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Subcritical water and supercritical carbon dioxide: efficient and selective eco-compatible solvents for coffee and coffee by-products valorization

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This review aims to establish the state of the art of the existing literature on the valorization of coffee and coffee by-products (*i.e.* green coffee, coffee husk, pulp, silverskin and spent coffee grounds) through the use of pressurized fluids as solvents, including subcritical water (SCW) and supercritical carbon dioxide (SC-CO_2). The first part reviews the exploitation, the composition, the properties and the ways of valorization of coffee beans and their by-products, highlighting their high potential as raw material. The second part is dedicated to subcritical H_2O and supercritical CO_2 applied to coffee and coffee by-products valorization, discussing the involved mechanisms, the parameters' influence and the superiority of subcritical H_2O and supercritical CO_2 in comparison to other solvents and techniques. Indeed, subcritical H_2O is considered as a super solvent, catalyst and reagent at the same time, being the most efficient technology for carbohydrate and polyphenol recovery as well as biocrude-oil production. Supercritical CO_2 is considered as a chameleon solvent, with unlimited tunability, able to selectively extract high value molecules but also compete with organic solvents in amount and quality of the produced extract. In addition, subcritical H_2O and supercritical CO_2 are complementary solvents, targeting together all the types of molecules in coffee and coffee by-products, leading to the development of a Green Solvent Bio-Refinery (GreSBiR) with sequential uses of subcritical H_2O and supercritical CO_2.

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1. Introduction

Bioeconomy is one of the most popular concepts of the XXIth century. It is defined as the production of chemicals, materials and/or energy from bio-resources, and the valorization of their by-products and waste. In this context, agricultural, forestry, aquatic or agrifood waste can be used as raw materials for new applications. For examples, agricultural by-products can be used to generate biohydrogen by fermentation processes for energy production[1] or biopolymers such as polyhydroxyalcanoate (PHA) for materials field.[2] Olive mill waste is a source of high value polyphenols such as hydroxytyrosol, a phenolic phytochemical with antioxidant properties.[3] Viticultural waste such as grape canes and stocks contains resveratrol and ε-viniferin, two powerful antioxidants.[4] Needles form pine tree waste are rich in proanthocyanidins, which are a class of polyphenols.[5] Invasive plants such as *Fallopia japonica or Fallopia sachalinensis* can be also valorized by extraction of the antioxidant extracts rich in triterpenoids and polyphenols they contain.[6] Aquatic waste such as microalgae have been studied for the production of biodiesel and glycerol as sub-product.[7] Moreover, other microalgae are rich in astaxanthine, terpenoid, and protein that are valuable compounds.[8] Indeed, many examples have reported the successful recovery of different biomolecules from agrifood waste, with high potential in pharmaceutical, nutraceutical and/or cosmetic fields.[9] In the same way, coffee and their by-products (*i.e.*, coffee pulp, husks, silverskins and spent coffee grounds) have been also widely studied these last years.[10]

Green chemistry aims to design chemical products and processes that are more environmentally benign, and that present reduced negative impacts to human health and environment.[11] Thus, the choice of coffee and its by-products as renewable feedstocks rather than petrosourced ones is in accordance with the seventh principle of green chemistry.[11]

Many extraction processes are based on the use of organic solvents, which may have certain drawbacks such as their use in large volumes, obtaining poor extraction selectivities and the generation of large amount of undesirable waste, making then the process expensive.[12] Moreover, organic solvents are hazardous for the operators in laboratories and industries due to their potential flammability, explosiveness, corrosivity and carcinogenic, mutagenic or reprotoxic properties.[13]

Hence, a myriad of new technologies and solvents have been developed to perform extraction more respectful for the environment. These include extractions assisted by non-conventional methods of activation such as ultrasound (US),[14–16] microwaves (MW),[6,17,18] pulse electric field (PEF)[19] or high voltage electric discharge (HVED).[20] Those methods are of great interest to increase extraction yields, reducing extraction times and energy costs.

