies, mainly those capable of extracting high added-value components to be used as food supplements and drugs. The next sections will deal in more detail on the application of these technologies on agro-industrial wastes.

3. New extraction technologies applied to agro-industrial wastes

The current trends for extraction of high added-value compounds from agro-industrial wastes are linked to the green technology methods. As the conventional techniques generally involve large amounts of organic solvents, high energy expenditure, and are time-consuming, the current trend is that they will be gradually replaced by new environmentally friendly extraction methods. These green extraction techniques

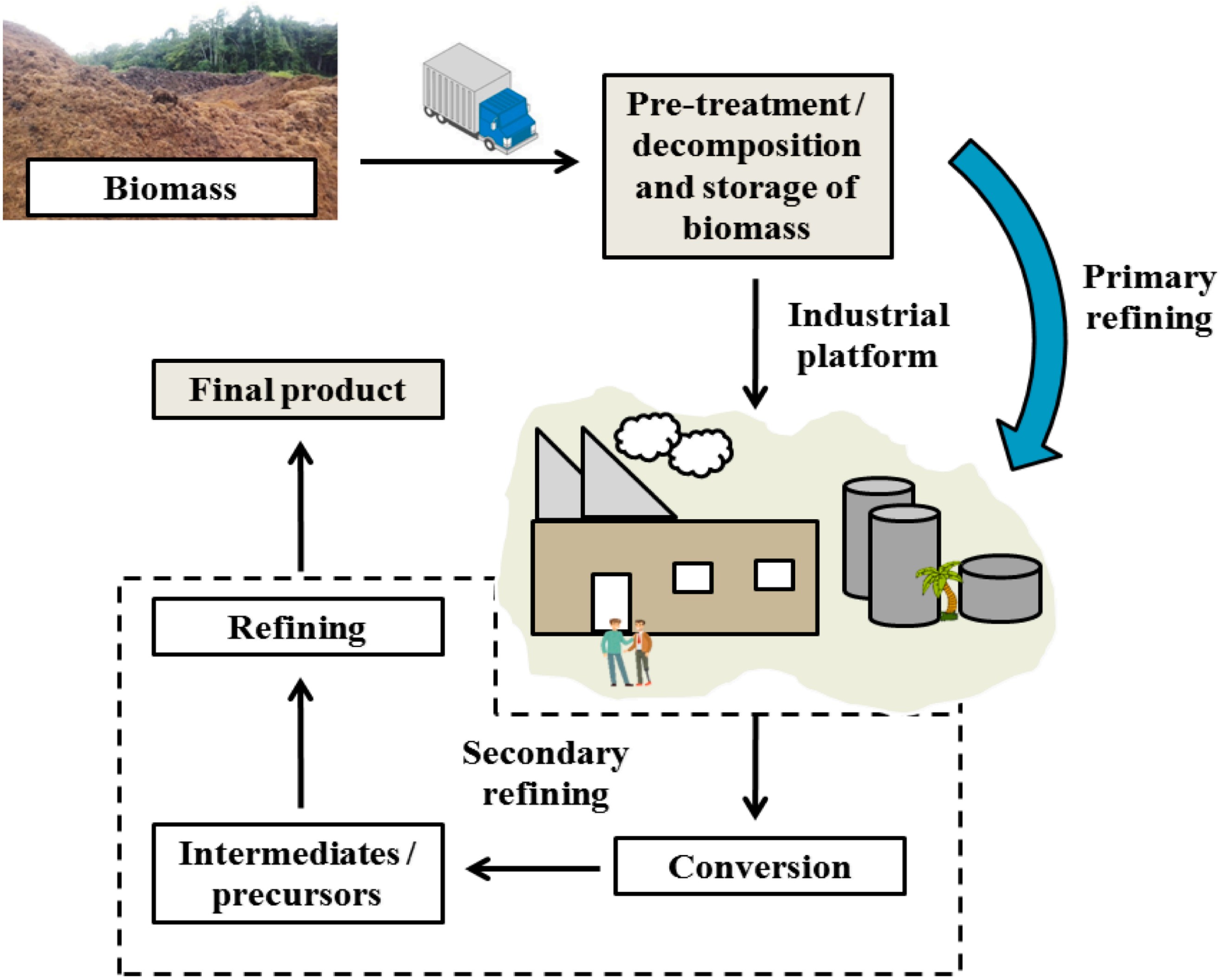

Fig. 3. Synthesis of a biorefinery in basic process terms, associating the main steps together with the second steps.

have greater applicability, are more selective in the recovery of products, and can contribute to the development of a more sustainable industry (Belwal et al., 2020). In order compare these technologies, Table 1 shows the advantages and disadvantages of different environmentally friendly extraction methods. In recent years, several works involving green extraction technologies have been intensively studied worldwide. Among these new technologies, it can be highlighted the supercritical fluid extraction (SFE), subcritical water extraction (SWE), ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE). Table 2 summarizes some recent applications of environmentally friendly extraction technologies on agro-industrial wastes.

3.1. Sub-and supercritical fluid extraction

In a few words, the supercritical extraction is known by the occurrence of changes in both temperature and pressure, which are capable to convert the gas in a supercritical fluid, making the liquid and gas phases indistinguishable. It is a mass transfer process, in which the convection in the supercritical solvent phase is usually the central transport mechanism (Soquetta et al., 2018).

Different from several other non-conventional techniques, supercritical fluid extraction (SFE) is a technique that has already crossed the barriers of the laboratory scale, since it has already been used industrially. In addition to it, CO_2 is the most used solvent on SFE because of its peculiar characteristics. According to Chemat et al. (2019), supercritical CO_2 is considered to be the ideal supercritical fluid due to its low critical temperature and pression (Tc = 31.1C, Pc = 7.38 MPa), which is an important advantage for the maintenance of bioactive compounds in extracts, in addition to be considered an inert solvent. The CO_2 is non-toxic, inexpensive, non-explosive, readily available, is easy to remove from the final product and it has a good extraction capacity due to its advanced penetration power. Additionally, it is generally recognized as safe (GRAS) solvent, which is not known to be hazardous for health and thus approved for use in foods (FDA, 2019). Other used solvents in SFE are propane, methanol, cooking gas (LPG), ethane, ethene, nitrous oxide, sulfur hexafluoride, n-butene, n-pentene and water (Da Silva et al., 2016). In the current scenario, supercritical fluids extraction is considered a favorable technology to take advantages of agro-industrial wastes since it allows to obtain several compounds with antioxidant activity that suggest applications in different fields such as pharmaceutical, food and cosmetic industries (Lizcano et al., 2019).

Table. 1
Advantages and disadvantages of different environmentally friendly extraction methods.

Extraction method	Advantages	Disadvantages
Supercritical Fluid Extraction (SFE)	- Environmentally friendly method - Preserve thermolabile compounds - Improved products properties - Improved yield - More selective - No solvent residue	- Requirement for elevated pressures - Relative high cost of initial investment
Subcritical water extraction (SWE)	- Environmentally friendly method - The solvent is water - Easier to perform - Few extraction steps - Lower maintenance cost	- Degradation of thermolabile compounds - Can oxidize or catalyze the hydrolysis of some compounds at elevated temperatures and pressures
Microwave-assisted extraction (MAE)	- High extraction rate - Reduced solvent usage - Improved extraction yield	- Non-selective - High power consumption - High capital cost
Ultrasound-assisted extraction (UAE)	- High extraction efficiency - Reduced extraction time - Use in thermosensitive compounds - Reduced installation cost - Easy maintenance - Reduced electrical energy consumption	- Non-selective - Decline of power with time

Subcritical water extraction (SWE) has also attracted the attention of the scientific community, as this technique provides several advantages, such as lower financial cost, greater safety, and efficiency of extraction, in addition to providing a modifying effect on the molecular structure, improving the biological activities of active ingredients. The studies carried out by Belwal et al. (2020), Soquetta et al. (2018), Da Silva et al. (2016) and Zhang et al. (2019) have already shown a very comprehensive approach on SFE and SWE concepts and fundamentals.

In terms of the applicability of SFE and SWE on biorefinery model, it is important to highlight that, after laboratory studies, the development of supercritical and subcritical fluid technology must pass through important stages of industrial plant design and economic analysis of the process. It is during the analysis stage of the industrial project that it is evaluated the pertinence of creating, modifying, expanding or even giving up the industrial plant.

Concentrating the discussion in general standings, by applying to all categories of agro-industrial waste exploration processes, two elements underlie decision-making: cost estimation and the admission of criteria for evaluating the merits for applying different investment alternatives (Knez et al., 2018). Although in the literature it is possible to find numerous articles on the economic viability of the process of extracting valuable products from waste using sub-and supercritical fluid technology, there is still no robust work addressing the assessment of industrial design at biorefinery level. In this regard, it is important to note that the industrial plant projects are mostly not presented in scientific articles, due to particular aspects related to patent rights and data privacy on industrial plants.

However, some review articles published recently (Ortiz, 2020; Knez et al., 2018) show that extraction plants or even other processes with supercritical fluids and other emerging technologies are commercially viable. As studies with these technologies advance, the use of integrated processes in series also advances, and have been used in several project models, proving to be an interesting strategy to expand production and reduce costs (Ortiz, 2020). Contextualizing, a work published by the authors Ortiz and De Santa-Ana (2017) shows that supercritical fluid technology improves biodiesel production. The researchers developed a self-sufficient energy process to produce 10,000 tons of biodiesel per year using supercritical methanol and propane as a cosolvent. After the process optimization, the equilibrium price of biodiesel was € 0.479 / kg of biodiesel, which was considered very competitive.

3.2. Ultrasound-assisted extraction (UAE)

Among the non-conventional extraction methods, ultrasound-assisted extraction (UAE) appears as one of the most viable in terms of cost. Therefore, it has been extensively studied on a laboratory scale in order to become feasible on an industrial scale. The ultrasound waves are used to cause disruption of cell walls that enable the release of target components in order to speed up diffusion and to increase mass transfer, in addition to permit a larger penetration of solvents into the ultrasound-radiated matrix (Chakraborty et al., 2020). These special effects, combined with the cavitation phenomenon and mechanical agitation, make the UAE a technique with low solvent and energy consumption, in addition to present reduced extraction temperature and time, which shows to be adequate for the extraction of thermosensitive compounds (Mena-García et al., 2019). A more in-depth information about the UAE

Table. 2

Recent applications of environmentally friendly extraction technologies on agro-industrial wastes.

Agro-industrial waste	Extraction method	Extracted compounds	Extraction yield (%)	References
Distillate liquor residues of *Arbutus unedo*	SFE	Phenolic compounds (pyrogallol, gallic acid, catechol, protocatechuic acid)	9.41	Alexandre et al. (2020)
Soybean residues from pressing oil extraction	SFE	Phenolic compounds and flavonoids	10.50	Alvarez et al. (2019)
Mango peel	SFE	Carotenoids	6.25	Sánchez-Camargo et al. (2019)
Onion residues	SFE	Oleoresin (Sulphur and pyruvate)	1.01	Devani et al. (2019)
Pistachio (*Pistacia vera* L.) hulls	SWE	Phenolic compounds (Flavonoids and gallotannins)	70.90	Ersan et al. (2018)
Satsuma mandarin (*Citrus unshiu* Markovich) peel	SWE	Flavonoids	60.00	Ko et al. (2016)
Custard apple peel	UAE	Pectin	8.90	Shivamathi et al. (2019)
Tomato processing wastes	UAE	lycopene	87.25	Rahimi and Mikani (2019)
Sour orange peel	UAE	Pectin	28.07	Hosseini et al. (2019)
Carrot juice processing waste	MAE	Carotenoids	77.48	Elik et al. (2020)
Jamun fruit (*Syzygium cumini* L.) seed	MAE	Polysaccharides	4.71	Abdullah Al-Dhabi and Ponmurugan (2019)
Cocoa bean shell	MAE	Proteins, polysaccharides and polyphenols	34.20	Mellinas et al. (2020)

SFE: Supercritical fluid extraction; SWE: Subcritical water extraction; MAE: microwave-assisted extraction; UAE: Ultrasound-assisted extraction; MAE: Microwave-assisted extraction.

fundamental principles can be found on Rutkowska et al., 2017; Lavilla and Bendicho, 2017 and Vinatoru et al., 2017.

3.3. Microwave-assisted extraction (MAE)

Microwave-assisted extraction is considered a young technique compared to ultrasound-assisted extraction. However, a considerable number of laboratories have developed researches on it, revealing the huge potential of this non-conventional energy source for extraction applications.

As definition, microwaves are radiation of the electromagnetic spectrum oscillating in frequency from 300 MHz (radio radiation) to 300 GHz. (Chen et al., 2017) The MAE has several advantages such as extraction selectivity, reduced installation cost, easy maintenance, as well as shorter extraction time, shorter time needed for preparing the process and shorter electrical energy consumption when compared to conventional methods. For more in-depth background information about MAE principles you should read this excellent review which was conducted by Vinatoru et al. (2017).

3.4. Viability aspects of SFE, UAE and MAE for industrial scale application

The feasibility of applying technologies (SFE, UAE and MAE) for the recovery of waste in a context of biorefinery on an industrial scale is still highly questioned. Although striking studies specific to each technology are needed, modern studies show that the technologies covered in this review can revolutionize the way of doing industry in the world. Considering the issues related to the trend towards verticalization of technologies based on the bioeconomy, it is possible to justify why these technologies should soon be the basis for industrial processes.

