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REVIEW

Recent Advances in the Processing of Agri-food By-products by Subcritical Water

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Abstract

The improper disposal of by-products from the agri-food industry raises global economic concerns. Therefore, proper management, development, and optimization of promising technologies like subcritical water processing can improve extraction and hydrolysis from by-products. Subcritical water acts as an acid catalyst, hydrolyzing by-products. Different residues from agri-food chains, such as pomace, peel, husk, seed, and straw have been used to obtain products, such as sugars, amino acids, phenolic compounds, pectin, and others. Furthermore, combining subcritical water with other technologies such as microwave, high-intensity ultrasound, and pulsed electric field can increase process efficiency, and promote sustainable economy. Therefore, this review addresses advances and trends in the role of subcritical water technology in treating by-product from the agri-food industry. By optimizing process variables (temperature, pressure, time, flow rate, and modifiers), hydrolysis and extraction of compounds can be maximized, minimizing degradation. Patents in the last five years have demonstrated the industry interest in subcritical water technology with high application prospects.

Keywords Bioactive compounds · Sugar production · Green emerging technologies · Extraction · Hydrolysis

Abbreviations

5-HMF	5-Hydroxymethylfurfural
BMIMAc	1-Butyl-3-methylimidazolium acetate
COM	Cost of manufacturing
DES	Deep eutectic solvents
FDCA	Furanedicarboxylic acid
GAE	Gallic acid equivalent
HIUS	High-intensity ultrasound
ILs	Ionic liquids
P	Pressure
PEF	Pulsed electric field
SDS	Sodium dodecyl sulfate
sCW	Subcritical water
SWE	Subcritical water extraction
SWH	Subcritical water hydrolysis
T	Temperature
TRS	Total reducing sugars
TPC	Total phenolic compounds

Introduction

The agri-food industry is one of the most important sectors in the world since it supplies fruits, vegetables, and products necessary to meet consumers' nutritional needs. However, the agri-food industry has also promoted climate change and social problems due to the generation of large amounts of waste due to poor practices during post-harvest (Green et al., 2020; Jeswani et al., 2021). Marić et al. (2018) reported that Europe's food processing industry generates around 100 million tons of waste annually. Therefore, agri-food waste can contaminate the soil due to landfill saturation and air through methane emission. Also, they generate economic

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and social problems due to the high final cost of the product, considering the loss during the post-harvest (Esposito et al., 2020; Morales-Polo et al., 2018).

The key difference between by-product and waste is that a by-product is a secondary product obtained incidentally in the manufacturing process of the main product. In contrast, waste do not add value to a product or service. By-product current use includes animal feed, while waste current destination includes composting, landfilling, or incineration. However, these waste discards affect the environment due to increased greenhouse gases and groundwater contamination (Costa et al., 2022). Therefore, sustainability has been incorporated into agri-food corporate strategies, considering the demand for clean processes to reduce food loss and waste generation (Esposito et al., 2020; Rabadán et al., 2019; Saldaña et al., 2015).

Biorefinery is a recent term used to present different possibilities for valuing by-products generated by agri-food and other industries (Caldeira et al., 2020; Saldaña et al., 2021). This concept considers using natural resources and by-products more comprehensively, developing new products, and reducing waste disposal. By-products are considered raw materials for recovering and producing various co-products (Saldaña et al., 2021). Then, many studies have proposed integrating green processes that provide more than one product from the same source (Landim Neves et al., 2020; Park et al., 2022; Ulvenblad et al., 2019). Other studies focus on treatments with subcritical water (sCW) technology of by-products to obtain fermentable sugars, phenolic compounds, proteins, and amino acids (Clauser et al., 2021; Di Domenico Ziero et al., 2020; Zhao & Saldaña, 2019; Cocero et al., 2018; Huerta & Saldaña, 2018; Knez et al., 2018; Saldaña & Valdivieso-Ramírez, 2015; Sarkar et al., 2014; Singh & Saldaña, 2011).

At sCW conditions, water dielectric constant is reduced by increasing its temperature. Therefore, thermal vibration occurs between the molecules, weakening hydrogen bonds. As a result, the surface tension decreases, and water quickly penetrates the matrix. A wide range of polarity as per temperature variation allows the extraction and fractionation of different compounds in the same process (Paini et al., 2022). Moreover, sCW acts as a catalyst, promoting the hydrolysis of proteins (Vo & Saldaña, 2023). Additionally, sCW has been modified by adding deep eutectic solvents and ionic liquids to achieve higher extraction yields (Sarkar et al., 2014). Other technologies such as high-intensity ultrasound, microwave, pulsed electric field, and enzymatic hydrolysis also have been combined with sCW, allowing higher process efficiency.

A search in the Scopus database using the keywords “subcritical water” and “food by-product/agricultural by-product” found forty-six publications (articles, reviews, book chapters, conference proceeding manuscripts) and two hundred and eighty-two patents published from 2017 to 2022 (Fig 1). Over the years, the number of publications on sCW to process by-products has grown. However, the number of patents has decreased in the last few years. As a result, patent production in 2022 decreased by 25% compared to 2020.

In this regard, the review addresses new trends involving sCW processing of agri-food by-products to obtain products reported in the 2017–2022 studies. Earlier reviews on sCW processing can be found somewhere else (Lachos-Perez et al., 2017a; Saldaña & Valdivieso-Ramírez, 2015). Thus, in this review, first, we discussed the operational conditions of sCW to extract and hydrolyze by-products. Additionally, this review reported sCW as a tool for extracting value-added compounds from agri-food industry by-products in a biorefinery concept. Furthermore, we presented new trends in sCW processing coupled with emerging technologies (microwave, high-intensity ultrasound, and pulsed electric field) and innovative solvents (deep eutectic solvents and ionic liquids) to obtain high product yields. Finally, studies on the economic feasibility and patents developed in the last five years using sCW were discussed.

The Role of Subcritical Water in Hydrolysis Processes

The product and process design trends include reducing the use and production of harmful substances, known as green chemistry (Song et al., 2018). sCW provides an efficient green approach to manage and valorize agri-food

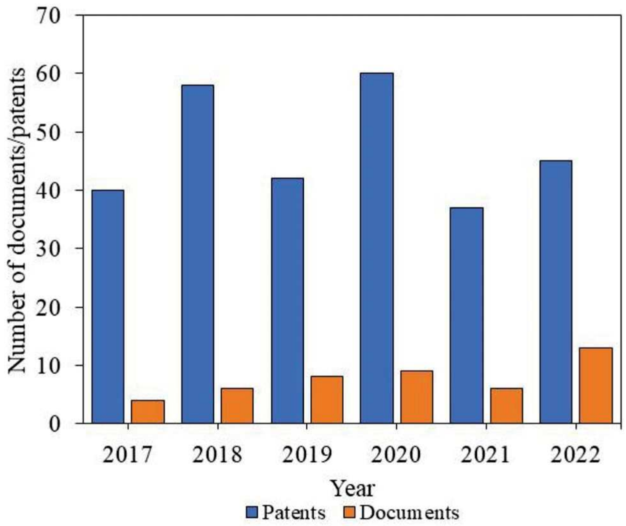

Fig. 1 Number of patents and documents in the Scopus database published from 2017 to 2022 using the keywords "subcritical water" and "food by-product/agricultural by-product"

by-products. Water in the subcritical state has a temperature above 100 °C or pressure below the critical point ((T_c) = 374 °C, critical pressure (P_c) = 221 bar). Water at room temperature has a high polarity and dielectric constant close to 80. However, increasing the temperature to 100 °C and 250 °C at 50 bar, the electric constant reaches 56 and 27, similar to some organic solvents (Aliakbarian et al., 2012). On the other hand, water in the supercritical state is above its critical point. Organic compounds are readily dissolved by water in the near-critical and supercritical regions up to complete miscibility. However, these statements hold for binary or quasi-binary systems (Brunner, 2009). Sub/supercritical water presents significant differences between the reaction media. The water concentration in H^+/OH^- at 300 °C and 220 bar is around 3×10^{-6} mol L^{-1}, while at 400 °C and 220 bar is 3×10^{-10} mol L^{-1} (Cocero et al., 2018). Therefore, sCW has a higher concentration of H^+ and OH^- ions, favoring ionic reactions, while supercritical water promotes radical reactions. Therefore, sCW operates by ionic mechanisms where the autohydrolysis of H_2O into hydronium H_3O^+ ions occur, producing an acidic atmosphere (Okolie et al., 2020).