Alternative solvents of extraction have been developed and studied over the years such as ionic liquids (ILs),[21] deep eutectic solvents (DES),[22,23] subcritical water (SCW),[24] supercritical CO_2 (SC-CO_2)[25] or solvent-free (pressing, extrusion, ball milling, instant controlled drop pressure).[26,27] However, after extraction, deep eutectic solvent and ionic liquid extracts suffer from the impossibility to recover the solute by a simple evaporation of solvent. It requires then an additional step such as solid–liquid extraction, liquid–liquid extraction or adsorption on column or addition of an antisolvent.[28,29] The physical extraction in the absence of solvent is generally not an efficient solution either since mechanical frictions induce high shearing and high temperature that can lead to the decomposition of heat-labile phenolic compounds and polymerization of phenolic compounds, reducing their extractability.[30]

Pressurized fluids such as subcritical water and supercritical carbon dioxide represent a very suitable alternative to the

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use of organic solvents. Water and carbon dioxide are cheap, available and non-toxic solvents. Subcritical water is perfectly adapted to recover polar and medium-polar solute and supercritical carbon dioxide is more adapted to recover apolar molecules. In a world aware of current and future environmental concerns, subcritical water and supercritical carbon dioxide represent top choice extraction solvents to reduce the environmental impact of the process.

Subcritical water (SCW) also called "*superheated water*", "*hot compressed water*" or "*pressurized hot water*" is liquid water at temperatures between 100 °C (373 K) under 1 bar and 374 °C (647 K) under 220 bars. This maximum temperature is related to the critical point of water that is reached at 374 °C and 220 bars when the heat of vaporization become equal to zero. The increase of temperature affects positively (i) the diffusion coefficient of water, (ii) the solubility of solutes, (iii) the diffusion of solutes and (iv) the water viscosity. In addition, a modification of specific physico-chemical properties of SCW are observed such as (i) the reduction of dielectric constant of water (ε = 80 at 25 °C, P_{atm} to ε = 27 at 250 °C, 50 bars) to become closer to that of ethanol (ε = 24) and methanol (ε = 33) and (ii) the acidification of water by self-ionization of water molecules.[31]

Supercritical carbon dioxide (SC-CO_2) means CO_2 at the supercritical state, with pressure and temperature exceeding the critical point of CO_2 at 31.1 °C and 73.8 bars. The supercritical CO_2 is in a homogeneous and hybrid state that presents both properties of liquids and gas. It reaches viscosities close to those of gas (0.02–0.12 mPa s at 40 °C) and its densities are close to those of liquids (700 to 1100 kg m^{-3}).[32,33] Variations of temperature and pressure allow to set the properties of supercritical CO_2 and to fit with different applications.[34] The most known extraction process with CO_2 used as supercritical fluid is the RESS (Rapid Expansion of Supercritical Solution) method, consisting in a two-steps process with (i) a first solubilization of the solute in SC-CO_2, followed by (ii) a precipitation of the solute by oversaturation in CO_2 gas.[35]

The aim of this review is to evaluate the contribution of subcritical H_2O and supercritical CO_2 for coffee and coffee by-products valorization. The review article is thus organized in two main parts: (i) the full description of the coffee and coffee by-products processes, composition and valorization (section 2) and (ii) the benefits of subcritical H_2O and supercritical CO_2 for the valorization of coffee and coffee by-products (section 3).

2. Coffee

Coffee is one of the most consumed beverages over the world after water, and it is the second most traded commodity after petroleum. According to International Coffee Organization, 9.4 million of tons of green coffee beans have been produced in 2018.[36] This raw resource is cheap, available and consequent amounts of by-products are resulting from the preparation of coffee beverage.

The following sections discuss the exploitation and the valorization of coffee and its by-products.

2.1. Coffee exploitation

Nowadays, 90% of coffee is produced in developing countries (Table 1).[37] Brazil is the biggest producer of coffee bean with 2.68 million tons in 2018 and represent almost a third of the world coffee production.[38] Close to 80 varieties of coffee exist, but two of them are mainly cultivated nowadays: *Coffea canephora*, mostly known as *Robusta* and *Coffea arabica*.