In a practical context, the application of technologies (SFE, UAE and MAE) in a biorefinery project must meet some criteria. The first one should be the understanding that each raw material has unique input processing and parameters. For instance, the processes for recovering fermentable sugars from lignocellulosic residues are different for each raw material. Therefore, a lignocellulosic waste biorefinery that uses one of the mentioned technologies must have an exclusive infrastructure for each specific raw material, or even an industrial plant capable of adapting to other process conditions. The second criterion is the possibility to scale up the technology used. In this sense, it is important to highlight that all technologies described in this paper have input and output parameters that can be used for scale-up studies. These mentioned criteria strongly help in the development of industrial projects (De La Rosa et al., 2019).

Extraction technologies can be adapted to meet specific demand. In the context of a biorefinery, supercritical fluid and subcritical fluid technologies can be used for biomass hydrolysis. Reactors can be developed to carry out controlled hydrolysis of biomass. In combination, a separation and purification system can also be coupled (Knez et al., 2018). **Figure 4** presents a summary of a sugarcane biorefinery scheme, using supercritical fluid technology for hydrolysis and production of fermentable sugars.

Another relevant aspect is the economic viability of industrial plants in the models of a biorefinery. Financial capital is undoubtedly a decisive factor in scale-up projects, especially when fixed and variable costs are considered. These terms have been widely used within the perspective of manufacturing cost of a process, which works as a highly reliable tool to predict the economic viability of a specific process. For a complete study of these parameters, some terms are applied as cost of raw material, fixed investment, cost of utilities and cost of operational labor (Zabot et al., 2018). Although few studies have explored the economic feasibility study in process with the use of waste, other studies applied to oilseed extraction processes have shown that capital amortization increases as the production capacity of the industrial plant increases (Duba and Fiori, 2019). In addition, it has been shown that although the use of financial resources at the beginning of projects is considered high, these resources are recovered within a short time (Zabot et al., 2018).

A relevant aspect considering the supercritical fluid technology, compared to the other described technologies, is associated with the low energy consumption of the processes, mainly considering the process of transformation of carbon dioxide phases. Optimizing the energy cost helps to reduce the production cost and increases the economic viability of the project. It is worth mentioning that the technologies covered in this paper have peculiarities regarding the energy cost that must be evaluated in isolation (Costa et al., 2018). The balance studies of entropy and enthalpy associated with equipment such as pumps, cooling baths, compressors and others, help to balance the energy cost balance (Costa et al., 2018).

Therefore, considering the indications and studies highlighted above, it can be inferred that the viability of the industrial implementation of the technologies reported in this paper (SFE, UAE and MAE) is considered promising. In addition, the ruled results show that these technologies have increments that justify studies and ample investment in their potential for expansion and scaling up. Thus, more studies should be conducted to expand the discussion on the use of these technologies on an industrial scale.

4. Agro-industrial wastes for pharmacological applications

The extraction of valuable components from agro-industrial waste using new technologies has been intensely reported in the pharmacological area (Ben Mohamed et al., 2016; Bezerra et al., 2018; Brenes

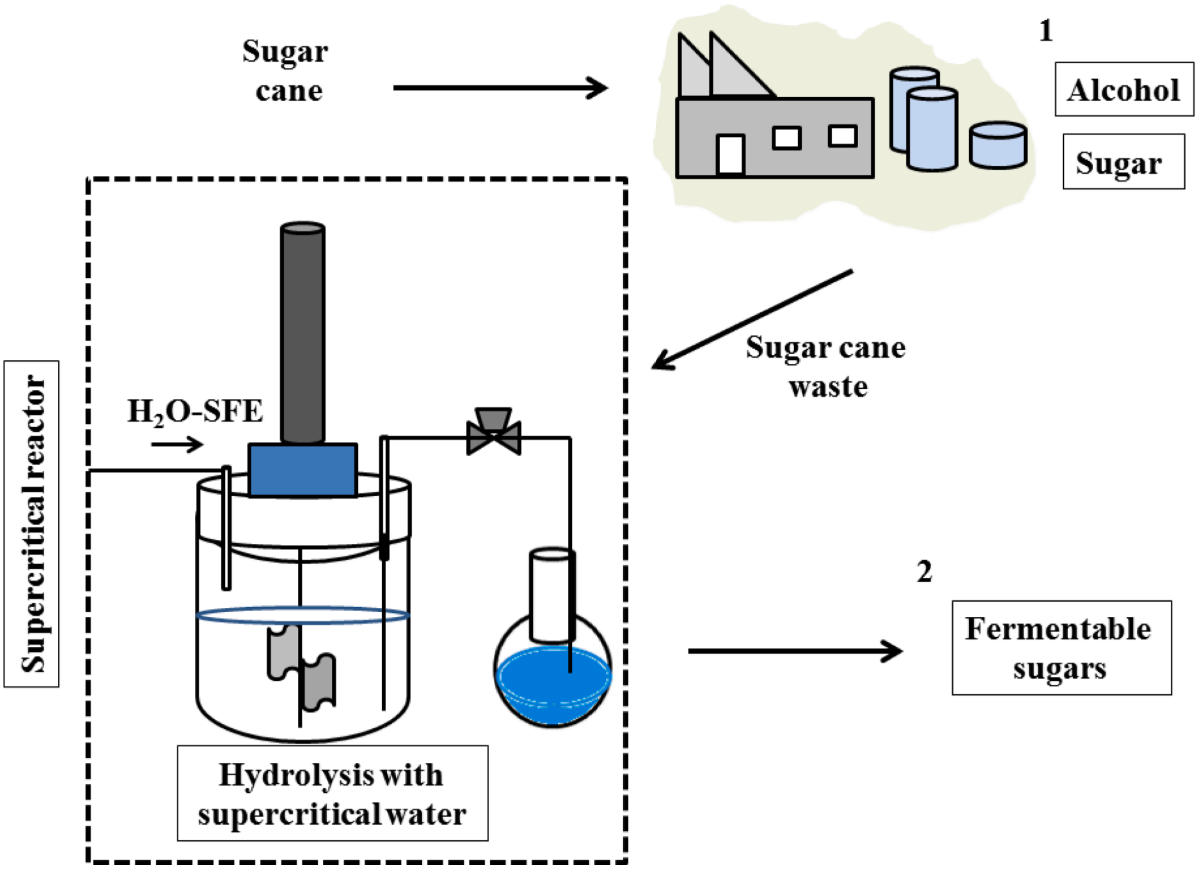

Figure. 4. Schematic summary representing a sugarcane biorefinery using supercritical fluid technology for hydrolysis and production of fermentable sugars. In step 1, we observe the main products of the sugar cane industry, while in step 2, we observe the products of supercritical hydrolysis.

et al., 2016; Espinosa-Pardo et al., 2017). In this context, the synthesis of drugs from unconventional methods and sources can be an alternative to those traditionally used, adding value and providing a sustainable setback to biomass produced on a large scale, mainly by the food industry. In recent years the agro-industrial waste have been studied for a more refined and ecological application to what would be simply discarded. Some potential applications of agro-industrial waste as delivery agents, nutritional pharmacology and as sources of biological activities will be discussed below.

4.1. *Delivery system*

Silk waste protein were studied as a possible electrospun nanocarrier for floating drug delivery of lafutidine, a gastro-retentive drug. In the study, the authors (Nangare et al., 2020) concluded that the system can act as a carrier, floating for 24 hours and releasing the drug, in addition to being biocompatible, biodegradable and presenting potential for gastro-retention. Mango peel waste was used in the study by Chaiwarit et al. (2020) as a source of pectin as a film-forming agent in film formulations. The study revealed that this source presented itself as a potential drug delivery system. Therefore, residues can act as biocomposites responsible for the storage of biomaterials or as a controlled delivery system for therapeutic agents releasing them in a controlled manner in the target organism, in addition to the possibility of replacing materials from non-renewable sources by biodegradable and environmentally friendly alternatives.

4.2. *Nutritional pharmacology*

Cocoa bean hulls is a by-product of the high value-added agribusiness due to its chemical composition that presents a high concentration in phenolic compounds with potential use in nutraceutical products. Mazzutti et al. (2018) studied obtaining these compounds using unconventional recovery techniques such as the integrated green-based process that consisted of a combined process between extraction with supercritical fluid (CO_2) followed by extraction with pressurized liquid (ethanol). The environmentally friendly method was considered a promising, technical and economical viable solution in the recovery of bioactive compounds such as cocoa lipids, caffeine and theobromine, suggesting the application in pharmaceutical products, adding value to the commonly discarded waste.

Similarly, grape seed oil was able to increase HDL-cholesterol and reduce LDL-cholesterol in treated patients; wistar rats treated with the oil for ten weeks showed a reduction in cholesterol levels in the liver due to a reduction in food intake (Beres et al. (2017). In the study by Klančnik et al. (2017) the extract from waste skins and seeds of Pinot noir grapes inhibited the adhesion of *Campylobacter jejuni* (gastrointestinal bacterial pathogen most commonly reported in humans) to polystyrene surface and pig small intestine epithelial (PSI) and human fetal small intestine (H4) cell lines, modulating the pathogen invasion and intracellular survival to these biotic and abiotic surfaces.

Notoriously, several classes of biomolecules such as phenolic compounds, phenolic acids, glycosylated compounds, terpenoids, alkaloids, peptides, fatty acids, proteins can still be part of the phytochemical composition of several agro-industrial residues that are discarded, but which still have great potential to be applied in human nutrition due to its potential antioxidant, antimicrobial, thermogenic activity that can act in a therapeutic way in the prevention and control of disorders, providing health benefits.

4.3. Potential biological activities in drugs

Mahato et al. (2018) presented research that reported biological activities with potential pharmacological applications of citrus waste. In the study, several *Citrus* species (*C. sinensis, C. sphaerocarpa, C. medica, C. unshiu, C. unshiu, C. reticulata, C. kawachiensis, C. depressa*) showed several effects such as hepatoprotective, immunosuppressive, antimicrobial, inhibitory on breast cancer metastasis, antiulcer, anti-obesity, antituberculosis, proangiogenic, anti-aging, anti-inflammatory, as well as the blood circulation improvement, and the enhancement of learning and memory. Some of these, attributed to phenolic compounds, flavonoids, polymethoxyflavonoids, tannins, saponins, essential oils, and polysaccharides.

Ballesteros-Vivas et al. (2019) proposed the valorization of mango seed kernel to improve the sustainability of the mango processing industry by obtaining the non-polar (fatty acids and lipids) and polar (polyphenols) fractions. The authors concluded that the fractions presented *in vitro* bioactivity, with antiproliferative activity exhibited against human colon adenocarcinoma cell line HT-29.

Beres et al. (2017) reported several beneficial effects of grape seed oil produced from solid waste generated by wine industries. Such effects were attributed to the antioxidant, anti-inflammatory and anti-apoptotic activities of the oil, which acted in reducing the inflammatory response through free radicals scavenge, improving the activity of antioxidant enzymes and also the responses down-regulate the gene expression levels of xanthine oxidase and inducible nitric oxide synthase.

The studies reported above highlight the high potential that agro-industrial waste can present, being valuable sources of bioactive compounds that can be converted into pharmacological products. Such forms of use can add value to these residues, which, in general, are simply discarded in the environment. In addition, Beltrán-Ramírez et al. (2018) highlight the growth of market interest in products from agro-industrial residues, demonstrating the trend of increased research and investments in the sector, such as the pharmaceutical industry that has been investing in research related to bioactive peptides and biocomposites, promoting the incorporation and valuation of more environmentally friendly materials.

5. Agro-industrial wastes as ingredient for food production

High amounts of waste are generated daily in the agri-food sectors. Such residues come from different stages of the production chain, which include the steps of harvesting, transportation, storage, industrial processing, commercialization and final consumption. Nevertheless, these residues (peels, seeds, among others) can provide several nutrients necessary for health, such as vitamins, minerals, fibers, carbohydrates and proteins, commonly presented in greater quantities than in other parts of the fruit. Most agro-industrial residues containing fats, natural dyes, enzymes, pigments, antimicrobials and antioxidants are natural food ingredients, additives and supplements with high added value that can be reused for industrial production in the development of new food products, becoming a viable alternative for both the economy and the environment (Bellemare et al., 2017). Some potential applications of agri-food waste as ingredient in food industries are discussed below.

5.1. Natural antioxidants

Recent studies have been highlighting various technologies for the reuse of agri-industrial waste as ingredients for food production. In this context, Gupta et al. (2019) studied the use of dry powder from fruit residues (pomegranate, grapes, lemon, apple and papaya) in order to investigate its potential in terms of natural pigments source, which showed excellent results. Furthermore, pigments from different fruit residues are beneficial to health. For instance, carotenoids obtained from pomegranate peel and tomato peel are commonly used as food dyes, bringing essential health benefits in the form of vitamin A precursor, improving skin health and helping with immune system defenses (Goula et al., 2017; Lima et al., 2019). In the same way, carotenoids from melon residues also provide health-promoting compounds since they have valuable antioxidants such as lutein and β-carotene (Benmeziane et al., 2018). These compounds are quite demanded since there is a greater request for natural antioxidants compared to the synthetic ones, due to its beneficial properties that include biocompatibility, low toxicity, economy, production and environmentally safe disposal.