sCW treatment has been used in a biorefinery concept by employing residual biomass to generate raw material for new products and reduce waste stream volumes (Lachos-Perez et al., 2017a; Saldaña et al., 2021). The sCW treatment limits the production of furans, which can inhibit the microbial and enzymatic biocatalysis step and biorefinery cascade processing (Jönsson & Martín, 2016). Furthermore, sCW treatment offers several advantages, such as acid/base substitution and a fast reaction rate. However, operating conditions influence these rates and the extent of reactions. Therefore, this section addressed the hydrolysis mechanism, main processing variables, and their influences on treating organic by-products.

Hydrolysis of Carbohydrates, Proteins, and Lipids

sCW convert wet biomass into chemicals and gases. Thus, disposal of industrial waste and domestic effluents is minimized or even avoided. Moreover, depending on the condition, the sCW presents mildly acidic characteristics and selectively hydrolyzes hemicelluloses without degrading cellulose (Ciftci & Saldaña, 2015). Also, sCW reduces the amounts of oxygen through decarbonization reactions, allowing the production of fuels with a higher H:C ratio. Therefore, the products of decarbonization reactions can be used as raw materials for chemical reactions, improving process efficiency (Knez et al., 2018).

sCW hydrolyze carbohydrates into fructose, glucose, maltose, furfural, and 5-hydroxymethylfurfural (5-HMF) without using enzymes or acids (Knez et al., 2018). Likewise, lignocellulosic plant matrices present in their composition cellulose, hemicellulose, and lignin. sCW hydrolyze the β-(1 $\rightarrow$ 4)-glycosidic bond of the cellulose structure, resulting in glucose monomers (Martínez et al., 2015). Hemicellulose is hydrolyzed into sugars (Huerta & Saldaña, 2018) and degraded into furfuraldehyde and other compounds. Lignin is hydrolyzed to produce phenolic monomers, oils, and gases (Liu et al., 2020).

The thermodynamic and mass transfer properties change as the pressure remains constant and the water is heated to the sCW conditions. Heated water has a decreased dielectric constant, increasing the solubility of lipids. Thus, sCW can extract oils and fats, replacing conventional solvents (Ravber et al., 2015). Free fatty acids hydrolysis produces long-chain hydrocarbons.

Regarding proteins, subcritical water hydrolysis (SWH) promotes breaking the C-N bond between the carboxyl and amine groups. At optimal conditions, amino acid yields can reach 10% at 250 °C (Knez et al., 2018). However, this value is lower compared to conventional methods. The subsequent degradation of amino acids due to deamination and decarboxylation reactions may explain this yield.

Hydrolysis Main Process Variables

The experimental design identifies significant main effects and variable interactions from a few experiments. The generated data systematically answer the experimental questions. The experimental design can follow the exploratory or optimization approach, depending on the available information (Sharif et al., 2014). The most studied variables in hydrolysis processes involving sCW are temperature, pressure, solvent-feed ratio (S/F), residence time, flow rate, use of inert gas, and catalyst.

Temperature

The increase in temperature changes the physicochemical properties of water, such as the dielectric constant, diffusivity, surface tension, and energy (Rivas-Vela et al., 2021). As the temperature increases, the nature of sCW changes, making the water a less polar molecule. Furthermore, sCW at higher temperatures accelerates hydrolysis, modifying the processing time and inducing irreversible reactions (Watchararuji et al., 2008). However, elevated temperatures can degrade compounds by promoting hydrolysis and oxidation reactions.

Additionally, above 300 °C, the water dielectric constant decreases. Therefore, the hydrolysis temperature must be adequate according to the compounds of interest. For example, Kim and Lim (2020) reported that increasing the temperature from 145 °C to 165 °C increased the extraction yield of hesperidin and narirutin from the SWH of *Citrus unshiu* peel. In addition to the hesperidin and narirutin extraction, they recovered sinensetin, nobiletin, and tangeretin. The hydrolysate-rich extracts could be used as a functional ingredient in the nutraceutical, pharmaceutical, and medicinal industries.

Pressure

Pressure is another critical variable in maintaining the subcritical state of the fluid. However, the pressure modulation analyzed separately from the vapor pressure value up to 100 bar has not significantly affected the hydrolysis performance (Rivas-Vela et al., 2021). Despite this, considering other factors, pressure can substantially affect hydrolysis by pressing water through pores that are usually inaccessible at room temperature (Essien et al., 2020). Although the SWH process is practically neglected from pressure, Cvetanović et al. (2017) increased the apigenin yield by 90%, increasing the pressure from 10 to 45 bar. High pressures facilitated the solvent's penetration into the sample matrix's pores. Likewise, it controls the formation of air bubbles inside the matrix, promoting the solvent to reach the analyte (Mustafa & Turner, 2011).

Residence Time, Flow Rate, and Solvent-feed (S/F) Ratio

The characteristics of the vegetal matrix and the water temperature determine the hydrolysis processing time. In general, low temperatures require more time and vice versa. It can be determined by fixing the processing time and evaluating other factors, such as temperature, its effects, and interactions (Zhang et al., 2019). Oliveira et al. (2022a) recovered fermentable sugars from canola waste by SWH at 230 °C. The hydrolyzate solutions were collected at ten different reaction times until a final time of 30 min. A higher hydrolysis rate was acquired for biomass harvested in 2019 than for the biomass harvested in 2020 in the first 600 s reaction. However, the hydrolysis rate remained constant over a more extended period (900 s). Moreover, high xylose and cellobiose content were acquired with all stalk and silique canola biomasses.

Although SWH occurs mainly in the static mode, for the continuous mode, the flow rate improves the hydrolysis rate through higher solvent flow in the plant matrix. Thus, faster hydrolysis with reduced residence time is performed. However, depending on the operating range, the flow rate may have a negligible effect on hydrolysis. Vedovatto et al. (2021) evaluated the SWH of soybean straw and hulls to obtain semi-continuously fermentable sugars at 180, 220, and 260 °C, 25 MPa for 15 min. According to the authors, a lower water flow rate resulted in higher yield of sugars due to the solvent reaching the desired temperature quickly in the reactor. Likewise, the residence time was sufficient for substantial dissociation of hemicellulose and cellulose.

The solvent/feed (S/F) ratio in continuous flow reactors is an essential variable in the sCW processes. Batch operation tends to accumulate higher concentrations of organic acid by-products than continuous operation. In this context, acids promote the autocatalysis of polymer depolymerization (Pourali et al., 2009; Prado et al., 2016). Thus, as the continuous operation does not have the benefit of autocatalysis, the S/F ratio should be evaluated. Torres-Mayanga et al. (2019a) analyzed the recovery of sugars and the formation of bioproducts from brewer's spent grains by SWH. The authors investigated hydrolysis at 140, 160, 180, and 210 °C, the flow rate of 10 and 20 mL min^{-1}, and the solvent/feed ratio (S/F) of 64, 80, and 112, using a semi-continuous system. Yields mainly depended on hydrolysis temperature and S/F ratio (< 64). Furthermore, the arabinose yield increased as the S/F ratio and flow rate increased.