Arabica coffee from Brazil and South American countries represents around 75% of the world production whereas Robusta coffee from Vietnam and African countries coffee represents the remaining 25%. Growing conditions of their trees are different. Arabica tree needs shade and soft temperatures, whereas Robusta tree can resist to harsh conditions of temperatures and humidity. Variation of composition is observed in terms of polysaccharides, lipids, bioactive molecules and caffeine as a function of the variety. For example, Arabica contains 0.8 to 1.5% of caffeine whereas Robusta contains 2.5 to 3.0% of this molecule. In any case, the treatment required for the transformation from green coffee bean to coffee beverage remains the same for both varieties.

2.2. Coffee treatments and composition

Many processes are required before obtaining the beverage from the coffee cherry, leading to the formation of by-products (Table 2). In addition, those by-products are composed of caffeine, tannins and polyphenols that could be possibly toxic for the environment.[39] After harvest coffee cherry, the three main steps required for obtaining the beverage are (i) drying or wet process, (ii) roasting process and (iii) brewing process.[10] Several by-products such as coffee husks (CH), pulp (CP), sil-

Table 1 The most important world coffee producers in 2018.[7]

	Production (million tons)	Word production (%)
Brazil	2.68	29.1
Vietnam	1.54	16.7
Colombia	0.75	8.2
Indonesia	0.67	7.3
Honduras	0.47	5.2
Ethiopia	0.47	5.1
Others	2.62	28.4

Table 2 Composition of green coffee and coffee by-products

	Sugars (%)	Lipids (%)	Proteins (%)	Caffeine (%)	Chlorogenic acids (%)
GCB	40–60	10–15	10	0.8–4	6–12
CH	70	0.3	7	0.65	—
CP	70	2	10	1.3	—
CSS	60	2	18	0.8–1.3	—
SCG	45–50	10–15	7–13	0–0.5	0.5–3