Ferri et al. (2020) reported that red grape marc is a good raw material for the production of bioactive molecules of industrial interest, as it provides a high content of phenolic compounds. Likewise, anthocyanin is another food additive with beneficial properties for health. It was extracted from grape marc after vinification, and it presented an anthocyanin content higher than in the grape peel, and even higher than in the wine, in addition to retain methoxylated and acylated pigments which are particularly more stable (Goula et al., 2017; Favre et al., 2019).

5.2. Functional components

The use of agro-industrial waste is also applied to the development of new food products, such as ingredients for cookies with functional properties, in which the extract of the pomegranate peel encapsulated with by-products from the orange processing industry was obtained, and the encapsulation enabled the retention of phenolic compounds without the loss of antioxidant activity, oxidation stability and sensory alteration in the quality of the product (Kaderides et al., 2020). Other promising residues with high added value have also been applied recently in bakery products. The goji berry residues have been applied as substitutes for different levels of wheat flour in the production of muffins and cookies, providing a significant increase in proteins, free phenolic compounds and soluble / insoluble dietary fibers. In addition, it showed good sensorial characteristics according to the flour replacement levels, presenting itself as a functional ingredient with excellent potential (Bora et al., 2019).

The use of soybean residue also made it possible to extract value-added products for use in the processing and development of functional foods, as it presented a significant amount of dietary fiber, proteins and isoflavones with good antioxidant activity potential (Nile et al., 2020).

5.3. Polysaccharides

Other important by-products for the food industry are the residues of edible mushrooms, which represent 20% of the total production, mainly composed of mushrooms with deformed lids and / or stems, which directly influences the rejection by retailers (Aguiló-Aguayo et al., 2017). However, they constitute a source of important compounds such as polyphenols and polysaccharides that contain various medical activities, including anti-tumor, anti-inflammatory, antibacterial, hypoglycemic and immune-enhancing activities, as well as terpenoids, vitamins (vitamin D2) and sterols (ergosterol) (Gong et al., 2020). Studies carried out recently revealed that residues from mushrooms are of potential value for the food industry. Correa et al. (2018) extracted and obtained compounds rich in ergosterol from *A. Blazei* commercially discarded. The extract was used as a fortifying ingredient in yoghurts, in which the ergosterol extract had good antioxidant properties and did not alter the nutritional profile of the product. Although the mentioned researchers have obtained a good yield in terms of ergosterol extraction, they used soxhlet technology, which is not an environmentally friendly method. In this situation, choosing a green extraction technology would be interesting from the environmental point of view and extract quality.

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Thus, the reuse and recovery of these agro-industrial wastes provide greater availability of value-added raw materials that can be used as ingredients in the food industry, contributing positively to the development of technological products of high biological value. In addition, they contribute to the environment, as they affect the reduction of waste disposal. However, quality parameters for obtaining and isolating biologically active compounds must be adopted, taking into account mainly the stability of the product and the use of an environmentally friendly extraction process.

6. Lignocellulosic residues for production of biomaterials

Lignocellulosic raw materials are natural, renewable, biodegradable, environmentally friendly matrices, which are available in large quantities and at low cost, with satisfactory and potential characteristics for industrial applications in different segments. The advantages of these matrices in comparison to synthetic inputs include: a great diversity of extractable loads from forest sources and agro-industrial residues; low density and reduced energy consumption; specific strength and modulus; reactive surfaces that can be easily modified and functionalized by different groups; high applicability in nanoparticle systems and possibility of recycling. In general, most of the lignocellulosic biomass is composed of 10-25% by weight of lignin, 20-30% of hemicellulose and 40-50% of cellulose (Fortunati and Balestra, 2019).

Lignin is the largest non-carbohydrate component of lignocellulosic biomass, which provides resistance and hydrophobicity to plant cell walls, protecting polysaccharides from degradation by microorganisms. This structure consists of a complex aromatic biopolymer, derived from the subunits syringyl, guaiacyl and hydroxyphenyl (Geun Yoo et al, 2020). Hemicelluloses are polysaccharides that make up the cell wall of vegetables, composed of monomeric units other than cellulose. The term hemicellulose comprises a heterogeneous class of linear and branched polysaccharides that include pentoses and / or hexoses (De Azeredo et al., 2018). Cellulose is a linear homopolymer, insoluble in water, of high molecular weight, formed by monomers of β-D-glycopyranosyl, joined by glycosidic bonds (1 → 4). Due to their flat and linear nature, cellulose molecules can associate with each other through hydrogen bonds over extensive zones, forming fibrous and polycrystalline bundles (Damodaran et al., 2018).

The lignocellulosic composition of some agro-industrial wastes is shown in the **Supplementary material (A)**. Different parts of vegetables are highlighted, such as husks and straws, in addition to bagasse from processing.

6.1. *Applications in the production of biomaterials*

The lignocellulosic compounds from agro-industrial wastes biomass can be used in the synthesis of biomaterials for different purposes, which include applications in the segments of biomedicine, engineering and pharmacy, through the synthesis of bioaerogels, biofilms, bionanocomposites and hydrogels. These nanocellulosic biomaterials can be used in tissue engineering scaffold, controlled drug delivery and biosensing (Fortunati and Balestra, 2019; Soorbaghi et al., 2019).

6.1.1. *Bioaerogels*

Bioaerogels consist of structures with interesting properties, such as high surface area, micro or nano porous structure and low density (Ubeyitogullari and Ciftci, 2020). Researchers reported the use of lignocellulosic materials in the production of bioaerogels (Zaman et al., 2020). Spongy aerogel based on corn straw was developed by Li et al. (2018) to capture oil. Shearing and lyophilization techniques were applied, providing the synthesis of biodegradable material. Rice husk silica aerogel was synthesized by Rajanna et al. (2015). This material was developed using the sol-gel technique, in a water-in-oil emulsion system. The characteristics of the product obtained enhance its use in controlled drug delivery systems. Hydrophobic aerogel from wheat husk ash was developed by Liu et al. (2015), using sol-gel technique, by drying at room pressure. Aerogels of cellulose nanofibrils were synthesized by Jiang and Hsieh (2014). These materials were developed from rice straws, containing characteristics of ultra-lightness, ultra-porosity, in addition to an excellent amphiphilic absorption, presenting potential for application in oil separation operations. Wheat straw lignin aerogels were synthesized by Perez-Cantu et al. (2014) by cross-linking with oligo (alkylene glycol) -α, ω-diglycidyl ethers and drying via supercritical CO_2. The materials produced can be applied in thermal insulation systems.

6.1.2. *Biofilms*

Biofilm of lignocellulosic components of the sugar processing bagasse was synthesized by Aradmehr and Javanbakht (2020), with the addition of chitosan and silver nanoparticles. The product made with high concentrations of lignin showed high flexibility and increased swelling properties. The hydrogel produced has antimicrobial and antioxidant potential. Nano-biofilm based on nanocellulose biopolymer derived from plant biomass was developed by Hossain et al. (2018). This investigation was carried out using corn leaf residues from the agro-industrial processing, without chemical treatment. The parameters of water absorption, odor, pH, cellulose content, shape, firmness, tensile strength, mineral composition were analyzed. The elaborated product can replace plastic derived from petroleum, once it is biodegradable.

6.1.3. *Bionanocomposites*

Bionanocomposite films of gelatin / nanocrystals of eucalyptus cellulose were developed by Leite et al (2020), using the continuous casting technique. The products produced presented satisfactory characteristics such as transparency, flexibility and thermal properties of UV barrier, with potential for applications in food packaging. Starch bio-composites of bengkoang / cellulose nanofibers from pineapple residues were synthesized by Mahardika et al. (2019) through ultrasound. The developed materials have tensile strength, better than fiber-free products, presenting potential for application in demands for systems based on renewable matrices, which are safe for food. Biocomposites containing chitosan were synthesized with rice straw cellulose nanocrystals by Xu et al (2018). The materials were synthesized by ultrasonic acid hydrolysis. The developed products have potential for applications in food packaging systems, controlled drug delivery and bio-sensing.

6.1.4. *Hydrogels*

Hydrogels consist of heterogeneous mixtures of two or more phases, in which the network of three-dimensional solids corresponds to the solid phase, and the water comprises the dispersing phase (Du et al., 2019). The production of hydrogels using lignocellulosic biomass is reported in the literature. Hydrogel based on polyvinyl alcohol reinforced with coconut shell cellulose was developed by Thinkohkaew et al. (2020). This material was produced using the alkali delignification technique. The elaborated product presents potential for applications in controlled drug delivery systems, artificial cartilage, dressings and cosmetics. Celery cellulose hydrogels were produced by Yan et al. (2019) using the phase inversion method. This research evaluated these materials for the administered release of short chain fatty acids. Hydrogels were synthesized with cellulose from tea residues and graphene oxide, in ionic liquid. This study indicates that hydrogels have good adsorption capacity and adsorption rate (Liu et al., 2017).

6.2. *Application in tissue engineering*

The research developed by Ghorbani et al. (2020) suggests the use of chitosan hydrogel reinforced with cellulose nanocrystals as scaffolding in tissue engineering, due to the increased proliferation of chondrocytes, indicating a possible application in the regenerative treatment of cartilaginous tissue. The study by Huerta et al. (2020) proposes the use of cellulose nanofiber hydrogel, with clove essential oil, as a scaffold in tissue engineering, due to the non-cytotoxicity in human gingival fibroblast cells. Investigations carried out by Chakraborty et al. (2018)

enhance the use of regenerated cellulose nanofiber scaffolding in bone tissue engineering. In this research, *in vitro* tests were performed for MC3T3-E1 osteoblastic cells, evaluating cell adhesion and proliferation in SEM and MTT assays. The study developed by Ko et al. (2018) with scaffolds composed of chitosan-g-D, L-latic acid and cellulose nanocrystals from lettuce leaves (*Lactuca sativa* L.) provides data on MTT cell characterization and viability, which enhance the application of these materials in tissue engineering. The study developed by Shaheen et al. (2018) showed that cell growth and cell adhesion were improved with the incorporation of cellulose nanocrystals in scaffolds consisting of chitosan / alginate / hydroxyapatite, enhancing applications in bone tissue.

7. Agro-industrial wastes as alternative source of energy generation

Agricultural crops are one of the main sources of food production worldwide, which play an important role in the distribution of income, generating a profound impact on the socio-economic dynamics. In a broader aspect, it influences the entire global economy (Prasad et al., 2018). Some agricultural crops such as cereals, legumes, oilseeds, sugar and tubers were the commodities that grew the most and produced the agro-industrial waste in the last 10 years. It is believed that at least 25 to 30% of all energy biomass produced in the world may be from agro-industrial waste, available potential that can be applied in the production of sustainable energy. In this framework, agro-industrial waste has been the focus of extensive research, concentrating on sustainable energy production (Prasad et al., 2018).

Some relevant questions about the economic and technological aspects of power generation, discussed below, pave the way for a more comprehensive understanding of the topic. Among them, we can highlight the need for new sources of energy material, depletion of fossil reserves, the considerable increase in pollution by conventional fuels and the need for sustainable management of energy sources (Prasad et al., 2020). The statements highlighted above are specific characteristics to be considered, taking into account the current energy generation status of the world.

Some of the current main problems are precisely the increase in agro-industrial wastes, dependence on fossil fuels and emission of greenhouse gases. In addition, there is a clear need to develop a sustainable economy and improve carbon-neutral energy production policies. It is known that agro-industrial residues are mainly rich in cellulosic material with a high fixed carbon content, which are ideal for use in the production of sustainable energy. Moreover, this biomass is rich in nitrogen, which is extremely important since it influences the carbon / nitrogen ratios. Due to the current needs already reported, several technologies have been developed for the production of sustainable energy such as bioconversion, enzymatic saccharification, two-stage anaerobic digestion, biochemical conversion, co-fermentation, anaerobic digestion, dark fermentation, among other technologies (Akbarian-Saravi et al., 2019; Kumar et al., 2019).

On the other hand, it is important to enhance that the entire process of energy production generates profound impacts, and are underlying several problems and challenges associated with environmental, sustainability, poverty and security issues (Prasad et al., 2020). Also, the production of energy from agro-industrial waste is subject to other needs that must be assessed, such as availability of biomass, assessment of environmental implications, planning and logistics, business plan, economic feasibility, cost-effectiveness, energy index net produced, social and economic impact, as well as the generation of emissions during production and consumption (Hiloidhari et al., 2017).

Biomass is usually divided into two main groups: woody biomass and non-woody biomass. Although this classic division does not include all the current state of the art on the subject, this division is used to understand how biomass can be applied to energy production. Woody biomass consists of more compact and large lignocellulosic materials, used for the production of thermal energy in industries, or even in households, where they are applied for food preparation and other activities. On the other hand, non-woody biomass can be applied in the most varied energy production processes, mainly due to the few processes of unitary operations necessary for the sample preparation used for energy production (Hanaki et al., 2018).

Technologies for the production of energy from biomass go through several stages, some more viable than others. However, in general, these technologies produce the most varied forms of energy. For instance, the conventional combustion process can be used to produce energy in the form of electricity, using biomass as a carbon source for burning in boilers, producing steam at high pressure, which can be applied in the movement of turbines used to generate electricity. Gasification technology is also applied in energy production using agro-industrial waste, where energy production can be applied for the production of mechanical work and electricity generation (Wang et al., 2019; Tian et al., 2019).