Moreira et al. (2023) evaluated the SWH of defatted rice bran at 230–260 °C, 100 bar, and S/F of 50 and 100. At 260 °C / S/F-100, a hydrolysis rate of 1.81 g/(100 g min) was obtained in the first 6 min of the reaction. However, for the 260 °C / S/F-50 assay, the hydrolysis rate was 1.01 g/(100 g min). This behavior was attributed to the longer residence time due to the low flow rate at the S/F of 100, which caused more significant degradation of sugars in other products.

Inert Gases and Catalysts Agents

Inert gases can be added to the system in hydrolysis processes employing sCW. These gases can be nitrogen, oxygen, or carbon dioxide. CO_2 reacts with water to form carbonic acid at high pressure and temperature. The dissociation of this acid increases the concentration of hydronium ions, which acts as an acid catalyst (Brunner, 2009).

Catalysts or modifying agents allow the modulation of hydrolysis to reduce reaction time or temperature. In addition to nitrogen, oxygen, and carbon dioxide, several compounds have been used, such as lactic acid, sodium bicarbonate, sodium chloride, and sodium hydroxide (Espinoza & Morawicki, 2012; Rivas-Vela et al., 2021). Degradation products such as ammonia, formic acid, acetic acid, and fatty acids also act as modifiers to increase the production of amino acids during hydrolysis (Espinoza & Morawicki, 2012). Marcet et al. (2014) observed up to a two-fold increase in the yield of amino acid recovery using nitrogen and oxygen as catalysts. Furthermore, the recovery time was reduced by half compared to trypsin digestion. The process occurred at 180 °C, 40 bar, and 120 min, with an oxygen flow of 1 L min^{-1}. The oxygen stream affected the interfacial properties of the peptides. On the other hand, the nitrogen stream resulted in hydrolysates with foaming and emulsifying properties similar to those obtained by enzymatic hydrolysis. Obtaining peptides from insoluble proteins was considered a faster and reagent-free method than enzymatic hydrolysis, reaching a yield of 95%.

Thermal Degradation Products

The glucose yield by sCW is lower than the obtained by conventional enzymatic methods probably due to degradation. Moreover, the degradation of fructose and glucose can result in products, such as acetic acid, furfural, levulinic acid, and gaseous products. Furfural and 5-HMF are inhibitory compounds derived from pentose and hexose sugar elimination reactions (Heer & Sauer, 2008; Palmqvist & Hahn-Hägerdal, 2000). Furfural is a by-product of formic acid, while 5-HMF is another cytotoxic derivative produced through catalytic dehydrogenation (Barbosa et al., 2021). Extensive reviews have reported various chemicals derived from furfural and 5-HMF, highlighting furfuryl alcohol and furanedicarboxylic acid (FDCA) with a purity of 99.5% (Mariscal et al., 2016; Torres-Mayanga et al., 2019b; Zhang & Huber, 2018). Furfuryl alcohol has applications in manufacturing industrial resins and as a precursor of levulinic acid and γ-valerolactone (Bui et al., 2013). On the other hand, FDCA can produce polyethylene 2,5-furandicarboxylate, which has similar properties to polyethylene terephthalate (Deshan et al., 2020).

sCW Extraction of Value-added Compounds

The subcritical extraction process involves three mechanisms during the transfer of active sites from the matrix to the extraction medium: diffusion, partition equilibrium, and convection (Zakaria & Kamal, 2016). The predominant step is the diffusion of the solute in the matrix, while the limiting step is the solute partition equilibrium. Yield, flow rate, and time describe these transport mechanisms through extraction kinetics (Nkurunziza et al., 2019). During extraction, the purge with inert gases like nitrogen prevents oxidation. Figure 2 illustrates a schematic of sub/supercritical equipment.

Water in the subcritical state as extracting solvent is environmentally friendly due to its non-flammability

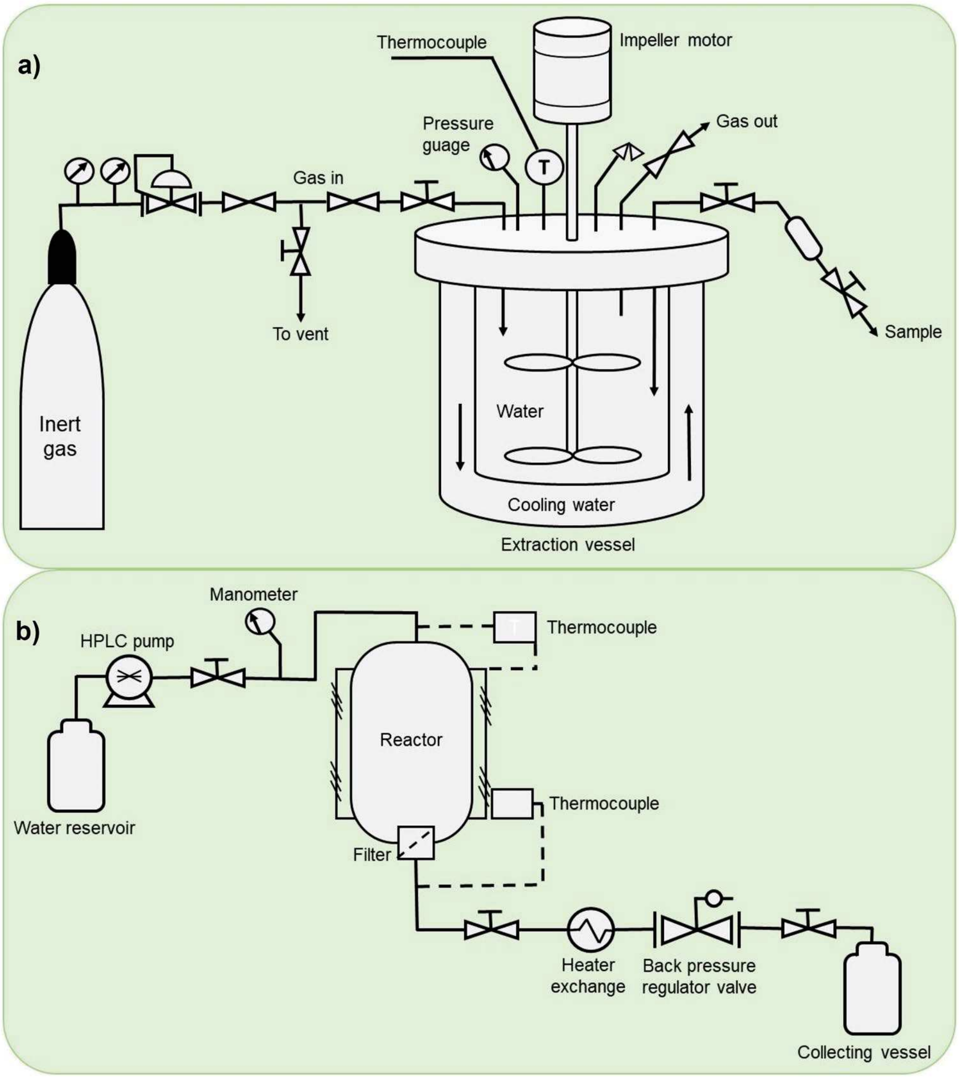

Fig. 2 Schematic of the apparatus used for sub/supercritical studies: **a** Batch system and **b** Semi-continuous system

and non-production of greenhouse gases and waste. The advantages of using sCW are its low cost, reproducibility, and low toxicity compared to some organic solvents. The change in temperature and pressure allows the separate extraction of high, medium, and weak polarity compounds. Moreover, water costs less than other solvents. Regarding the disadvantages, heat-sensitive compounds can be degraded due to the increase in temperature (Benito-Román et al., 2022).

Additionally, sCW is more corrosive than water under ambient conditions and can catalyze or accelerate the oxidation of compounds. Removal of moisture from the extraction solution may require additional methods such as dehydration, evaporation, or precipitation. Figure 3 displays the advantages and disadvantages of subcritical water extraction (SWE).