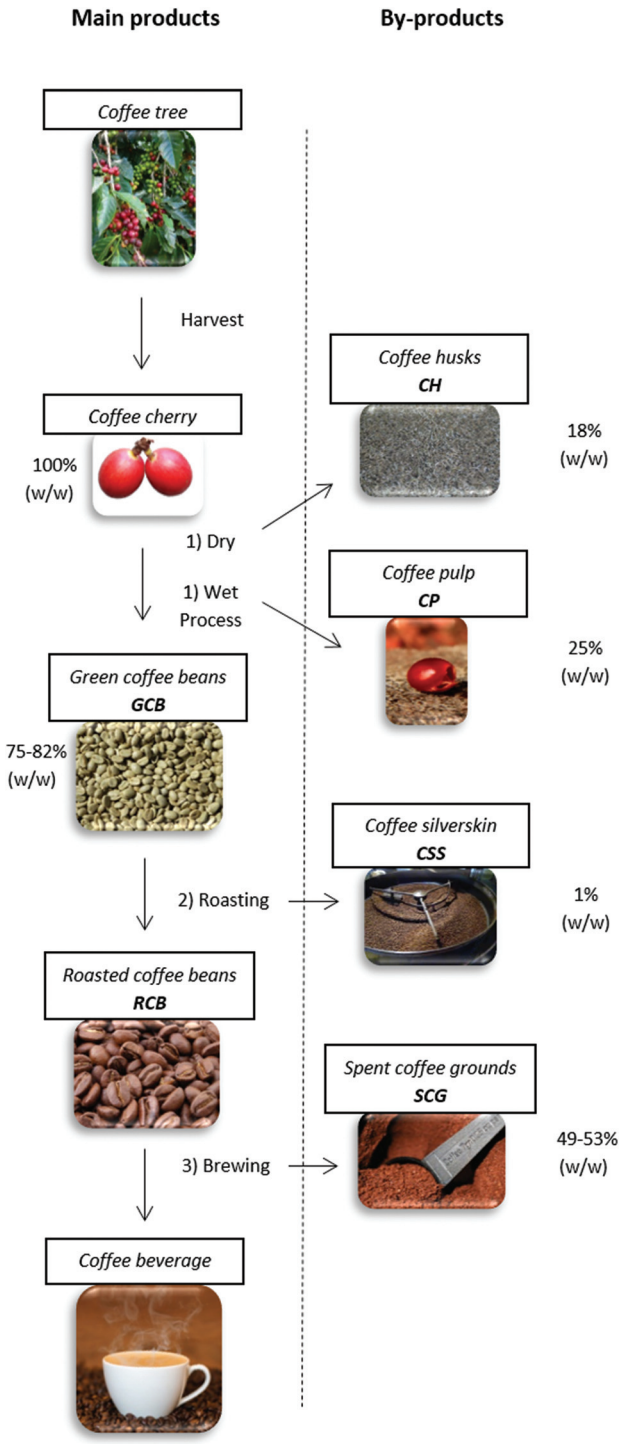

Fig. 1 Coffee processes and their by-products.

verskin (CSS) and spent coffee grounds (SCG) result from the processes of coffee treatment (Fig. 1) that have been largely described in literature.[10]

Dry or wet processes aim to extract the core of coffee cherry and to recover the green coffee bean. Dry method also called *cherry method* consists in drying and mixing the freshly harvested coffee cherry for 12–15 days until it is totally dry.[10] The peel removed during the dry process is called coffee husk. About 0.18 ton of husk is produced for 1 ton of coffee cherry. The husk is composed of more than 70% of carbohydrates, 15% moisture, 7.0% protein, 5% ash, 0.3% lipids, and 0.65% of caffeine (w/w).[10,40] Wet method consists in removing coffee cherry pulp with a pulper before drying operation that longs 24 to 36 h for Arabica and 72 h for Robusta. The by-product recovered during the wet process is called coffee pulp. About 0.33 ton of pulp is produced for 1 ton of coffee cherry. The pulp is composed of 50% carbohydrates, 20% fibers, 10% proteins, 5% tannins 2% lipids and 1.3% caffeine (w/w).[41]

Green coffee beans obtained are composed of about 30–50% of insoluble polysaccharides, 10% of soluble carbohydrates, 10–15% of lipids, 10% of proteins, 6–12% of chlorogenic acids and 0.8–4% of caffeine (w/w). Contents in lipids and insoluble polysaccharides are higher for Arabica whereas contents in chlorogenic acids and caffeine are higher for Robusta.[42] Despite this interesting composition, green coffee bean is tasteless and odorless and a roasting process is necessary to give it flavor and odor.

Roasting process consists in a pyrolysis of the green coffee beans at 200 to 250 °C during 0.75 to 25 min. Many of the compositional changes occur during this step and are due to the Maillard reaction that gives thus to the coffee beans their aromas.[43] Roasting step also removes a peel to beans that is called coffee silverskin. Although it only represents 1% of initial mass,[10] the large amounts of coffee beans that are roasted make it an important by-product of coffee production. Coffee silverskin is composed of 60% carbohydrates, 18% proteins, 2% lipids, 7% ashes, 7% moisture and 0.8–1.3% caffeine (w/w).[44] Roasted coffee beans obtained keep almost same composition as green coffee beans in terms of carbohydrates, lipids and proteins. Main differences are the important degradation of chlorogenic acids, up to 90% and caffeine, up to 25% depending on the roasting intensity that can be light, medium or dark.[45]

To finally obtain coffee beverage, grinding and brewing process are required. Brewing process consists in an extraction with water at 100 °C. Boiling water is flowed through the grinded roasted coffee beans by gravity or under pressure giving a flavored coffee beverage. Remaining grinded roasted coffee beans that are not soluble in water and constitute then a solid waste with high moisture content that is called spent coffee grounds. Thereby, 0.65 ton of spent coffee grounds is produced for 1 ton of green coffee beans.[10] The spent coffee grounds is composed of 45–50% carbohydrates, 10–15% lipids, 7–13% proteins, 0.5–3% chlorogenic acids and 0–0.5% caffeine (w/w).[46]

2.3. Valorization of coffee and coffee by-products

The valorization of coffee and coffee by-products is mainly related to (i) their chemical composition and (ii) their availability, accessibility and quantity generated.