The non-woody biomass is converted into oil through the pyrolysis process used for combustion, producing heat and energy. Additionally, wet biomass and other residues are used for the production of hydrogen and biogas, using fermentation processes in solid and submerged cultures, in addition to the anaerobic digestion process. Biomasses rich in sugar and polysaccharides such as starch, pectin, cellulose and chitin are used for the production of bioethanol, through various biotechnological and biochemical processes such as enzymatic hydrolysis, saccharification and fermentation. (Usman Khan et al., 2019; Kumar et al., 2019). Broader aspects of the use of biomass in energy production, informative data on the availability of surplus residues from agricultural crops, management of agricultural residues, burning of residues and their consequences, energy potential, technologies for cost evaluation and process planning can be consulted in the following works (Prasad et al., 2020; Zubair et al., 2020; Jiang et al., 2020; Cai et al., 2018).

The production of energy from biomass is undoubtedly a very interesting alternative, especially considering all technological and economic aspects. The development of the energy production processes discussed in this paper elucidate the importance of extensive investment in research and technologies applied to the energy generation field. Finally, further studies on aspects related to the development of joint processes, such as extraction and purification, and studies on the use of supercritical CO_2 as a catalyst for energy production are still required. In the next section, a didactic approach will be conducted with the aim of broadening the discussion for future trends and new investment opportunities.

8. Future trends and new investment opportunities

The basic pillars for the development of a sustainable society must explicitly pass through the development of efficient technologies, with moderate cost, ecologically correct and that have parameters that facilitate the increase of scale for industrial production. The role of an ecologically correct waste reuse industry is precisely to guarantee the well-being of the planet and to contribute to the economy and society (Marwaha et al., 2018). In this context, it is possible to look to the future of the reuse industry as promising, especially when we consider advances, trends and new investment opportunities.

The technologies for extracting value-added compounds from waste have undergone major changes. New, more efficient, innovative and ecologically correct technologies are gaining ground in academic productions. The technology of supercritical and subcritical fluid for hydrolysis of biomass and extraction of bioactive compounds from waste is already a reality. Several recent works (Bezerra et al., 2018; Da Costa., 2018; Lachos-Perez., 2020; Pedras et al., 2020) demonstrate that it is possible to apply these technologies for the extraction and hydrolysis of biomass. Supercritical fluid technology is an innovative and emerging proposal that offers many opportunities for investment and the development of new business plans. MAE and UAE also have great prospects for scaling up.

Another emerging technology, with ideal characteristics for processing waste and extracting valuable resources, is deep eutectic solvent technology. The technology was first reported by Abbott et al. (2004) and is based on a mixture of two or more hydrogen bond acceptor and hydrogen bond donor compounds that act on the degradation of the physical structure of a given biomass. The technique emerged as an alternative in the pre-treatment of biomass, showing similarities to conventional ionic liquids, but with the advantage of having less toxicity, greater biodegradability, lower cost, easy preparation, low volatility, thermal stability, high conductivity and improved enzymatic compatibility (Pan et al. 2019; Lin et al. 2020; Xue et al., 2019; Loow et al., 2018). Recent works (Mamilla et al., 2019; Yi et al., 2019; Thi et al., 2019; Li et al., 2019; Ling et al., 2020) showed that eutectic solvent technology can be applied to various types of waste processing. In addition, the development and improvement of these technologies will open up new markets with clear opportunities for new investments, contributing to the advancement of a more sustainable economy.

The use of waste for the recovery of added value compounds is undoubtedly one of the major current challenges. The development of viable industrial processes is still a challenge due to several problems such as development of suitable industrial plants, cost reduction for the recovery of added value compounds, consumer market, among others. However, expectations can be considered encouraging, especially when we compare the latest efforts to implement projects of biorefineries and pilot plants for the production of enzymes, polymers and edible biomass from fungi and yeasts (Narra et al., 2020).

The expectations for the development of cheaper and ecologically correct energy production processes using residual biomass have been undergoing radical changes. The growing number of companies and biorefineries interested in developing processes for the production of sustainable energy is one of the most relevant aspects of the current state of the art on the reuse of waste. In Europe, until 2018, more than 40 biorefineries were cataloged using lignocellulosic materials for sustainable energy production. Great challenges and many opportunities arise with the development of these new industries. The technology developed by these companies provides key elements linked to biorefining, including raw material supply, processing methods, cost and market analysis (Hassan et al., 2018).

Several companies throughout the world have shown growing interest in the use of residual biomass. In 2012, Beta Renewables installed the world's first cellulosic ethanol industrial operating plant. With the success of this initiative, other companies began to develop industrial plants for the reuse of waste such as Crescentino, in Italy, in 2015. In addition to the mentioned companies, others have been implementing technologies for the use of cellulosic material for the production of ethanol and other compounds in countries such as India, Brazil and China (Rosales-Calderon et al., 2019).

Although the energy production industries and or even value-added compounds industries are still in few number and less competitive, in the last decade these industries has made significant progress. In this context, the production and commercialization of cellulosic ethanol has been gaining space, mainly due to the low cost of the substrates that are readily available. Regarding these aspects, we can consider a promising future, especially when we observe new companies investing in the development of industrial processes and plants for the use of waste, as observed in 2015 with the implantation of a cellulosic ethanol factory by the company Abengoaabriu, in the Kansas, USA (Hassan et al., 2018).

Concerning the promising aspects, it is interesting to evaluate that the commercial use of agro-industrial wastes for the generation of bioenergy and other valuable products can generate many direct and indirect employments, as well as assist in the development of a new method of dealing with waste management. In addition, there is a growing possibility for new investments such as the creation of startups and or even new companies to act directly or indirectly on business models related to the reuse of waste. Biomass will be the most real and viable future energy source to the detriment of conventional ones. A more efficient and accessible planning, improvement and business models for commercial use should continue to be developed and studied.

9. Conclusions

Agro-industrial waste is no longer seen as a problem, but is now seen as an opportunity. Studies aimed at reusing waste in a sustainable manner have advanced significantly on laboratory scale and have begun to be implemented on industrial scale. Also, the concept of biorefinery is already being applied, despite being at an early stage with needs for improvements. Energy generation from agro-industrial waste biomass and the production of biomaterials have gained space, presenting promising growth trend. Therefore, the agro-industrial wastes can help in the development of various products, promoting new investment opportunities that satisfy both economic and environmental concerns. However, further studies are still needed regarding the applications of SFE, UAE and MAE on an industrial scale. Moreover, greater government incentives are needed to generate more opportunities for research and technological development, encouraging the bioeconomy through sustainable production alternatives, and consequently improving society's quality of life.

Declaration of Competing Interest

The authors declare no conflict of 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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Supplementary materials

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CAPÍTULO II

Supercritical fluid technology as a tool to valorize bacuri fruit (*Platonia insignis* Mart.) shell.

(Tecnologia de fluido supercrítico como ferramenta para a valorização da casca do fruto do bacuri (*Platonia insignis* Mart.)

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Supercritical fluid technology as a tool to valorize bacuri fruit (*Platonia insignis* Mart.) shell.

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ABSTRACT

Bacuri (*Platonia insignis* Mart.) is a fruit composed of up to 70% shell, a fraction often discarded as agro-industrial waste. Therefore, the purpose of this work was to study the bacuri shell through the application of supercritical technology in order to valorize this waste by separating its resin, which is the main barrier for its industrial application, as well as to evaluate the extraction process parameters studying the influence of particle size, pressure and cosolvent use. The extracts obtained were also analyzed in terms of phenolic compounds and antioxidant capacity (ABTS). The extraction results showed that the applied technology was able to separate the resin, which is the first report described in the literature. Furthermore, the smaller particle size (0.25 mm) exhibited the most prominent impact on extraction rate, providing good yields of lipid extracts (up to 10.09 ± 0.02 %) and ethanoic extracts (up to 13.78 ± 0.41%). The obtained extracts presented good levels of phenolic compounds, which was associated with its high antioxidant activity. Thus, the application of supercritical technology added value to the bacuri shell, enabling new strands for industrial use of this agro-industrial waste with potential applications in the food, pharmaceutical and cosmetic industries, encouraging the circular economy and the bioeconomy of the Amazon region.

Keywords: Agro-industrial waste, Valorization, Bioeconomy, Resin separation, SFE

1. INTRODUCTION

In an era where the concept of bioeconomy and circular economy has been widely discussed and encouraged, the application of clean technologies envisioning the use and recovery of agro-industrial waste has been the focus of relevant studies worldwide (Patermann and Aguilar, 2021; Grafström and Aasma, 2021). Currently, the agro-industrial waste are no longer seen as a problem, but as a great ally for the development of a sustainable industry, since they can help in the development of several products, promoting new investment opportunities that satisfy both economic and environmental concerns, in addition to generating income and regional development (Freitas et al., 2021).

In this scenario, the bacuri fruit (*Platonia insignis* Mart.), very popular in the Amazon region, stands out as a relevant source of agro-industrial waste, since it presents low pulp yield (10% to 18%) and high percentages of shell (64% to 70%) and seeds (13% to 26%), the last two being commonly discarded as waste (Jacomino et al., 2018). Despite having a high percentage of shell, studies emphasizing the use of this fraction are still very rare. The studies available in the literature focus on pulp and seed evaluations, and few alternatives have been raised for the use of the shells (Cavalcante et al., 2020).

Although bacuri shell has an aroma very similar to that of the pulp, its use is still very limited due to the presence of a yellow colored resin that exudes from its mesocarp (Villachica et al., 1996; Mourão and Beltrati, 1995.). Currently, this resin is considered the main barrier for the technological use of bacuri shell. Thus, an efficient process emphasizing the total or partial separation of this resin has been the object of interest for many industries, since the bacuri shell has several components of economic interest (Ribeiro et al., 2021).

The decoction technique is the current state of the art for removing the resin from the bacuri shell. It is a method where the shells are subjected to heating with water for a period up to 120 minutes, usually carried out in tanks or pans provided with heating means. After the proper decoction time, a part of the resin is removed by the action of high temperature. After the appropriate decoction time, a part of the resin is removed by the action of high temperature. When separating from the shell, the resin fraction starts to occupy the surface region of the boiling water, which is changed and the procedure is repeated until the resin is completely removed. The other fraction of resin adheres strongly to the entire internal surface of the tank (Sabará et al., 2018)

The decoction technique has several disadvantages, such as the use of high temperatures for a long period of time, causing the loss of thermosensitive compounds present in the bacuri shell. In addition, there are problems related to the difficulty of cleaning the utensils (tanks or pans) used in this technique, due to the strong adhesion of the resin to its internal surfaces. Consequently, another disadvantage is related to the technical complexity of scaling up the method to industrial levels due to resin adhesion problems in equipment and utensils.

Previous studies suggest the possibility of using the bacuri agroindustrial waste in several industrial segments, since they have compounds with important biological and nutritional potential (Ribeiro et al., 2021; Chendynski et al., 2020). For instance, the bacuri shell fat is rich in free fatty acids such as palmitic, oleic, linoleic, α-linolenic, and stearic acids (Monteiro et al., 1997), presenting high morelloflavone content with antioxidant and antiglycation activity that can add value to the product (Ribeiro et al., 2021). Despite all these advantages, there is no real perspective on the industrial use of bacuri shell due to the limitations attributed to its resin. To the best of our knowledge, there has been no work carried out applying the supercritical technology process envisioning the valorization of bacuri fruit shell, emphasizing its processing aspects related to the separation or minimization of its resin, raising the possibilities of using this agro-industrial waste for products development.

In this context, the application of a clean technology, such as supercritical fluid extraction (SFE), can open new horizons for the use of bacuri shell, generating new possibilities and prospect in terms of industrial applications. SFE is a technique known for being environmentally friendly due to the lower energetic consumption, reduction of organic solvents and short operation times (Soquetta et al., 2018). Therefore, the purpose of this work was to study the application of sequential SFE to bacuri fruit shell by studying its process parameters such as particle size, pressure and use of cosolvent, as well as analyzing the extracts obtained in terms of phenolic compounds content and antioxidant capacity. Additionally, the first report on the separation or minimization of bacuri fruit shell resin using SFE was carried out, providing information that can help in the industrial application feasibility of this agro-industrial waste, aiming at the valorization of this fruit and encouraging the bioeconomy development.

2. MATERIALS AND METHODS

2.1. Raw Materials

The fruits of bacuri (*Platonia insignis* Mart.) were purchased in the municipality of Cametá, State of Pará, Brazil (2° 15′ 15″ S, 49° 30′ 44″ W) (Sisgen: A870E9C) and were transported to the Extraction Laboratory of the Federal University of Pará. The fruits initially went through a pre-processing step, where they were washed and sanitized. After this step, the fruits were cut manually with the aid of a stainless steel knife. Then, the shells were separated from the pulp and seeds. The shells were cut into small cubes (L = 0.8cm) and taken to the freeze-drying stage, where they were frozen at a temperature of -18°C and subsequently dehydrated in a freeze-dryer (model, JJ Científica, LJI015, Brazil). After lyophilization, the samples were comminuted in a knife mill (model TE 631/1, TECNAL, São Paulo, Brazil). The samples were vacuum packed in polypropylene bags, stored and kept under refrigeration at a temperature of 5 ºC for further analysis and extraction.