Studies have shown sCW as a promising solvent capable of isolating phytochemical compounds from natural sources (Saldaña & Valdivieso-Ramírez, 2015). This green solvent is ideal for the food and pharmaceutical industry since it avoids using organic solvents, allowing the extraction of nutraceuticals from food and herbaceous plants (Mustafa & Turner, 2011). In addition, sCW presents a high selectivity to extract antioxidant compounds such as carnosol, rosmanol, carnosic acid, methyl carnosate, and some flavonoids such as cirsimaritin and genkwanin (Ibañez et al., 2003). Furthermore, high extraction rates, yields, and the simultaneous extraction of hydrophilic and lipophilic compounds can be achieved by controlling process conditions. However, although its hydrophilic nature facilitates the extraction of various products, the formation of unwanted products and the degradation of compounds can affect human health, depending on the concentration.

Table 1 presents examples of compounds extracted and hydrolyzed from plant by-products using sCW. The compounds that have been most extracted using sCW are phenolic compounds, proteins, carbohydrates, and lipids. Furthermore, the agri-foods that have been most explored as sources of these compounds are peels and pomaces.

Mikucka et al. (2022) recovered bioactive compounds from distillery vinasse under subcritical conditions, evaluating temperature, solid/solvent ratio, and extraction time. The response surface methodology and principal component analysis indicated that extraction time and temperature had a more significant effect on the antioxidant activity of the extracts. A 30 min SWE and 1:15 (w:v) solid-solvent ratio yielded the highest total phenolic content (4.9 mg GAE/g dry matter) and total flavonoid content (1.24 mg quercetin equivalent/g dry matter) at 140 and 200 °C, respectively. During extraction, the contact surface of the solvent with the solid increases due to the disruption of the cell wall matrix, increasing the mass transfer rate (Xu et al., 2016). The behavior can increase the solubility of phenolic compounds since there is a breakage of hydrogen bonds (Kheirkhah et al., 2019). However, extraction times greater than 30 min can cause oxidation and degradation of polyphenols (Mikucka et al., 2022).

In another study, Lachos-Perez et al. (2017b) hydrolyzed sugarcane bagasse with temperatures between 190 and 260 °C and pressures from 90 to 160 bar to obtain sugars. Pressure played a minor role in total reducing sugar (TRS) yields. The ANOVA indicated that the TRS yield strongly depended on temperature ($p < 0.05$). Temperature increases reduced TRS yields, indicating that the degradation and carbonization rates are higher than the hydrolysis rate (Mayanga-Torres et al., 2017). Additionally, at 200 °C, the thermal

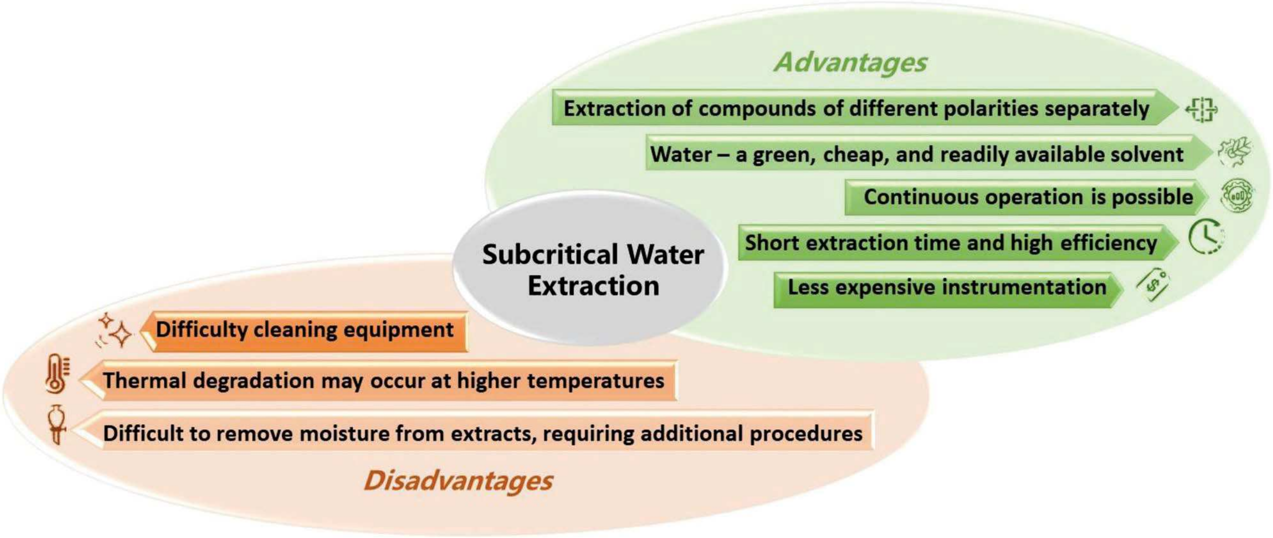

Fig. 3 Advantages and disadvantages of SWE

Table 1 Overview of compounds extracted and hydrolyzed from plant matrices by sCW

Plant matrix	Goal	Experimental condition	Yield / Main results	Reference
Apple pomace	Dissolving fermentable sugars and assessing the effects of treatment on the solids	T: 80–120 °C P: 10–30 bar Operating mode: batch	sCW treatment altered the structure's thermal degradation. Furthermore, the condition of 100 °C, 10 bar, dilution factor = 20, and process time of 30 min activated the cellulose.	(Paini et al., 2021)
Brewers' spent grains	Recovering of sugars and amino acids	T: 80, 130, and 180 °C P: 150 bar Flow rate: 5 mL min^{-1} Operating mode: semi-continuous	Hydrolysis at 180 °C for a single reactor indicated the highest yield of monosaccharides (47.8 mg g^{-1} carbohydrates). The composition indicated xylose and arabinose as the main sugars and low levels of furfural (310.7 μg mL^{-1}), 5-HMF (< 1 mg L^{-1}), and organic acids (0.343 mg mL^{-1}). The main amino acids recovered from the hydrolyzate were tryptophan (223.1 μg mL^{-1}), aspartic acid, valine (66.1 μg mL^{-1}), lysine (26.7 μg mL^{-1}), and glycine (16.1 μg mL^{-1}).	(Sganzerla et al., 2022)
Citrus unshiu peel	Extraction of flavonoids and determination of the functional properties of the hydrolysate	T: 145–175 °C P: 50 bar Flow rate: 0.75–2.25 mL min^{-1} Operating mode: semi-continuous	Increasing the temperature from 145 to 165 °C increased the yield of hesperidin and narirutin. At 160 °C, monoglycosides and aglycones were obtained. The sum of hesperidin, monoglycosides, and aglycones was correlated to antioxidant activity, while hesperidin and naringenin were related to inhibitory enzyme activities.	(Kim & Lim, 2020)
Coffee waste residues (powder and defatted cake)	Extraction of reducing sugars and phenolic compounds	T: 150, 175, 200, and 250 °C P: 225–300 bar Flow rate: 10 mL min^{-1} Operating mode: semi-continuous	The maximum recovery of the reducing sugars was 6.3% (150 °C, 300 bar) and 8.79% (175 °C, 225 bar) for the defatted coffee powder and cake. The cake residue indicated a higher total phenolic compounds (TPC) yield of 55.31 mg TPC GAE (Gallic Acid Equivalent)/g compared to the powder, whose value was 26.64 mg GAE/g.	(Mayanga-Torres et al., 2017)
Corn stover	Establish an integrated ethanol-methane fermentation system	T: 190 °C P: N/A Operating mode: batch	The pretreatment improvement indicated the degradation of 60% of hemicellulose and 50% of lignin, demonstrating stability in the performance of ethanol and methane fermentation as the number of cycles increased.	(Wang et al., 2018)