Despite the discrepant composition between green coffee bean (GCB), coffee husk (CH), coffee pulp (CP), coffee silver-

skin (CSS) and spent coffee grounds (SCG), similar way of valorization are studied since the nature and proportion are quite similar between the different coffee by-products CH, CP, CSS and SCG (Table 2).[47] Main difference of way of valorization is related to the high lipidic content of GCB and SCG. GCB is also atypical with high chlorogenic acid content. The concentration of chlorogenic acids significantly decreases after roasting, hence, the antioxidant activity remains similar.[48] This is due to the formation of Maillard reaction products such as melanoidins and transformation of chlorogenic acids into derivatives such as chlorogenic acids, lactones or phenylindans that exhibit high antioxidant properties.[43,48,49] As a consequence, even if CSS and SCG present different chemical composition of polyphenols compared to GCB, CH and CP, the way of valorization into high antioxidant extract remains the same (Table 3).

As presented in Fig. 1, SCG is the main coffee by-product representing 49–53% w/w of the coffee fruit, followed by coffee pulp (25% w/w), coffee husk (18% w/w) and coffee silverskin (1% w/w).

In addition, coffee by-products are produced at different stages of coffee processes resulting in major differences of their accessibility. For example, coffee husk and coffee pulp are generated by coffee growers, limitating geographically the valorization of such by-products to coffee producer countries. Coffee silverskin are obtained all around the globe but only roaster companies are generating this by-product. Spent coffee grounds are produced all over the planet by everybody, in particulars in household, coffeeshops, hotels or soluble coffee industries. Then, the possibility to give higher economic value to this waste is not only valuable for industry but also for the collectivities and public authorities, especially in terms of waste management.[50]

2.4. Characterization of coffee and coffee by-products extracts

Numerous technics of characterizations are used to evaluate the nature of the final product like antioxidant extract or biocrude oil. The following section gives a brief description of all the major analysis performed with coffee extracts in order to better discuss the effects of subcritical H_2O and supercritical CO_2.

2.4.1. Carbohydrates extracts

2.4.1.1. Total sugar content (TSC). The total sugar content (TSC) is a colorimetric test in food science that aims to measure all carbohydrates such as mono-, di-, oligo-, polysaccharides, proteoglycans, glycoproteins and glycolipids without distinguishing the nature of the species.[51] Two simple procedures have been developed as phenol-sulfuric acid assay also called "Dubois method"[52,53] and anthrone-sulfuric acid.[54–56] The phenol and anthrone-sulfuric tests lean on the hydrolysis of sugars into furfural or 5-hydroxymethyl-2-furaldehyde

Table 3 Main ways of valorization of coffee and coffee by-products

Raw material	Valorized fraction	Area	Applications	Value	Ref.
CP, CH, CSS, SCG	Entire resource (raw)	Animal food	Protein food for ruminants	+	66–68
CP, CH, CSS, SCG	Entire resource (raw or transformed)	Agriculture	Fertilizers, soil amendment, compost	+	69 and 70
SCG	Entire material (raw)	Agrifood	Substrate for edible mushrooms culture (Pleurotus, Flammulina vetulipes)	+	40 and 71
CP, CH	Entire resource (raw)	Agrifood	Cascara beverage (infusion)	+	72–74
SCG	Entire resource (transformed)	Building material	Raw (fill road embankment), geopolymer (cement), composite (thermal insulator, clay brick)	+	75–78
SCG	Entire resource (raw or transformed)	Depolluting material	Raw (Cu^{2+} adsorption), bioelastomer ($60\%_{SCG}$/$40\%_{silicone}$ Pb^{2+}/Hg^{2+} adsorption), composite (SCG/chitosan drugs adsorption), activated carbon (volatile organic compounds VOC adsorption)	+	79–82
CP, CH, CSS, SCG	Entire resource (transformed)	Energy/depolluting material	Biocrude oil, biochar (pyrolysis) Biogas (anaerobic digestion)	++	83–85
CP, CH, CSS, SCG	Carbohydrates	Energy	Bioethanol (fermentation)	++	86 and 87
SCG	Lipids	Energy	Biodiesel (triglycerides transesterification)	++	88
CP, CH, CSS, SCG	Carbohydrates	Polymers	Biopolymer PolyHydroxyAlkanoate (PHA, enzyme *B. cepacia*)	++	89
SCG	Lipids	Polymers	Biopolymer PolyHydroxyAlkanoate (PHA, enzyme *C. necator*)	++	90
GCB, RCB, CP, CH, CSS, SCG	Caffeine	Agrifood, pharmaceutical, nutraceutical, Cosmetic	Ingredient in sodas, energy drinks, painkillers, slimming cream	+++	91–93
CP, CH, CSS, SCG	Carbohydrates	Nutraceutical	Bioactive sugars, dietary fibers (hydrolysis)	+++	94–96
GCB, SCG	Lipids	Cosmetic	High value oil (ingredient moisturing cream)	+++	97 and 98
GCB, CP, CH, CSS, SCG	Polyphenols (chlorogenic acids, melanoidins)	Nutraceutical, cosmetic	Antioxidants and anti-inflammatory extracts, pills for body weight loss (Svetol®), anti-aging and anti-UV cream	+++	99–103