2.2. Particle size

An amount of 50 g of comminuted sample was sieved on Tyler's standard series sieves and placed on a magnetic sieve shaker for 15 minutes. Different particle sizes (20, 35 and 60 mesh, equivalent to 0.84, 0.50 and 0.25 mm, respectively) were selected for the extraction in order to study the influence of particle size on the global extraction yield. The material retained in the sieves was properly collected and packed in polypropylene bags.

2.3. Bed characteristics

The true density was determined using the Nitrogen (N) automatic gas pycnometer Anton Paar 5200e. The bulk density was determined by the mathematical ratio between the mass and volume of the freeze-dried bacuri shell, according to Equation 1. The bed porosity was determined through Equation 2.

$$\rho_b = \frac{m_s}{V_s} \quad (1)$$

$$\varepsilon = 1 - \frac{\rho_b}{\rho_t} \quad (2)$$

Where: ρ_b is the bulk density, ρ_t is the true density, m_s is the sample mass, V_s is the sample volume, and ε is the bed porosity.

2.4. Proximate composition

The proximate composition of the freeze-dried bacuri shell was determined by analyzing the moisture, lipids, proteins, ash and carbohydrate contents, based on AOAC Standard Method (2000). The moisture content was obtained by drying the sample in an oven at 378.15 K, until constant weight. The ash content was determined by incinerating the samples in muffle heated to 873.15 K. The lipid content was obtained by the Soxhlet method, using petroleum ether as a solvent. Protein content was quantified using the Kjeldhal method, using 6.25 as a factor for nitrogen conversion. Crude fiber content was determined by the Van Soest method. The carbohydrates were calculated from the difference between 100 and the sum of moisture, ash, lipids, crude fiber and proteins.

2.5. Sequential Supercritical Extractions: CO_2–SFE (Extraction with Supercritical CO_2) and CO_2+EtOH–SFE (Extraction with Supercritical CO_2 and Ethanol)

The sequential extraction experiments were carried out in a supercritical extraction plant on a laboratory scale using the Spe-edTM SFE from Applied Separations (model 7071, Allentown, USA), equipped with 10 mL cell and cylinder containing CO_2 (99% purity, White Martins, Brazil). The global yield isotherms were determined through extractions with 2 g of bacuri shell. All extractions were carried out at 313.15 K of temperature, 20, 30 and 40 MPa of pressure and mean particle size of 0.84, 0.50 and 0.25 mm, under CO_2 densities of approximately 828, 927, and 991 kg/m^3, and

CO_2+Ethanol densities of approximately 903, 948, and 980 kg/m^3, as shown in Table 1. For the calculation of these densities at this temperature and pressures, it was used the Aspen Hysys software (Aspen One 8.6), which applies the cubic state equation of Peng and Robinson (1976) with binary interaction parameters zero. The extraction period was divided into two stages: static period of 1800s and dynamic period of 7200s. The dynamic period was subdivided into two phases in which the first 3600 s was used only supercritical CO_2 in order to extract the lipophilic compounds (fats), and in the other 3600 s it was used the supercritical CO_2 with ethanol as cosolvent (85:15, *v/ v*) in order to obtain the most polar extracts (ethanolic extracts). The CO_2 mass flow was $8.85\text{x}10^{-5} \pm 2.95\text{x}10^{-6}$ kg.s^{-1}. For ethanolic extracts, the residual solvents were evaporated in a CentriVap centrifuge (model 78100, Labconco, Kansas, EUA), under vacuum, at 313.15 K. The global yield (on a dry basis) was determined using Equation 3. Each condition was performed in duplicate.

$$Y_{(\%db)} = \left(\frac{m_o}{m_s\left(1-\frac{U_S}{100}\right)}\right)100 \qquad (3)$$

Where: $Y_{(\%db)}$ is the global yield in dry basis, m_o is the obtained extract mass, m_s is the sample mass used and U_s is the percentage moisture of the freeze-dried bacuri shell.

2.6. Resin separation assessment

After the supercritical extraction process, the bacuri shell cake retained in the extraction cell was duly collected and submitted to qualitative and quantitative analysis in order to assess resin separation. For the qualitative analysis, a trinocular stereoscope (Model LM310BZ-45, Lumen, Brazil) with image amplitude of up to 40x coupled with a high definition camera was used, where the samples were evaluated for the presence of characteristic resin particles. For comparison purposes, the samples were also evaluated before being submitted to the supercritical fluid extraction process. For the quantitative analysis, the samples were submitted to the soxhlet extraction process through extract yield quantification using different solvents (ethanol and hexane) in order to evaluate the removal of the lipid and resin fraction from the bacuri shell.

2.7. Total Phenolic Compounds (TPC)

Total phenolic compounds were determined according to the methodology described by Singleton et al. (1999) and Georgé et al. (2005). Initially, extract samples were solubilized in acetone (1:9 v/v). For the analysis, it was used 500 µL of the extract diluted in distilled water, 250 µL of Folin-Ciocalteau (Tedia, Brazil) at 1.00 N and 1250 µL of sodium carbonate solution (99.5%, Vetec, Brazil) at 7.5% (m:v). After the reaction at room temperature in the dark environment, absorbance was measured at 750 nm using an ultraviolet-visible spectrophotometer (Model UV-M90, Bel Engineering, Italy). Quantification was performed using gallic acid (98.0%, Vetec, Brazil) as a standard for constructing the calibration curve. The standard curve for gallic acid was made from a 500mg/L (m/v) stock solution, where 14 concentration points (0.83 to 17.25 mg / L) were used, according to the straight-line equation $y = 0.0487 x + 0.0129$, where y is the absorbance and x is the concentration. From the linear equation, the content of total phenolic compounds was calculated and the results were expressed in mg of gallic acid equivalent per gram of extract on a dry basis (mg EAG / g db). The analysis was performed in triplicate.

2.8. Antioxidant Activity (AA)

The antioxidant activity of bacuri shell fat and ethanolic extract was determined by the ABTS method, as described by Nenadis et al. (2004). Initially, extract samples were solubilized in acetone (1:9 v/v). The 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) or (ABTS•+) radical was prepared by the reaction of 7mM ABTS•+ with 2.45 mM potassium persulfate, kept at room temperature and stored in the dark for 16 hours. The ABTS solution was diluted in ethyl alcohol until obtaining a solution with an absorbance of 0.70 (± 0.05) at 734 nm, using a UV-VIS spectrophotometer (model UV-M90, Bel Engineering, Italy). The decay of the absorbance value at 734nm was measured after six minutes of reaction. The Trolox standard curve was made from a 2000 μmol/L stock solution, where 6 concentration points (0 to 20 μmol/L) were used, according to the straight-line equation $y = 0.0003\,x + 0.0171$, where y is the absorbance and x is the concentration. From the linear equation, the antioxidant activity was calculated and the result was expressed in micromol of Trolox equivalent per gram of sample on a dry basis (μmol TE/g db). The analysis was performed in triplicate.

2.9. Statistical Analysis

For all results, the means and standard deviations were calculated. The results of total phenolic compounds and antioxidant activity were submitted to the Tukey test, at a significance level of 5% (p <0.05). Statistica Kernel Release 7.1 (StartSoft Inc., Tulsa, OK, USA) and Excel 2000 SR-1 (Microsoft, Troy, NY, USA) were used as tools.

3. RESULTS AND DISCUSSION

3.1. Characterization of the raw material

Figure 1 shows the bacuri fruit shell at different stages of pre-processing that preceded the extraction with supercritical fluid.

-Insert Figure 1 here-

Through Figure 1b, it is possible to observe that, after dehydration, the bacuri mesocarp presented a spongy appearance, lightweight structure and with the presence of many internal pores. In Figures 1b, 1c and 1d, it is possible to observe the bacuri shell resin in different conditions and image zoom. The resin was easily distinguished from the material of the bacuri shell, as it presents an amorphous structure and a differentiated color (brown). To the best of our knowledge, there are no specific studies on bacuri resin, and even the works that deal with this raw material usually do not address this part of the process. However, according to general scientific knowledge, resins exude when there is an incision or infection in the shell, and usually act as a plant defense agent (Langenheim, 2003). Furthermore, resins are usually produced in specialized superficial glands or internal ducts (Nagy et al., 2000), as is the case of bacuri fruit. Therefore, due to its high adhesion capacity (sticky feature), the separation of the resin from the shell becomes challenging to carry out.

3.2. Proximate Composition

The proximate composition of the freeze-dried bacuri fruit shell showed moisture content equal to 9.80 ± 0.30%; ash content of 1.98 ± 0.13%; lipid content equal to 10.48 ± 0.07%; crude fiber content of 28.42 ± 0.65%, protein content of 2.55 ± 0.05% and total carbohydrates of 46.77%. The results showed that the bacuri fruit shell is predominantly composed of carbohydrates, followed by lipids. Since studies in the international literature containing the proximate composition of the bacuri fruit shell are still rare, these results are important to broaden the knowledge of the composition of this agro-industrial waste in the scientific community.

3.3. Bed characteristics

The real density of the freeze-dried bacuri fruit shell was 1499.00 ± 3.99 kg/m^3. The bulk density was equal to 246.55 ± 0.99, 247.43 ± 0.86 and 317.58 ± 1.8 kg/m^3 for particle sizes of 0.84, 0.50 and 0.25 mm, respectively. The bed porosity was 0.84 ± 0.00, 0.83 ± 0.00 and 0.79± 0.00 for mean particle sizes of 0.84, 0.50 and 0.25 mm, respectively. According to Eliasson et al. (2017), these differences in bulk density and bed porosity might be because the smaller particles were more densely packed. These bed parameters are important for the mass transfer rate of supercritical fluid extraction, since they are directly associated to the possible problems related to bed packing and the occurrence of preferential paths.

3.4. Global yield isotherms

The global yield isotherm of bacuri fruit shell extracts obtained by CO_2 -SFE at 313.15 K can be seen in Figure 2a. The highest yield (10.09 ± 0.02 %) was obtained under the conditions of 0.25 mm particle size, 40 MPa and density of 991 kg/m^3, while the lowest yield (5.34 ± 0.01 %) was obtained in the conditions of 0.84 particle size, 20 MPa and density of 828 kg/m^3. The results showed that the increases in pressure and density promoted an increase in extraction yield in all conditions investigated. This occurred because the increase in pressure caused an increase in CO_2 density, increasing its solubility power, which provided higher yields. According to Silva et al. (2016), pressure variations under isothermal conditions define the performance of an SFE system, since this parameter has a great influence on fluid hydrodynamics, solubility and mass transfer.

-Insert Figure 2 here-

Additionally, the results showed that the smallest particle size studied (0.25 mm) provided higher extraction yields at 40 MPa. According to Eliasson et al. (2017), this can be explained by the increase in the contact surface between the sample particles and the solvent, as well as the reduction of obstacles to the mass transfer in the extraction bed. Smaller particles result in a shorter diffusion distance, which allows for faster extraction. Therefore, this confirms that particle size has a direct influence on the overall yield of bacuri fruit shell extraction with supercritical CO_2. However, care must be taken in relation to particle size reduction, since very fine particles can cause bed packing or formation of preferential paths, thus reducing extraction efficiency and yields. In the case of bacuri shell, these undesirable behaviors did not occur, suggesting that the studied particle sizes provided adequate solvent passage through the extraction bed.

The global yield isotherm of bacuri fruit shell extracts obtained by CO_2+EtOH-SFE at 313.15 K can be seen in Figure 2b. The highest yield (13.78 ± 0.41%) was obtained under conditions of 0.25 mm particle size, 40 MPa and density of 980 kg/m^3, while the lowest yield (7.11 ± 0.44%) was obtained under conditions of 0.5 mm particle size, 40 MPa and density of 980 kg/m^3. For the smallest particle size studied (0.25 mm), it was observed that the addition of the cosolvent (ethanol) caused an increase in the extraction yield as the pressure and density of the solvent increased. However, an opposite behavior was observed for the particle sizes of 0.50 and 0.84 mm. This could be because larger particles increase the diffusion path and the obstacles for the passage of the cosolvent through the extraction bed. Furthermore, the sampling process of the material inserted in the extraction cell must be improved in order to avoid errors arising from non-representative samples, since there may be differences in solute concentration between the samples studied, which may have contributed to the behavior described above.

The results showed that the addition of ethanol as a cosolvent favored the extraction mainly of the polar compounds that were not extracted in the previous step, which was carried out without cosolvent. Therefore, the sequential extraction process allowed obtaining extracts with different profiles, since in the first step, CO_2 favored the extraction of lipophilic (nonpolar) components, and in the second step, the addition of ethanol as a cosolvent favored the extraction of the predominantly polar characteristics compounds.

3.5. Resin Separation

One of the main purpose of this work, for being an important industrial demand, the separation of resin from the bacuri shell was successfully carried out through the application of supercritical fluid technology. After performing the sequential extractions using supercritical CO_2 and ethanol as cosolvent, it was possible to obtain three products, one of them was the bacuri shell retained in the supercritical extraction cell with no visual evidence of resin. Some authors (Mourão and Beltrati, 1995; Yamaguchi et al., 2014; Villachicca et al., 1996) had already reported that bacuri resin is soluble in some organic solvents such as ethanol, but up to then, there were no reports in the literature of a consolidated separation process for this resin. Based on this information and the knowledge of the high solubility and selectivity power of supercritical fluid extraction, after several preliminary tests, it was possible to develop this methodology by parameterizing all process steps, from the raw material preparation to obtaining the material without the resin.