Table 1 (continued)

Plant matrix	Goal	Experimental condition	Yield / Main results	Reference
Distillery stillage	Extraction of bioactive phenolic compounds	T: 25, 80, 140, 200, and 260 °C P: 41.4 bar Operating mode: batch	SWE of 30 min indicated the highest extraction yield for the total content of polyphenols and phenolic acid (140 °C) and total content of flavonoids (200 °C). Most of the total phenolic acid content was present in the free form (88%). Ferulic and p-coumaric acids had an antioxidant effect on the extracts.	(Mikucka et al., 2022)
Jabuticaba (*Myrciaria cauliflora*) peel	Evaluate the operational performance of semi-continuous flow hydrothermal pretreatment to obtain bioproducts (monosaccharides, organic acids, and inhibitors)	T: 60–210 °C P: 150 bar Flow rate: 5 mL min^{-1} Operating mode: semi-continuous	The highest sugar yields (177.5 mg g^{-1}) occurred at 60 °C, yielding 74.2 and 103.8 mg g^{-1} for glucose and fructose, respectively. Citric acid was the main organic acid obtained, reaching a concentration of 30.8 mg g^{-1} for the heat treatment at 60 °C. However, the highest concentration of total organic acids occurred at 135 °C (40.1 mg g^{-1}). For the authors, the hydrolysis time should be reduced, and the S/F ratio should be optimized.	(Barroso et al., 2022)
Olive pomace	Obtaining oil enriched with sterol and phenols using hydrothermal pretreatments	T: 160, 180, and 200 °C P: 4.9, 9.8, 15.7, and 24.5 bar Operating mode: batch	The pretreatment recovered 54–76% of oil and 18–32% of β-sitosterol. The authors suggested the sequential treatment, starting with a steam explosion followed by sCW with a temperature above 200 °C to obtain multiple fractions and recover olive pomace.	(Seçmeler et al., 2018)
Onion skin waste	Pectin recovery and oligomers identification	T: 105–180 °C P: 50 bar Flow rate: 2.5 mL min^{-1} Operating mode: semi-continuous	The pectin extraction yield reached up to 9% at 145 °C. sCW induced the recovery of hairy pectin regions. After hydrolysis, the solid showed potential for use as a fuel.	(Benito-Román et al., 2022)
Orange peel	Extraction flavanones hesperidin and narirutin	T: 110, 130, and 150 °C P: 100 bar Flow rate: 10, 20, and 30 mL min^{-1} Operating mode: semi-continuous	The maximum yield of hesperidin (189 $mg/g_{extract}$) and narirutin (22 $mg/g_{extract}$) occurred at 150 °C with a flow rate of 10 mL min^{-1}. These values represented 21% of the flavonon compounds in the extract.	(Lachos-Perez et al., 2018)

Table 1 (continued)

Plant matrix	Goal	Experimental condition	Yield / Main results	Reference
Orange peel	Sequential extraction of flavonoids and recovery of cellulose sugars	T: 200, 225, and 250 °C P: 100 bar Flow rate: 10, 20, and 30 mL min^{-1} Operating mode: semi-continuous	At 150 °C and 10 mL min^{-1}, the highest yields of hesperidin and narirutin (22.9 and 1.9 mg/g orange peel) were obtained. At 200 °C, there were excellent yields of arabinose (7.14%) and glucose (13.44%).	(Lachos-Perez et al., 2020)
Passion fruit peel	Extraction of oligosaccharides	T: 100–245 °C P: N/A Operating mode: batch	At 150 or 175 °C within 4.5 or 5.5 min, the highest amount of oligosaccharides (21%) had galacturonan as the main component (65%). These conditions promoted the extraction and hydrolysis of pectin.	(Klinchongkon et al., 2017)
Pressed palm fiber, coconut husk, defatted grape seed, and sugarcane bagasse	Evaluating the addition of CO_2 in sCW to obtain sugars and by-products	T: 250 °C P: 200 bar Operating mode: semi-batch	The addition of CO_2 increased the content of reducing sugars by 15 and 56% for coconut husk and grape seed. However, adding CO_2 did not change the sugar yield for palm fiber and sugarcane bagasse.	(Prado et al., 2017)
Red wine grape pomace	Recovering hemicellulose oligomers and phenolic compounds	T: 25–190 °C P: 100 bar Flow rate: 5–10 mL min^{-1} Operating mode: semi-continuous	The residue extract was rich in oligomers and showed phenolic compound contents of up to 29 g/100 $g_{extract}$ with antioxidative activity compared to gallic acid.	(Pedras et al., 2020)
Sugarcane straw	Obtaining simple sugars and other valuable compounds	T: 190, 200, 225, 250, and 260 °C P: 9, 10, 12.5, 15, and 160 bar Flow rate: 10 mL min^{-1} Operating mode: semi-continuous	Hydrolysis at 200 °C provided the highest yield of total reducing sugars (32.1%) with 2.1% glucose and 2.3% xylose. Temperatures greater than or equal to 190 °C indicated char in the treated samples.	(Lachos-Perez et al., 2017b)
White wine grape pomace	Extraction of carbohydrates and phenolic compounds	T: 170, 190, and 210 °C P: 100 bar Flow rate: 5–10 mL min^{-1} Operating mode: semi-continuous	The highest recovery of carbohydrates (85%) and phenolics occurred at 210 °C. In addition, 60 g of residue provided 6.6 g of an extract rich in phenolic compounds with a phenolic compound content higher than 100 mg/$g_{extract}$.	(Pedras et al., 2017)

T temperature, *P* pressure

effects and the generated hydroxide and hydronium ions are balanced between hydrolysis, carbonization, and sugar degradation (Lachos-Perez et al., 2017b).

Subcritical Water Combined with Other Technologies

sCW coupled or in sequence with other technologies can increase process efficiency by recovering high contents of bioactive compounds or producing more fermentable sugars from agri-food by-products. Table 2 presents an overview of studies employing sCW coupled or in sequence with high-intensity ultrasound (HIUS), microwave, pulsed electric field (PEF), and enzymatic hydrolysis technologies.

Subcritical Water and High-intensity Ultrasound

The HIUS technology employed in extraction processes is based on the application of acoustic waves at frequencies from 20 to 40 kHz and high intensities (≥ 1 W/cm^2) into the liquid medium (Kumar et al., 2021; Strieder et al., 2021). This energy promotes acoustic cavitation in extraction media, generating pores and ruptures on the vegetable's cell walls (Fan et al., 2020). Although known as a non-thermal technique, the waves propagated in the liquid medium increase the pressure and temperature (Costa & Almeida Neto, 2020). In this way, HIUS has been used as pretreatment coupled with sCW to facilitate sCW penetration in the vegetable cells, improving the extraction of phytochemical compounds. Also, HIUS accelerates reaction rates by improving mass and heat transfer rates and reducing processing time (Martins Strieder et al., 2020; Zhao et al., 2019). As a disadvantage, it contributes to forming free radicals, which can degrade bioactive molecules. Table 2 presents studies that integrated our coupled HIUS to sCW to increase extraction yields.

Elmi Kashtiban and Esmaiili (2019) and Park et al. (2022) pretreated grape skin and spent coffee with HIUS to favor the sCW extraction of flavonoids, phenolics, antioxidants compounds, and reducing sugars. According to them, the cavities promoted by acoustic cavitation on the cell structures of the grape skin and spent coffee exposed phytochemical compounds to sCW, increasing the extraction yield. The coupling of HIUS and sCW also increased the extraction of cinnamaldehyde from cinnamon barks, reducing the extraction time to 10 times that of steam distillation (Guo et al., 2021). However, a higher extraction time (over 25 min) at 140 °C probably thermally degraded the cinnamaldehyde. In this sense, temperature control is essential when coupling ultrasound technology, as it provides heat to the system (Urango et al., 2022).