(5-HMF) that form a conjugated system with phenol or anthrone. The result is expressed with a calibration curve of glucose (g_{GLU} per 100 $g_{dry\ material}$). For lignocellulosic material, this assay is efficient (i) to define the total sugars of a biomass or (ii) to evaluate the influence of extraction parameters on the sugar content of a produced extract.

2.4.1.2. Reducing sugars (RSs). A reducing sugar is defined as any sugar reacting as reducing agent because of a free aldehyde or free ketone function its bears. As such, all monosaccharides are considered as reducing sugar. It is important to note that monosaccharides are dietary sugars with applications in agrifood and nutraceutical. Furthermore, the transformation step for the production of reducing sugar from lignocellusic material is called the saccharification. It is generally performed by enzymatic, or acid or alkaline hydrolysis. The saccharification is the preliminary step before the transformation of reducing sugars into bioethanol.

The "Reducing Sugars" (RSs) is a colorimetric assay in food science that aimed to measure all the reducing sugars without distinguishing between species (*DNS method*).[57,58] RSs is a relevant test to (i) determine dietary sugars amount in an extract and (ii) to evaluate the interest of subcritical H_2O to induce saccharification.

2.4.1.3. Sugar profile. Lignocellulosic material is a complex matrix of lignin, hemicellulose and cellulose. Di-, oligo-, polysaccharides such as hemicellulose and cellulose are macromolecules composed of 2 (di-), 3–10 (oligo-) or >10 (poly-) monosaccharides building blocks. Cellulose is a homopolymer composed of 100–3000 glucose molecules combined at the $\beta(1 \rightarrow 4)$ position. Hemicellulose is a heteropolymer that can be composed of glucose, xylose, mannose, galactose, rhamnose or arabinose. Coffee polysaccharides are mainly composed of galactose, mannose, glucose and arabinose patterns.[59]

The nature of those monosaccharides can be determined after hydrolysis of the biomass or extract by HPLC with a Refractive Index detector (RI),[60] Evaporative Light Scattering Detection (ELSD),[61] Electrochemical Detection (ECD)[62] or UV-Visible/Diode Array Detector (DAD) after derivatization with 1-phenyl-3-methyl-5-pyrazolone (PMP).[63,64]

$$\text{Sugar profile} = \frac{\text{Amount of specific sugar}}{\text{Amount of total specific sugar}} \quad (1)$$

Other chromatographic methods have also been studied in the literature.[65] Sugar properties are related to their chemical structure hence, the determination of sugar profile (eqn (1)) is relevant (i) to define the chemical structure of sugars in extract and (ii) to evaluate the influence of SCW on the sugars extraction selectivity or their *in situ* transformation.

2.4.2. Antioxidant extracts

2.4.2.1. Total polyphenol content (TPC). The Total Polyphenol Content (TPC) also called "Folin–Ciocalteu assay" is a colorimetric assay in food science that aims measuring the total polyphenols without distinguishing the species.[99,104] The result is expressed with a calibration curve of standard like gallic acid ($mg_{GAE}\ g^{-1}_{extract}$ or $mg_{GAE}\ g^{-1}_{dry\ matter}$ or $mg_{GAE}\ L^{-1}$) that is the most common standard. Some papers also refer the use of caffeic acid or catechin as standards.