-Insert Figure 3 here-

According to the results obtained, in all studied extraction conditions there was solubilization of the bacuri shell resin, which could be qualitatively verified through the absence of characteristic particles of the resin in microphotographs (Figure 3) obtained by trinocular stereoscope. Resin separation was also quantitatively confirmed through soxhlet extractions of the sample by means of different solvents (ethanol, hexane and petroleum ether), in which the presence of resinous and lipid material was not detected, confirming that the extraction process using supercritical CO_2 and ethanol as a cosolvent, under the conditions studied, was able to remove resinous and lipid components from the sample.

Considered as the main barrier to the industrial use of bacuri shell, resin separation has been an object of interest for many industries. In view of this, the present work presents a separation process that uses an environmentally friendly technology, which is capable of removing the resin at low temperatures, preserving the thermosensitive compounds present in the bacuri shell. This technique has the potential to replace the current state of the art for resin separation from bacuri shell (decoction process) which uses high temperatures for long periods of time and which faces problems related to cleaning the utensils used due to the strong adherence of the remaining resin.

Despite being a promising process capable of providing important advances for the use of agro-industrial waste from the bacuri fruit, it is important to emphasize that the aforementioned process was carried out in a laboratory scale and that the process optimization and scale-up studies need to be carried out to elucidate and provide information on its applicability at industrial levels. In addition, short, medium and long-term economic feasibility studies must also be carried out.

3.6. Total Phenolic Compounds (TPC)

Phenolic compounds are a well-known class of antioxidants due to the hydroxyl groups in their structure, which stabilize intermediate radicals by donating an electron and a hydrogen atom (Cheynier, 2012). The analysis of total phenolic compounds (TPC) estimates the content of all compounds that belong to the subclasses of phenolic compounds present in the extracts. Table 1 shows the results of phenolic compounds from ethanoic extracts from the bacuri fruit shell, where it is observed that the highest content (140.89 ± 4.42 mg GAE/g db) was obtained in the extraction with SC–CO_2 + 15% EtOH at 30 MPa, 313.15 K, solvente density of 948 kg/m^3 and mean particle size of 0.84 mm, while the lowest content (62.45 ± 1.05 mg GAE/g db) was obtained at 40 MPa, 313.15 K, solvente density of 980 kg/m^3 and mean particle size of 0.25 mm. The results indicate that the extract obtained from the bacuri fruit shell is rich in phenolic compounds, presenting values higher than those found in other important agro-industrial waste such as cocoa shell, 35.11 ± 1.57 mg GAE g^{-1} (Hernández et al., 2019); Sacha Inchi shell, 41.97 ± 1.05 mg GAE g^{-1} (Sanchez-Reinoso et al., 2020); groundnut hull, 13.84 ± 0.51 mg GAE g^{-1} (Prakash et al., 2018) and coconut shell, 22.44 ± 1.42 mg GAE g^{-1} (Rodrigues et al., 2008). This high content of phenolic compounds may be correlated to the high concentration of the biflavonoid moreloflavone found in bacuri shell extracts, recently investigated by Ribeiro et al. (2021).

-Insert Table 1 here-

In terms of process, these results demonstrate that the operating conditions, as well as the use of cosolvent, directly impacted the final result of phenolic compounds, which is confirmed by the predominance of statistically significant differences (p-value <0.05) between the extraction conditions studied. As the extraction with supercritical CO_2 allowed the removal of lipophilic fractions in the first stage of extraction, the subsequent step (with cosolvent) was carried out in a bed with less interference, which allowed a higher concentration of polar bioactive compounds available for extraction. Therefore, the need for a pre-treatment with supercritical CO_2 is essential to obtain an extraction bed with greater availability of polar bioactive compounds. This explains the fact that phenolic compounds were not detected in the extracts obtained in the first stage with supercritical CO_2 (without cosolvent), being below the limit of detection of the analysis (LOD = 1.22×10^{-4} kg/m^3), thus indicating that these compounds were concentrated in defatted beds obtained in the second stage of extraction. This behavior is consistent in terms of polarity of the solvents used, since phenolic compounds are polar substances and supercritical CO_2 is a non-polar solvent. It is noteworthy that, at this stage of the research, it was not possible to correlate the results of phenolic compounds and the studied extraction conditions, suggesting the need for future improvement studies in terms of raw material sampling and process optimization.

The high content of phenolic compounds extracted from the bacuri fruit shell by SFE reveals to be a promising strand for using this agro-industrial waste in the industrial scenario. The results obtained demonstrate that the supercritical extraction technology was able to preserve these compounds due to the use of low temperatures, in addition to being an ecologically correct option.

3.7. Antioxidant Activity (AA)

Table 1 shows the results of antioxidant activity (ABTS) of lipophilic (fats) and ethanolic extracts obtained from the bacuri fruit shell. Regarding lipid extracts, the highest antioxidant activity (1877.06 ± 23.52 μmol TE/g db) was obtained in the extraction with SC–CO_2 + 15% EtOH at 20 MPa, 313.15 K, solvente density of 828 kg/m^3 and mean particle size of 0.25 mm, while the lowest content (1391.11 ± 5.23 μmol TE/g db) was obtained at 40 MPa, 313.15 K, solvente density of 991 kg/m^3 and mean particle size of 0.84 mm. The results show that at 20MPa, the mean particle size variation (from 0.25 to 0.84 mm) had no significant effect (*p*-value <0.05) in terms of antioxidant activity, but when compared to other pressure conditions, there is a predominance of statistically significant differences. In addition, the results revealed a high antioxidant potential of lipophilic extracts in all conditions studied, with values higher than those found in other agro-industrial waste such as buriti shell, 382.90 μmol TE g^{-1} (Rudke et al., 2019) and avocado shell, 791.50 ± 35.90 μmol TE g^{-1} (Daiuto et al., 2014). Regarding the ethanolic extracts, the highest antioxidant activity (1452.88 ± 11.76 μmol TE/g db) was obtained in the extraction with SC–CO_2 + 15% EtOH at 30 MPa, 313.15 K, solvente density of 948 kg/m^3 and mean particle size of 0.50 mm, while the lowest content (737.80 ± 19.60 μmol TE/g db) was obtained at 40 MPa, 313.15 K, solvent density of 980 kg/m^3 and mean particle size of 0.50 mm. The results for these extracts also show the predominance of significant differences between the extraction conditions analyzed, in addition to revealing high antioxidant activities in all conditions studied.

The antioxidant activity of bacuri fruit shell extracts was recently described by Ribeiro et al. (2021), who attributed its high bioactivity to the presence of the biflavonoid morelloflavone, because it is the major compound found in the extract, in addition to being a compound in which the high antioxidant activity was previously reported by Gontijo et al. (2012). Ribeiro et al. (2021) also correlated the high antioxidant activity of bacuri shell with its anti-glycant activity, suggesting that the presence of morelloflavone is responsible for many bioactivities, including antiglycation activity. Products with anti-glycation properties are highly desirable in the dermocosmetics industries, since these compounds can act to prevent and combat the glycation effect on the skin, preventing cell hardening that cause premature aging of the skin, minimizing the appearance of wrinkles and marks of expression (Shin et al., 2015). Additionally, Ribeiro et al. (2021) revealed that bacuri shell extract has promising anti-inflammatory activity *in vivo*, evaluated through the paw edema protocol after its incorporation into a liquid-crystalline drug carrier system, reducing edema by up to 31%, an effect similar to that obtained by dexamethasone, which makes it interesting for the pharmaceutical industry as well. It is noteworthy that, in addition to the shell, the antioxidant activities of the pulp (Freitas et al., 2018) and seeds (Costa Júnior et al., 2013) of bacuri fruits have already been described previously, whose activities have been attributed to the presence of phenolic compounds and also the presence of alpha-and gamma-mangostin xanthones present in these fractions.

Despite the lack of information in the literature about the bacuri shell, the data provided previously, together with the data obtained in this present work, suggest that this fraction of the fruit has value-added components, confirmed by the presence of phenolic compounds that are associated to its high antioxidant capacity. As it is a non-explored by-product, there is still a lot to be studied in terms of its bioactivity and extraction methods optimization. However, it is already possible to state that the barriers that banned the use of this agro-industrial waste are increasingly smaller and that its industrial feasibility is more palpable, since process parameters for obtaining and characterizing its components have recently become more elucidated.

4. CONCLUSION

The application of supercritical fluid technology enabled the valorization of the bacuri fruit, since this technology was able to separate the resin that exudes from its shell, which, until then, was considered the main barrier for the industrial use of this agro-industrial waste. This new resin separation process has potential to replace the current state of the art (decoction technique), solving the problems and limitations of the old method. Furthermore, the process proposed in this work is considered an environmentally friendly technology and capable of providing excellent global yield rates. In terms of lipid extracts, the highest yield (10.09 ± 0.02 %) was obtained under the conditions of 0.25 mm particle size, 40 MPa and density of 991 kg/m^3. Regarding ethanolic extract, the highest yield (13.78 ± 0.41%) was obtained under conditions of 0.25 mm particle size, 40 MPa and density of 980 kg/m^3. Additionally, extracts from the bacuri fruit shell showed significant levels of phenolic compounds that are correlated with its high *in vitro* antioxidant activity, which may be attributed to the bioactive compound morelloflavone. Therefore, bacuri shell extracts have potential for applications in the food, pharmaceutical and dermocosmetic industries, encouraging the bioeconomy in the Amazon region. In addition to adding value to the by-product, its use makes it possible to reduce the amount of waste disposed of in the environment.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Table 1. Operating conditions of CO_2–SFE and CO_2 + EtOH–SFE of bacuri fruit shell (*P. insignis* Mart.) and characterization of the obtained extracts in terms of phenolic compounds and antioxidant activity.

Samples	Mean particle size (mm)	Pressure (MPa)	ρ Solvent (kg/m^3)	Total Phenolic Compounds (mg GAE/g d.b.)*	ABTS (µmol TE/g b.s.)*
Fats (CO_2 –SFE)	0.25	20	828	n.d.	1877.06 ± 23.52 ^{a}
		30	927	n.d.	1687.98 ± 5.64 ^{b}
		40	991	n.d.	1694.14 ± 28.86 ^{b}
	0.50	20	828	n.d.	1864.13 ± 47.04 ^{a}
		30	927	n.d.	1509.36 ± 16.11 ^{d}
		40	991	n.d.	1639.94 ± 24.61 ^{bc}
	0.84	20	828	n.d.	1823.48 ± 20.90 ^{a}
		30	927	n.d.	1629.47 ± 18.29 ^{c}
		40	991	n.d.	1391.11 ± 5.23 ^{e}
Ethanolic extracts (CO_2+EtOH– SFE)	0.25	20	903	78.72 ± 3.35 ^{e}	1297.67 ± 19.60 ^{b}
		30	948	118.36 ± 0.86 ^{b}	1256.10 ± 39.20 ^{bc}
		40	980	62.45 ± 1.05 ^{f}	851.44 ± 0.00 ^{f}
	0.50	20	903	90.19 ± 2.76 ^{d}	1006.65 ± 9.60 ^{d}
		30	948	116.90 ± 4.94 ^{b}	1452.88 ± 11.76 ^{a}
		40	980	122.30 ± 3.89 ^{b}	737.80 ± 19.60 ^{g}
	0.84	20	903	104.46 ± 6.89 ^{c}	1017.74 ± 54.88 ^{d}
		30	948	140.89 ± 4.42 ^{a}	917.96 ± 7.84 ^{e}
		40	980	112.53 ± 0.93 ^{bc}	1195.12 ± 54.88 ^{c}

* Different letters in the same column, per sample, showed a difference in significance level of 5% ($p < 0.05$); ABTS: 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid); CO_2 –SFE: extraction with supercritical CO_2; CO_2+EtOH–SFE: extraction with supercritical CO_2 and ethanol; n.d: not detectable.