HIUS coupled with sCW was also studied by Fan et al. (2020) to extract polypeptides from *Spirulina platensis*. The extraction rate increased from 10.3 to 41.3% by coupling HIUS to sCW. Acoustic cavitation made protein wrapped inside cells much easier to be released into the sCW solution. sCW changed these proteins' structure, accelerating the formation of peptides. Higher ultrasound power (250 W) decreased the SWE yield, while higher temperature (160 °C), pressure (150 bar), and processing time (80 min) maintained the same extraction results. Then, acoustic energy favored extraction, but higher power probably increased the temperature in the medium, promoting thermal degradation. The best condition to obtain peptides from the microalgae was 153 °C, 221 W, 100 bar for 64 min, acquiring an extraction rate of 74%.

Subcritical Water and Microwave

Microwave-assisted sCW processes have been studied to extract phytochemical compounds and pretreat lignocellulosic materials (Table 2). Its advantage includes fast volumetric heating without surface overheating. On the other hand, inhomogeneous heating and limited penetration depth can lead to hot and cold spots that are difficult to control (Gut 2022). This technology sources thermal energy through electromagnetic waves at the frequencies of 915 MHz and 2450 MHz, improving the mass transfer rate (Wen et al., 2020). Therefore, microwave technology has coupled to sCW to promote fast heating of the system, accelerating the process.

Moirangthem et al. (2021) statistically extracted the same anthocyanins content (about 62.8 mg/100 g) from black rice straw employing microwave-assisted sCW at 90 °C for 5 min and methanol at 60 °C for 20 min. The authors demonstrated the efficiency of coupling these two technologies (sCW and microwave). However, high temperatures at 160 °C of sCW promoted anthocyanin thermal degradation.

Microwave-assisted sCW also acted as an acid catalyst in the pretreatment of Indian black rice straw by disrupting the waxy silica surface, breaking down the lignin–hemicellulose complex, and partially removing silicon and lignin (Moirangthem et al., 2022). In this sense, these associated technologies facilitated the action of enzymes on black rice straw for its hydrolysis, enhancing glucose production from 25 to 50%.

Subcritical Water and Pulsed Electric Field

PEF technology employs high-intensity pulsed electric fields (10–80 kV cm^{-1}) sourced by two electrodes in the sample to promote membrane disruption through electroporation (Barbosa-Canovas et al., 2000). The advantages of PEF extraction are the low energy demand and the alteration

Table 2 Overview of technologies coupled or in sequence with sCW

Plant matrix	Goal	Technology/ Combination mode	Main results	Reference
Siah-Sardasht grape skin	Extraction of phenolic compounds	HIUS/Sequence	Ultrasound pretreatment (400 W at 21 kHz and 50 °C for 30 min) followed by SWE at 150 °C, 40 bar, for 30 min allowed the maximum extraction of total flavonoid and total phenolics, improving the antioxidant capacity of the extract.	(Elmi Kashtiban & Esmaiili, 2019)
Spent coffee ground	Oil removal and fractionation of bioactive compounds	HIUS/Sequence	Ultrasound pretreatment (400 W at 60 Hz and 40 °C for 30 min) followed by SWE at 180 °C and 40 mg/600 mL significantly increased total phenolic compounds, total flavonoid content, and reducing sugar values correlating with improved antioxidant activities by 2,2-Diphenyl-1-Picrylhydrazyl and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid assays.	(Park et al., 2022)
Cinnamon barks	Extraction of cinnamon oil	HIUS/Coupled	The extraction time of SWE was the shortest and equivalent to 1/10 of steam distillation. Optimal conditions were 140 °C, 25 min, 50 bar, 8 mL g^{-1}, 145 W, 18.5 kHz acquiring 1.78 g/100 g of cinnamon oil.	(Guo et al., 2021)
Spirulina platensis	Production of peptides	HIUS/Coupled	The extraction rate increased to 74% at process conditions of 153 °C and 221 W for 64 min.	(Fan et al., 2020)
Manipur black rice (*Chakhao*) bran and straw	Extraction of anthocyanin	Microwave/Coupled	Microwave-assisted sub-critical water extraction at 90 °C for 5 min presented an extraction efficiency of 85.8%.	(Moirangthem et al., 2021)
Indian black rice (*Chakhao Poireiton*) straw	Production of fermentable sugar	Microwave/Coupled	Pretreatment (100–200 °C for 5 min) did not drastically impact the sugar composition but enhanced the release of glucose after black rice enzymatic hydrolysis from 25 to 50%.	(Moirangthem et al., 2022)
Green Tea (*Camellia sinensis*)	Extraction of catechins	PEF/Sequence	The highest extraction yield of total catechin (44.35 ± 2.00 mg g^{-1}) was acquired at PEF treatment conditions of 2 kV cm^{-1} during 60 s and sCW at 130 °C.	(Hwang et al., 2021b)

Table 2 (continued)

Plant matrix	Goal	Technology/ Combination mode	Main results	Reference
Citrus unshiu peel	Extraction of hesperidin and narirutin	PEF/Sequence	The PEF increased the amounts of hesperidin and narirutin extracted by 22.1% and 33.6%, respectively. The best condition for hesperidin was: PEF treatment at 120 s, combined with SWE at 150 °C for 15 min, while for narirutin was PEF treatment at 120 s, integrated with SWE at 190 °C for 5 min.	(Hwang et al., 2021a)
Onion skin	Extraction of quercetin	PEF/Sequence	Pretreatment with PEF at 2.5 kV cm^{-1} for 15 s and SWE at 145 °C for 15 min improved the quercetin extraction by 33.22% (yield 19.25 mg g^{-1}).	(Kim et al., 2022)
Corn meal	Extraction of antioxidant compounds	PEF/Sequence	The treatment achieved the highest extraction yield by employing 2.51 kV cm^{-1} and 127.91 °C.	(Hosseini et al., 2021)
Sugarcane straw	Obtain fermentable sugars and second-generation ethanol	Enzymatic hydrolysis/Sequence	Integrating sCW and enzymatic hydrolysis increased fermentable sugar yield (2.40 ± 0.01 g L^{-1} of xylose and 8.9 ± 0.6 g L^{-1} of glucose) than subcritical pretreatment. In addition, the hydrolysis disrupted the lignocellulosic matrix facilitating the enzymatic accessibility of cellulose.	(Oliveira et al., 2022b)
Coconut husk	Evaluating the effect of surfactants in the pretreatment by SW for sugar production	Surfactant-assisted SW and enzymatic hydrolysis/ Sequence	The surfactant-assisted sCW and enzymatic hydrolysis generated the highest sugar yield (5.55 g L^{-1}) for the subsequent biofuel process. Sodium dodecyl sulfate (SDS) surfactant increased the production of reducing sugar at 150 °C by facilitating cellulose and hemicellulose solubilization in sCW. In this condition, the accessibility of water to hydrolyze hemicellulose and cellulose was increased.	(Muharja et al., 2019)

of cell permeability, promoting minimal thermal degradation (Bocker & Silva, 2022). Its disadvantages are the high cost-effectiveness, which depends on the conductivity of the environment. A high conductivity reduces the effectiveness and specificity of the electroporation phenomenon (Martínez et al., 2020). The phenomenon promotes the disintegration of the cells, increasing the diffusion of bioactive compounds from the cellular matrix. In addition, sCW polarity can be modified to enhance the extraction of organic compounds. Therefore, these technologies have been combined to extract higher contents of bioactive compounds, such as flavonoids and phenolic compounds, from different raw materials, as shown in Table 2.

PEF pretreatment of green tea leaves allowed an extraction yield 15.43% higher in catechin than untreated leaves by destructing the leaves' vacuoles and exposing these stored compounds to sCW (Hwang et al., 2021b). PEF as pretreatment to sCW also increased the recovery of hesperidin and narirutin from *Citrus unshiu* peel waste and quercetin from onion skin (Hwang et al., 2021a; Kim et al., 2022). However, the studies need to assess the intensity of the conditions applied. Hosseini et al. (2021) observed an increase of 86% in the extraction efficiency of phenolic compounds from corn meal by increasing the PEF intensity from 0 to 2.5 kV cm^{-1}. But, they verified a lower extraction of phenolic compounds by increasing the PEF intensity from 2.5 to 4.5 kV cm^{-1} and the sCW temperature from 130 to 150 °C. Higher intensities of PEF probably degraded the internal structure of the corn grains, closing the outlet ducts and disfavoring the extraction. While the high temperatures may have caused wall damage, leading to less phenolic compounds extraction from the corn meal.

Subcritical Water and Enzymatic Hydrolysis

sCW disrupts lignocellulosic matrices, increasing the enzymatic accessibility of cellulose (Muharja et al., 2018). Thus, enzymatic hydrolysis has been performed with sCW to increase hydrolysis yields, producing high amounts of sugar for subsequent biofuel, ethanol, and biohydrogen processes (Table 2). For that, agri-food by-products such as wheat straw, sugarcane straw, coconut husk, and agave bagasse have been used as a source of sugars.

The conversion efficiency of sugarcane straw to xylose and glucose was also improved by integrating sCW and enzymatic hydrolysis (Oliveira et al., 2022b). SWH pretreatment disrupted the lignocellulosic matrix of sugarcane straw, increasing the enzymatic accessibility of cellulose.

Muharja et al. (2018, 2019) integrated sCW and enzymatic hydrolysis to produce reducing sugars from coconut husk. Muharja et al. (2018) observed better hydrolysis results using sCW at 160 and 180 °C and 80 bar for 60

Table 2 (continued)

Plant matrix	Goal	Technology/ Combination mode	Main results	Reference
Coconut husk	Developing methods to hydrolyze the residue into sugars and carry out the fermentation of the hydrolyzate to hydrogen	Enzymatic hydrolysis/Sequence	sCW using 160 and 180 °C at 80 bar for 60 min increased the total reducing sugar production. Integration of sCW, enzymatic hydrolysis, and fermentation resulted in hydrogen with a maximum total yield of 0.279 mol mol^{-1} of sugar consumed at 150 °C, 80 bar, SF–3.25.	(Muharja et al., 2018)
Agave bagasse	Fractionation of agave bagasse	Enzymatic hydrolysis/Sequence	Agave bagasse was a promising raw material for developing second-generation biorefineries. The best sCW conditions were: 190 °C for 50 and 30 min. The maximum conversion yield (cellulose to glucose) by enzymatic hydrolysis was 61.62%.	(Singh et al., 2021)

min. These conditions broke the hemicellulose bonds to its monomers (xylose, arabinose, and fructose) through reactions of dissolution. Thus, the action of enzymes in the production of reducing sugars was favored, reaching a yield of 8.60%. The use of surfactants (PEG, Tween 80, and SDS) on sCW as pretreatment to perform enzymatic hydrolysis of coconut husk was studied by Muharja et al. (2019). They observed the highest sugar yield and the lowest degradation of monomeric or oligomeric sugar, reducing energy consumption by combining sCW assisted by SDS and enzymatic hydrolysis. SDS surfactant increased the production of reducing sugars close to 5.5 g L^{-1} at 150 °C by forming a surfactant micelle in this sCW condition. The hydrophilic groups of micelles may favor the cellulose and hemicellulose solubilization in sCW. In this condition, the accessibility of water to hydrolyze hemicellulose and cellulose increased. Thus, the hydrophobic and hydrophilic interaction between lignin and SDS produced the highest delignification and solubilization of monomeric sugar during sCW treatment.

Agave biomass acquired during tequila production also showed promising characteristics as a raw material for developing second-generation biorefineries. Singh et al. (2021) pretreated agave biomass with sCW, selecting the operating conditions based on the increased cellulose content (> 50%). The enzymatic hydrolysis allowed a maximum conversion yield of cellulose to glucose of up to 61.62% (5.86 g L^{-1}) in industrial bagasse for 72 h. Thus, the process demonstrated the possibility of using different raw materials as sources of reducing sugars to produce fuels.

Subcritical Water and Alternative Solvents

sCW presents higher miscibility than water at room temperature and pressure, favoring the simultaneous extraction of hydrophilic and lipophilic compounds. However, in many cases, there is an interest in extracting a specific compound. Thus, an alternative is the addition of deep eutectic solvents (DES) or ionic liquids (ILs) to sCW, modifying its characteristics to favor a selective and efficient extraction (Essien et al., 2020; Sarkar et al., 2014). Few studies reported sCW associated with other solvents to hydrolyze or extract compounds from raw materials. Some examples are presented as follows.

Subcritical Water and Deep Eutectic Solvents

DES is formulated by mixing a hydrogen bond acceptor with a hydrogen bond donor. These associations produce a network favoring the solvation of a specific class of compounds through interactions and presenting a melting point at a single temperature lower than the melting point values of the separate constituents (Benvenutti et al., 2019). Thus, DES are biodegradable solvents that have allowed the extraction of target compounds, reducing the thermal degradations by high temperatures (Essien et al., 2020). Its advantages include easy preparation without further purification, lower toxicity, and higher biodegradability compared to ILs when prepared with natural components (Boateng, 2023; Murador et al., 2019). However, in this case, the viscosity of the DES is not an issue as they have been added to sCW as modifiers to increase extraction yields.

Saravana et al. (2018) studied adding DES to sCW to extract polysaccharides (fucoidan and alginate) from brown seaweed. The authors evaluated seven DES combinations: choline chloride with 1,2-propanediol, glycerol, ethylene glycol, 1,3-butanediol, 1,4-butanediol, urea, and propanedioic acid. Each type of DES presented a particular influence on the solvent's viscosity, solubilization capacity, and polarity, resulting in different extraction yields. Moreover, the authors studied the effects of temperature (100, 125, and 150 °C), pressure (50, 60, and 70 bar), water content (50, 60, and 70%), and liquid-to-solid ratio (30, 40, and 50 mL g^{-1}) on the extraction of alginate and fucoidan. The first verification observed by them was that choline chloride mixed with glycerol or ethylene glycol allowed the highest extraction of alginate than other DES combinations. The highest fucoidan recovery was observed using choline chloride mixed with glycerol. The recovery yields observed by adding a DES in sCW were at least twice that obtained from water/HCl as a solvent. This result was associated with the steric hindrance of three hydroxyl groups of glycerol that can weaken the interactions between the polysaccharide and the chloride anion. Among molar ratios, 1:2 (mol/mol) was the best to extract the polysaccharides. Moreover, the extraction yield was higher for DES with 60% water for both polysaccharides than with 50 or 70%. An intermediate liquid-to-solid ratio (40 mL g^{-1}) was the best to extract the polysaccharides. The best extraction conditions were between 120 and 140 °C and 30 bar.

sCW with DES also was studied by Machmudah et al. (2018) to enhance the extraction of phenolic compounds from pericarps of mangosteen. sCW at 160 °C added to DES destroyed the cell wall of mangosteen pericarps, depolymerizing lignin and thus releasing phenolic compounds like xanthone to the solvent. DES produced from citric acid and alanine (molar ratio of 1:1) improved the dissolution capability for water-soluble and macromolecular compounds separated from the pericarp. Furthermore, the xanthone extraction yield increased from 3.24 to 6.76 mg g^{-1} of dried sample by increasing the volume of DES addition from 10 to 30% at the same extraction temperature. Thus, demonstrating the DES's strong intermolecular interactions enables the extraction at high temperatures.