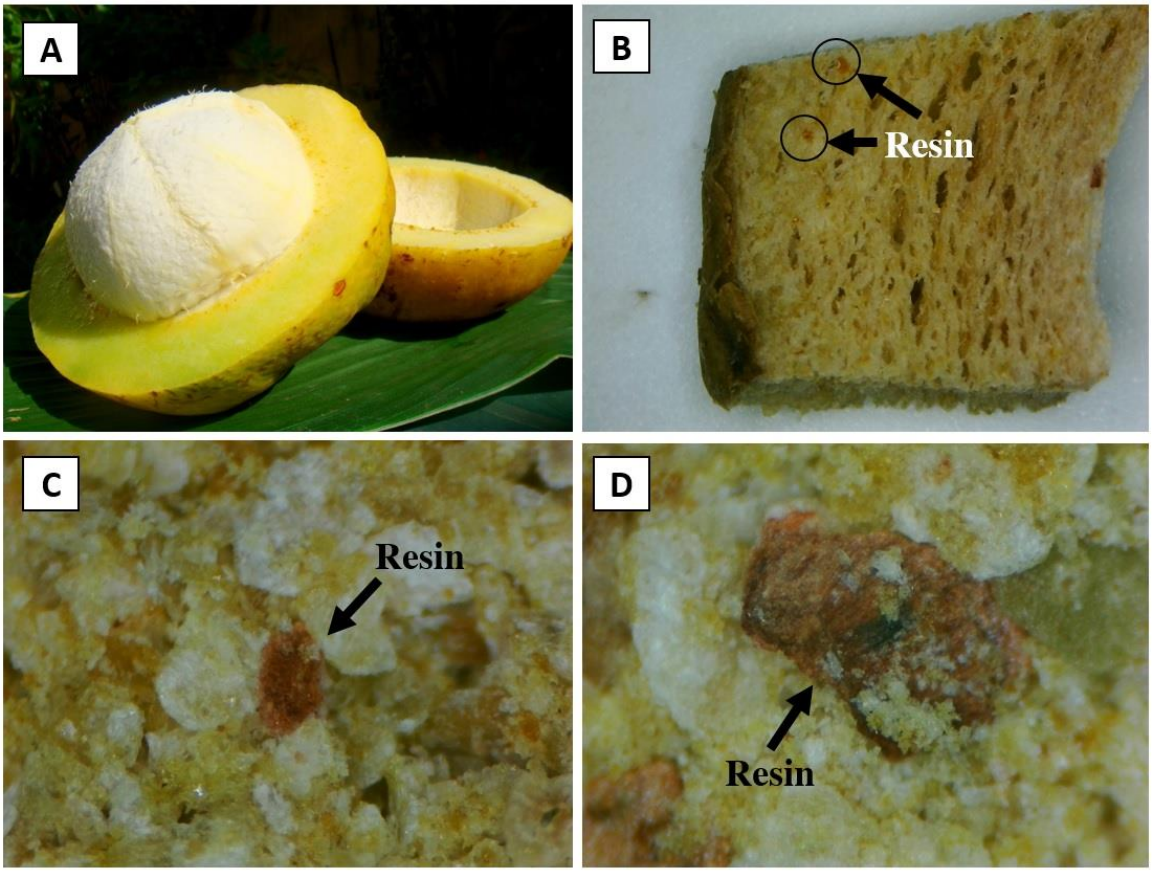


Figure 1. Bacuri fruit shell in different stages: (A) slitting of fresh bacuri; (B) cross-section of the freeze-dried bacuri shell magnified 15x in a trinocular stereoscope; (C) magnified by 30x and (D) magnified by 40x.

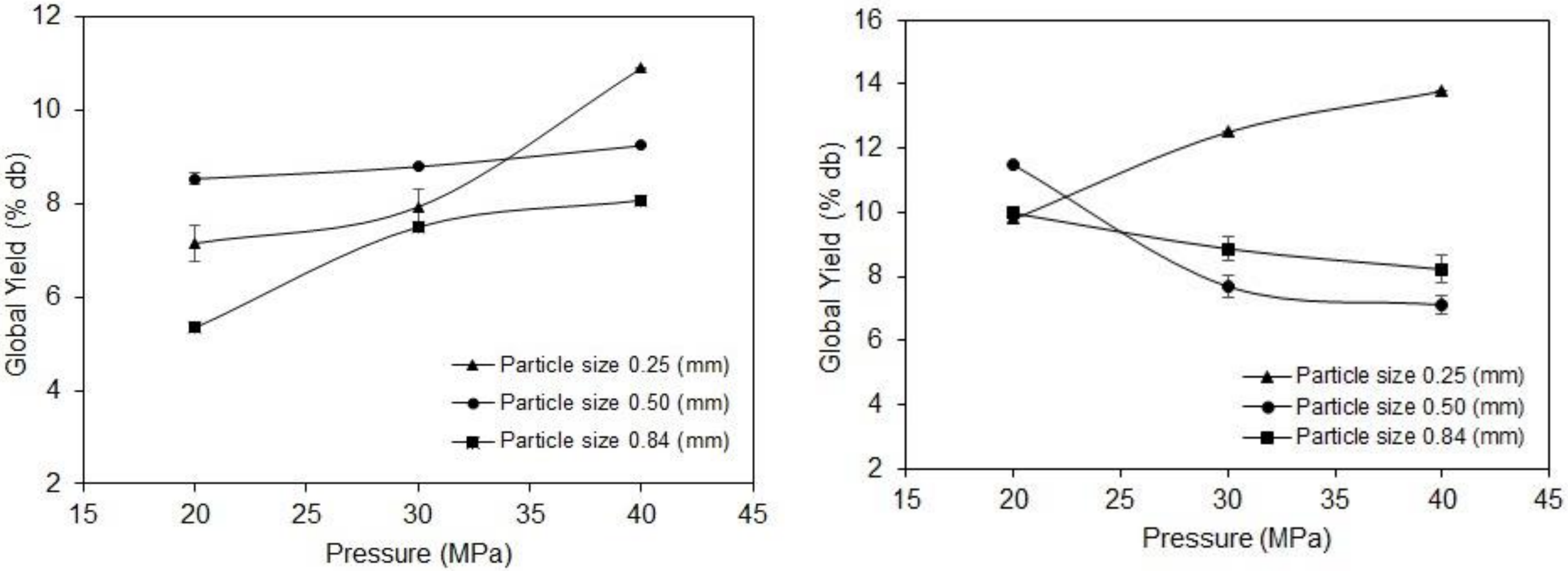


Figure 2. Global yield isotherms of bacuri fruit shell. Fig. 2A (left) - Yield *versus* pressure extracted with supercritical CO_2 at 313,15 K; Fig. 2B (right) - Yield *versus* pressure extracted with supercritical CO_2 + ethanol at 313,15 K.

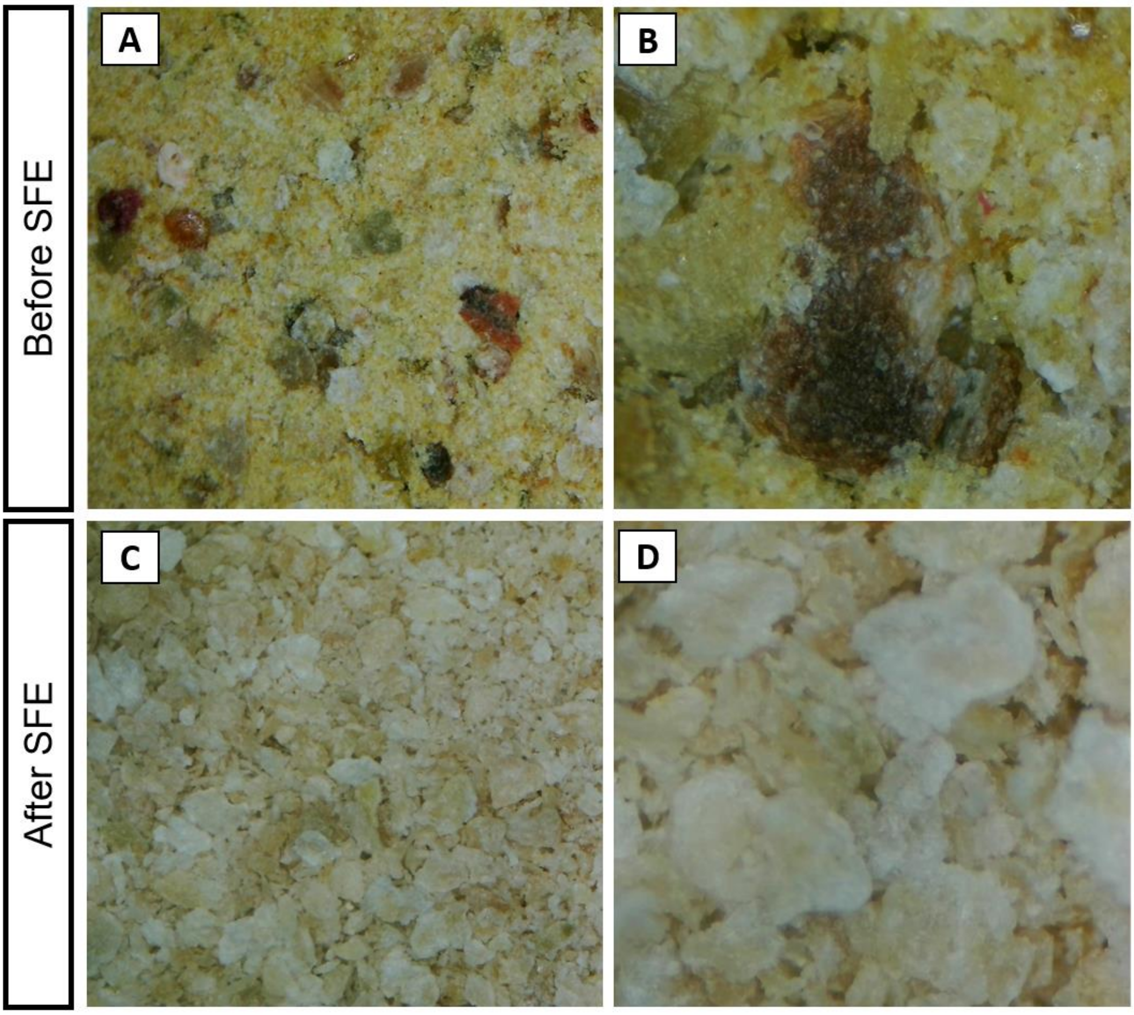


Figure 3. Microphotography of freeze-dried bacuri peel before (A and B) and after (C and D) the application of supercritical technology. A and C (10x zoom); B and D (30x zoom).

CAPÍTULO III

PATENTE:

Processo para a separação da resina da casca do fruto do bacuri (*Platonia insignis* Mart.) utilizando a tecnologia de fluido supercrítico

Lucas Cantão Freitas, Letícia Maria Martins Siqueira, Raul Nunes de Carvalho Junior

Patente em processo de depósito no Instituto Nacional da Propriedade Industrial- INPI

TÍTULO

[001] Processo para a separação da resina da casca do fruto do bacuri (*Platonia insignis* Mart.) utilizando a tecnologia de fluido supercrítico.

CAMPO DE UTILIZAÇÃO

[002] A presente invenção refere-se ao desenvolvimento de um processo para a separação da resina presente na casca do fruto do bacuri, utilizando o CO_2 supercrítico como solvente e etanol como cosolvente. A casca do bacuri compreende aproximadamente 65-70% da massa total do fruto. No entanto, a resina presente em sua casca dificulta o aproveitamento industrial dessa importante fração, o que geralmente é descartada como resíduo. Atualmente, essa resina é considerada a principal barreira para o aproveitamento industrial da casca do bacuri. Dessa forma, um método eficiente de separação ou minimização dessa resina tem sido objeto de interesse de muitas indústrias, uma vez que a casca do bacuri possui compostos de interesse econômico. Além disso, a presente invenção refere-se a um processo que utiliza uma tecnologia limpa, ecologicamente correta, que é capaz de remover a resina a baixas temperaturas, preservando os compostos termosensíveis presentes na casca do bacuri, como algumas vitaminas e compostos bioativos. Após a separação da resina, a casca do bacuri torna-se uma matéria prima viável para ser utilizada a nível industrial em diversos segmentos, antes limitada pela acentuada presença de resina.

ESTADO DA TÉCNICA

[003] A técnica de decocção é o método mais utilizado para a remoção da resina do bacuri atualmente. Trata-se de um método onde as cascas são submetidas ao aquecimento com água por um período de até 120 minutos, geralmente realizada em tanques ou panelas providas de meios de aquecimento. Após o devido tempo de decocção, uma parte da resina é removida pela ação da alta temperatura. Ao separar-se da casca, uma fração de resina passa a ocupar a região superficial da água de fervura, a qual é trocada e o procedimento é repetido algumas vezes até a completa remoção da resina. Essa técnica também é utilizada para a remoção de resina das cascas, comumente realizada de forma artesanal para a produção de cremes e mousses da casca do bacuri,

uma vez que esta parte do fruto apresenta o mesmo aroma da polpa, possuindo uma aceitabilidade sensorial muito acentuada entre os apreciadores do fruto (MATTIETTO et al., 2006).

[004] A técnica de decocção apresenta algumas desvantagens. A primeira delas é o uso de temperaturas elevadas por um longo período de tempo, ocasionando a perda de compostos termosensíveis que estão presentes na casca do bacuri, reduzindo uma parcela relevante de sua riqueza nutricional e funcional. A segunda desvantagem está relacionada com a dificuldade de limpeza dos utensílios (tanques ou panelas) utilizados nessa técnica, uma vez que, após o fim do processo de decocção, a resina fica fortemente aderida em toda a superfície interna dos utensílios utilizados. Consequentemente, a terceira desvantagem está relacionada com a dificuladade técnica de escalonamento do método para níveis industriais devido aos problemas de aderência da resina nos equipamentos e utensílios (VILLACHICA et al., 1996; MOURÃO; BELTRATI, 1995)

[005] A tecnologia de extração por fluido supercrítico é uma técnica conhecida por ser ecologicamente correta devido ao menor consumo energético, redução de solventes orgânicos e reduzido tempo de operação. Nesse processo há a ocorrência de mudanças tanto de temperatura quanto de pressão, acima de seus pontos críticos, que são capazes de converter o solvente em um fluido supercrítico, tornando as fases líquida e gasosa indistinguíveis. É uma técnica de transferência de massa, no qual a convecção na fase supercrítica do solvente costuma ser principal mecanismo de transporte (SOQUETTA et al., 2018).

[006] Em termos de solvente, o CO_2 é o mais utilizado na extração com fluido supercrítico devido a sua baixa temperatura e pressão críticas ($T_c = 31{,}1°C$, $P_c = 7{,}38$ MPa), que é uma vantagem importante para a manutenção de compostos bioativos em extratos. Além disso, o CO_2 é atóxico, barato, seletivo, não explosivo, altamente disponível, é fácil de remover do produto final e possui uma boa capacidade de extração devido ao seu alto poder de penetração (CHEMAT et al., 2019). Paralelamente, o etanol é bastante utilizado como cosolvente do processo, a fim auxiliar na extração dos componentes polares (MELO et al., 2014).