Subcritical Water and Ionic Liquids

ILs are organic salts formed by an organic cation and an organic or inorganic anion, which present a lower melting point than their pure compounds. These alternative and reusable solvents have high thermal stability, negligible vapor pressure, and high hydrophobicity (Herce-Sesa et al., 2021). ILs offer numerous advantages for carrying out organic reactions since product recovery is easier and the catalysts can be recycled. However, its relatively high cost compared to conventional organic solvents makes its use as an additive in solvents. ILs formed by cations derived from 1-alkyl-3-methylimidazolium, combined with anions such as acetate, chlorate, and bromide, have been used to extract several compounds (Benvenutti et al., 2019; Sarkar et al., 2014). However, pure ILs presenting long alkyl chains and large sizes of nonpolar parts increase the van der Waal's interactions, thus causing difficulting in the extraction of other compounds. In this sense, mixing ILs with water may minimize this limitation, reducing the solvent viscosity (Vo Dinh et al., 2018).

Gereniu et al. (2018) and Vo Dinh et al. (2018) combined ILs and sCW to extract carrageenan and phenolic compounds from seaweeds. The addition of 1% 1-Butyl-3-methylimidazolium acetate (BMIMAc) to the sCW at 150°C/50 bar with 1:80 g mL^{-1} (solid to liquid ratio) promoted the highest carrageenan recovery (78.75%) from the Solomon Islands red seaweed (Gereniu et al., 2018). This extraction yield was higher than the acquired by SWE (71%) and a conventional method (55%). BMIMAc has demonstrated a higher capability to depolymerize cellulose than other ILs because of the mobility of the acetate ion. Moreover, sCW temperature and pressure facilitated the IL penetration into the sample matrix, increasing mass transfer and solubilizing the carrageenan in the solvent.

Likewise, Vo Dinh et al. (2018) studied 1-Butyl-3-methylimidazolium tetrafluoroborate $[C_4C1im][BF_4]$ addition to sCW at different temperatures (from 100 to 250 °C) and molarity (0.25–1.00 M) to extract phenolic compounds from brown seaweed. IL favored the solvation of the phenolic compounds in the sCW at 175 °C, increasing the extraction yield. However, a reduction in phenolic compounds recovery was observed by increasing the IL molarity in the sCW. Thus, the best molarity of IL in the sCW was 0.25 M. This result is probably due to the better solvation of the water in the matrix at lower content of IL.

One of the first publications was on the removal of total carbohydrates and phenolics from barley hull using sCW and ionic liquid (Sarkar et al., 2014). The authors reported that the highest phenolics extraction (189.1 ± 3.1 mg/g hull) was obtained using pressurized aqueous ionic liquid. The anionic species facilitated removal of phenolics from barley hull by-product. More studies are required to evaluate the addition of ionic liquids to sCW for extraction of compounds from other agri-food by-products.

Patents and Economic Aspects Related to Processes Employing Subcritical Water

The techno-economic feasibility study allows the scale-up of processes performed at laboratory scale. This information allows the evaluation of emerging technologies that are not yet available at industrial scale. For example, some studies have reported sCW economic feasibility on the recovery of bioactive compounds and the production of sugars by hydrolysis (Essien et al., 2021; Sganzerla et al., 2021) using SuperPro Designer and Aspen Plus® by Aspen Technology software. The cost of manufacturing (COM) considers economic parameters such as fixed capital investment, cost of raw material, operational labor, and cost of utilities. Moreover, the COM calculation considers that the industrial-scale extraction performance (yield) was the same as obtained on the laboratory scale.

Essien et al. (2021) performed a techno-economic comparison between SWE and ethanol extraction to obtain phenolic compounds from kãnuka leaves. Although ethanol extraction was carried out at ambient pressure, this process requires the recovery and reuse of the solvent. Thus, it requires adding extra process units to the extraction. In this sense, the estimated energy consumption process was higher for ethanol extraction than for SWE. Besides higher energy consumption, ethanol extraction presented a lower extraction yield than SWE. The same phenolic compound content was acquired with 1 h of SWE and 8 h of ethanol extraction. Thus, the COM for the ethanol extraction was 4.6% higher than for the SWE, considering the same pilot scale due to the cost of ethanol compared to water. In this way, SWE presented a competitive process against ethanol extraction.

Sganzerla et al. (2021) performed a techno-economic evaluation to produce sugars from brewer's spent grains employing SWH. They analyzed two production scales: 10 L (pilot plant) and 500 L (industrial plant), coupled or not to a separation system. They demonstrated that the COM to produce sugars was reduced by 80% when increasing the production from 10 to 500 L. However, coupling the separation system to the SWH increased the COM to 4-fold. This result was expected, considering that the sugars separation system is the most expensive operation due to the high costs of fixed capital investment. These two assessments demonstrated several costs involved, such as feedstock pre-treatment, solvent preparation, extraction/collection, ethanol recovery, total electricity, electricity demand per kg feed, power consumption per kg product, SWH plant cost, steam, and others in sCW processes. However, few studies have addressed this type of analysis.

According to Fig. 1, the number of patents on sCW highlighted the industry interest in this technology. In addition, many publications reported biofuel production processes using waste or plant materials (Aoki, 2021; Forster-Carneiro, 2015; Kumar et al., 2018). For example, Kumar et al. (2018) presented an sCW industrial system for processing plant materials to produce biofuel (sugars and oil), biochar, and raw materials for other industries (pulp for manufacturing paper and cellulose). This system included a pre-processing module and a two-stage extractor with temperature, pressure, and residence time control. In addition, Forster-Carneiro (2015) proposed a system to produce ethanol, hydrogen-rich, and methane-rich biogas from biomass and waste coupling sCW and semi-continuous or continuous gasification.

In addition, many studies have proposed sCW to extract phytochemical compounds from plant materials. For example, Vitrac et al. (2019) proposed an sCW extraction to recover volatile compounds and phenolic compounds in the same extract from some medicinal plants (*Helichrysum*, *Rosmarinus*, *Eucalyptus*, *Inula*, *Laurus*, *Rosa*, *Thymus*, *Mentha*, *Citrus*, *Lavandula*, *Cupressus*, *Salvia*, *Picea*, *Pinus*, *Jasminum*, *Anthemis*, *Lippia*, *Myrtus*, *Lilium*, *Arnica*, *Cinnamomum*, *Crocus*, *Cananga*, *Pelargonium*). The "dynamic" extraction method by percolation, where sCW continuously circulates through the raw material, was performed between 150 and 175 °C.

Other inventors used sCW technology in a step of the process to obtain a product, like the patent of Kobayashi et al. (2021). This invention treated sugar with sCW in a buffer solution for a short time to produce rare monosaccharides (D-gulose) and disaccharides (lactitol). In addition, Mishima and Tokunaga (2019) proposed using sCW to produce microcapsules using cellulose nanofibers as a coating component. In this case, the sCW was employed during the mixture and microencapsulation of the coating material and core particles. The core was composed of a stream of fluid. Another stream of fluid formed the coating. The microcapsule would have a delayed release of actives, with the second act being released first after the outer coating has degraded and the first act being released last.

Conclusion and Future Perspectives

Agri-food by-products are discarded in large quantities worldwide. Thus, this review discussed recent advances over the past five years in treating these by-products using sCW technology. Its advantages include reduced extraction time and increased heat and mass transfer, resulting in high yields. Through controlling variables, mainly temperature, pressure, and time, the technology has stood out due to its selectivity in obtaining bioactive compounds by changing chemical affinity related to the polarity of the molecules. Furthermore, sCW coupled or in sequence with other technologies has increased process efficiency by increasing the recovery of bioactive compounds or producing higher yields of fermentable sugars from agri-food by-products. The patents and techno-economic evaluations demonstrated the powerful perspective for developing future research focused on large-scale operation for industrial equipment design. Thus, the technology would alleviate environmental and energy issues.

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Declarations

Competing Interest The authors declare no conflict of interest.

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