INVENÇÃO

[007] O processo de remoção da resina presente na casca do fruto do bacuri utilizando a tecnologia supercrítica é uma técnica com diferencial tecnológico que utiliza uma tecnologia emergente e ambientalmente correta, sem o uso de elementos tóxicos ao meio ambiente. Além disso, diferente da técnica de decocção que é uma técnica rudimentar que emprega altas temperaturas, o novo método é realizado a temperaturas brandas (40°C) que preservam grande parte dos compostos termosensíveis presentes na matriz vegetal. Ademais, trata-se de uma invenção cuja a técnica é provida de controle operacional. As limitações relacionadas à dificuldade de limpeza da resina dos utensílios utilizados na técnica de decocção também são sanadas pela nova técnica, uma vez que são realizadas duas extrações consecutivas, sendo que na última delas o etanol é adicionado no processo como cosolvente da extração, arrastando a resina remanecente no interior do equipamento. O método consiste em dois estágios principais: a etapa de pré-tratamento da matéria-prima e a etapa de extração supercrítica.

DESCRIÇÃO DETALHADA DA INVENÇÃO

[008] De acordo com a presente invenção, o método de separação da resina da casca do fruto do bacuri (*Platonia insignis* Mart.) consiste em dois estágios principais: (I) pré-tratamento da matéria-prima e (II) extração supercrítica consecutiva. No estágio (I) estão inclusos os processos de higienização, corte, liofilização, cominuição e granulometria. O estágio (II) compreende à extração consecutiva utilizando apenas o CO_2 supercrítico, na primeira etapa, e o CO_2 supercrítico mais etanol (EtOH) como cosolvente do processo, na segunda etapa.

[009] Inicialmente, na etapa de higienização, frutos maduros de bacuri são submetidos a um pré-processamento, onde se realiza a lavagem e sanitização.

[010] Após a sanitização, os frutos são cortados ao meio com auxílio de uma lâmina de aço inoxidável. Em seguida, as cascas são separadas da polpa e das sementes. As cascas são cortadas em forma de pequenos cubos e levadas para a etapa seguinte.

[011] As amostras são submetidas ao processo de liofilização, onde são congeladas em temperatura de -18ºC e posteriormente desidratadas em liofilizador, visando a remoção da massa de água da casca do bacuri a um teor de umidade inferior a 10%.

[012] Após a etapa de liofilização, as amostras são cominuídas em moinho de facas a fim de aumentar a superfície de contato e expor a resina com o objetivo de facilitar a sua remoção/extração.

[013] Uma determinada quantidade de material cominuído é peneirada em peneiras da série padrão de *Tyler* e colocadas em agitador de peneiras magnético por 15 minutos. O material retido nas peneiras é devidamente coletado e embalado.

[014] No estágio (II), a extração supercrítica é realizada utilizando uma planta de extração supercrítica em escala laboratorial. Trata-se do equipamento *Spe-ed*^{TM} *SFE* (modelo 7071, Allentown, EUA) da *Applied Separations*, acoplado com compressor de volume interno de 19,7 L da Schulz S/A (modelo CSA78, Joinville, Brasil), cilindro com CO_2 com 99.9% de pureza, recirculador Polyscience (modelo F08400796, Nilles, EUA) e medidor de vazão de CO_2 na saída do sistema da *Alicat Scientific* (modelo M 5SLPM, Tucson, EUA), com o sistema operacional da unidade.

[015] Uma determinada quantidade de amostra de casca de bacuri liofilizada a 60 mesh é adicionada na célula de extração a qual, posteriormente, é conectada ao sistema de extração por fluido supercrítico até atingirem as condições operacionais desejadas.

[016] Depois de alcançadas as condições desejadas, inicia-se a extração em duas etapas consecutivas: etapa estática, com duração de 30 minutos e a etapa semi-contínua, com o tempo total de extração de 2 horas (marcadas a partir do fim da etapa estática), compreendendo duas extrações consecutivas de 1 hora cada, sendo a primeira hora apenas com a circulação do CO_2 supercrítico e a segunda hora com CO_2+EtOH (proporção de 85% e 15%, respectivamente).

[017] Após o tempo total de extração, é feita a despressurização do sistema. Em seguida, a casca do bacuri sem resina é coletada diretamente da célula de extração.

[018] Analisando o material retido na célula, os resultados obtidos mostram que, na condição de extração estudada, ocorreu a solubilização da resina da casca do bacuri, o que pôde ser constatado qualitativamente através da ausência de partículas características da resina em microfotografias obtidas por estereoscópio trinocular. A separação da resina também foi confirmada quantitativamente através de extrações via soxhlet da amostra com diferentes solventes (etanol, hexano e éter de petróleo), nas quais não foram detectadas presença de material resinoso e lipídico, ratificando que o processo de extração utilizando CO_2 supercrítico e etanol como cosolvente, nas condições estudadas, foi capaz de remover os componentes resinosos e lipídicos da amostra.

[019] Em vista disso, a presente invenção apresenta um processo de separação que utiliza uma tecnologia limpa, ecologicamente correta, que é capaz de remover a resina a baixas temperaturas, preservando os compostos termosensíveis presentes na casca do

bacuri. Essa técnica possui potencial para substituir o atual estado da arte de separação da resina da casca do bacuri (processo de decocção) que utiliza altas temperaturas por longos períodos de tempo e que enfrenta problemas relacionados à limpeza dos utensílios utilizados devido à forte aderência da resina remanescente.

REIVINDICAÇÕES

1. PROCESSO PARA A SEPARAÇÃO DA RESINA DA CASCA DO FRUTO DO BACURI (*Platonia insignis* Mart.) UTILIZANDO A TECNOLOGIA DE FLUIDO SUPERCRÍTICO, **caracterizado por** reivindicar o uso do processo que compreende as seguintes etapas sequenciais: higienização, corte, liofilização, cominuição, granulometria e extração consecutiva com fluido supercrítico.
2. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a extração supercrítica é realizada com CO_2 (solvente) e etanol (cosolvente).
3. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a etapa de corte é realizada para aumentar a superfície de contato e facilitar a liofilização da casca do bacuri.
4. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a etapa de liofilização é realizada para a remoção da massa de água da casca do bacuri a um teor de umidade inferior a 10%.
5. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a etapa de cominuição é realizada em moinho de facas para a redução do tamanho de partícula e o consequente aumento da superfície de contado da casca do bacuri na célula de extração supercrítica.
6. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a etapa de granulometria é realizada em peneiras da série padrão de *Tyler* visando a separação de frações granulométricas mais finas da casca de bacuri liofilizado e cominuído.
7. PROCESSO, de acordo com a reivindicação 1, **caracterizado pelo** fato de que a torta remanescente no interior da célula de extração supercrítica trata-se da casca do bacuri sem resina.
8. PROCESSO, de acordo com a reivindicação 1 e 7, **caracterizado pelo** fato de que o uso de temperaturas brandas (≤40°C) preservam grande parte dos compostos termosensíveis presentes na casca do bacuri.
9. PROCESSO, de acordo com as reivindicações 1 e 7, **caracterizado pelo** fato de que, após o processo de extração supercrítica, a casca cominuída de bacuri sem resina, possa ser usada industrialmente, sem problemas relacionados à aderência da resina no interior dos equipamentos.

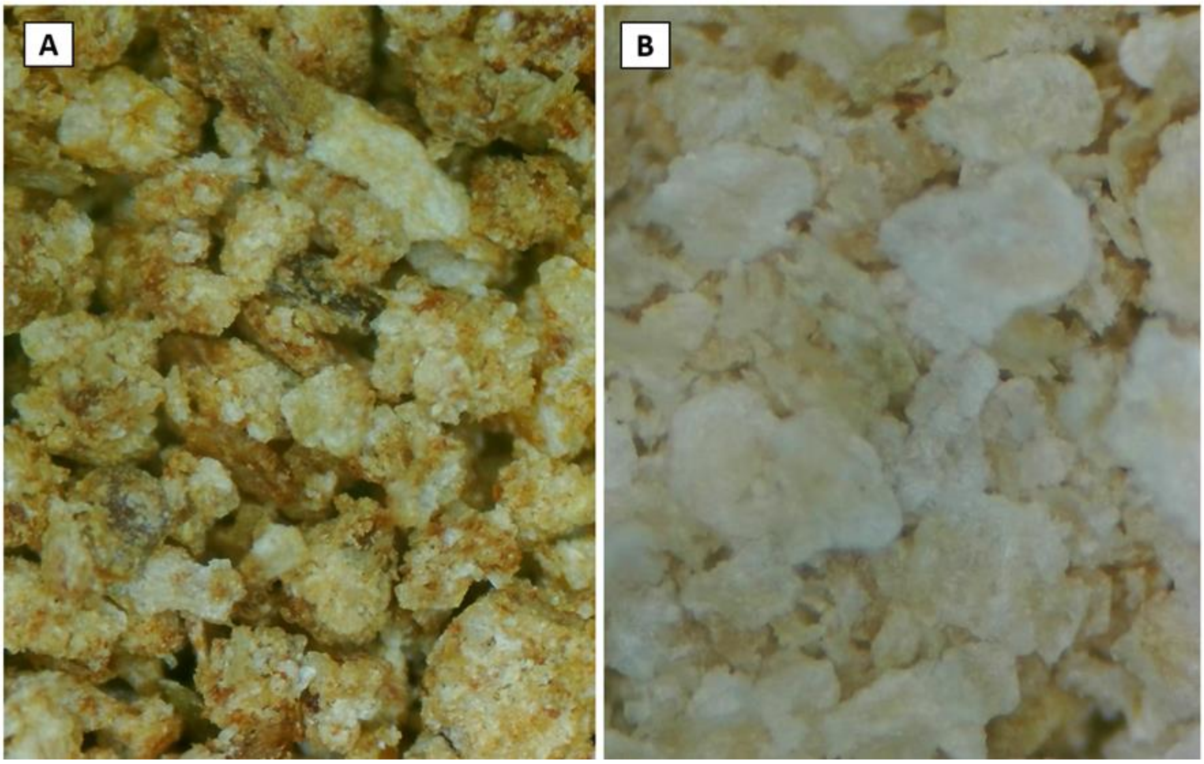
RESUMO

PROCESSO PARA A SEPARAÇÃO DA RESINA DA CASCA DO FRUTO DO BACURI (*Platonia insignis* Mart.) UTILIZANDO A TECNOLOGIA DE FLUIDO SUPERCRÍTICO

A presente invenção refere-se ao desenvolvimento de um processo para a separação da resina presente na casca do fruto do bacuri utilizando a tecnologia de fluido supercrítico. O método consiste em dois estágios principais: (I) pré-tratamento da matéria-prima e (II) extração supercrítica consecutiva. No estágio (I) estão inclusos os processos de higienização, corte, liofilização, cominuição e granulometria. O estágio (II) compreende à extração consecutiva utilizando o CO_2 supercrítico como solvente e etanol como cosolvente do processo. Após a remoção da resina, a casca do bacuri torna-se viável para ser utilizada em diversos segmentos industriais, antes limitada pela acentuada presença deste componente.

DESENHOS

Figura 1: Microfotografia da casca do fruto do bacuri antes (A) e depois (B) da aplicação da tecnologia supercrítica.



4 CONCLUSÃO GERAL

A tecnologia supercrítica possibilitou a remoção da resina da casca do fruto do bacuri, que atualmente é considerada a principal barreira para o aproveitamento tecnológico desse subproduto agroindustrial. O processo de separação da resina, que gerou uma patente devido ao seu ineditismo, possui potencial para substituir o atual estado da arte (processo de decocção), eliminando algumas limitações do antigo método. Além disso, o novo processo é considerado uma tecnologia *eco-friendly* que reduz os impactos ao meio ambiente. A extração sequencial com CO_2 supercrítico revelou que a granulometria de 60 mesh (0.25 mm), a 313.15 K e 40 MPa, apresentou os melhores rendimentos globais de extração, proporcionando resultados satisfatórios. Os extratos obtidos apresentaram acentuado conteúdo de compostos fenólicos, o qual foi correlacionado com a sua elevada atividade antioxidante. O uso de uma temperatura branda e de um processo de extração de alta seletividade pode ter contribuído para a manutenção desses compostos nos extratos, sugerindo que as condições aplicadas preservam esses componentes, principalmente os termosensíveis. Mediante aos resultados obtidos nesse estudo, correlacionados aos já existentes na literatura, pode-se inferir que a casca do bacuri é um subproduto agroindustrial que apresenta grande potencial de aplicabilidade em diversos segmentos industrias como na indústria cosmética, farmacêutica e de bionanomateriais. No entanto, por ser o primeiro trabalho nesse âmbito, mais estudos relacionados a otimização dos processos de extração e a caracterização de seus extratos, assim como da torta residual, devem ser realizados a fim potencializar a sua viabilidade industrial. Além disso, sugere-se futuros estudos de aumento de escala e viabilidade econômica a curto, médio e longo prazos, inserindo esse importante subproduto agroindustrial no panorama de estratégias para o incentivo da bioeconomia da região Amazônica.