2.4.2.2. Total flavonoid content (TFC). The Total Flavonoid Content (TFC) is a colorimetric assay in food science that aims measuring the total flavonoids without distinguishing the species.[105,106] The assay is based on the complexation of aluminium ($AlCl_3$) with flavonoids. Two main procedures have been described in the literature[105] The result is expressed *via* the calibration of standard such as catechin, quercetin or rutin for examples.

2.4.2.3. Antioxidant capacity (AOC). Antioxidant Capacity (AOC) assay is a colorimetric assay that aims measuring the level of oxidative species inhibition of a solution or extract. Several tests have been developed such as 2,2-diphenyl-1-picrylhydrazyl (DPPH), ferric ion reducing antioxidant power (FRAP) and/or 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), oxygen radical absorbance capacity (ORAC) assays.[107,108] DPPH results have been reported as percentage of radical inhibition like DPPH (Table 4, entries 3 and 4),[109] half effective concentration EC_{50} (Table 4, entry 5)[110] or inhibition concentration at 50% IC_{50} (Table 4, entry 15).[111] IC_{50} or EC_{50} is the most used expressed result of DPPH with calibration curve of Trolox, an antioxidant specie. The use of Trolox is also reported in literature as Trolox Equivalent Antioxidant Capacity (TEAC) for the different antioxidant capacity assays (DPPH, ABTS, FRAP, ORAC). TEAC can be expressed in $\mu mol_{TE}\ g^{-1}$, $mmol_{TE}\ g^{-1}$, $\mu g_{TE}\ g^{-1}$ or $mg_{TE}\ g^{-1}$, (Table 4, entry 1).[112] Otherwise, another standard such as ascorbic acid equivalent in $mmol_{AAE}\ g^{-1}$ or $\mu mol_{AAE}\ g^{-1}$ is also used (Table 4, entry 6).[113]

2.4.2.4. High performance liquid chromatography (HPLC) – polyphenols. Chlorogenic acids are the main polyphenols in coffee and coffee by-products.[114,115] Chlorogenic acids are composed of hydroxycinnamic acids like caffeic, coumaric or ferulic acids bonded to the –OH function of quinic acid core in position 3, 4 or 5 (Fig. 2).

Hence, chlorogenic acids can be quantified by HPLC-MS or HPLC-DAD (325 nm) in equivalent of one marketed chlorogenic acid, 5-caffeoylquinic acid.[116] Secondary polar metabolites from methylxanthines, flavonoids, and anthocyanins families have been observed in the extracts by HPLC-UV. The major secondary metabolites identified and quantified in coffee extracts are caffeine (methylxanthines) and catechin (flavonoids) at 280 nm and cyanidin-3-rutinoside (anthocyanins) at 520 nm (Fig. 3).[117–119]

2.4.3. Biocrude oil and biochar

2.4.3.1. Higher heating value (HHV). The heating value also called "calorific value" or "heat of combustion" is defined as the energy content of a biomass fuel. This parameter is considered as one of the most important characteristic parameters for designing calculations and numerical simulations of thermal system.[120] The largest heating value (HHV) refers to the heat released from the fuel combustion with the original

Table 4 SCW for coffee and coffee by-products valorization

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
1	Spent coffee grounds	110–190 °C 50 bars 15–75 min 10–70 mL g^{-1} DM	TPC, ABTS, DPPH, HPLC (CGA)	High antioxidant extract	TPC = 88.3 mg_{GAE} $g^{-1}_{extract}$ ABTS = 886.5 μmol_{TE} $g^{-1}_{extract}$ DPPH = 382.8 μmol_{TE} $g^{-1}_{extract}$ (179 °C, 36 min, and 14.1 mL g^{-1}_{SCG})	112
2	Spent coffee grounds	180–240 °C 20–60 bars 10 min 27 mL g^{-1} DM US/MW N_2/CO_2 modifier	TPC, TFC, RSs, proteins, ABTS, DPPH, MIC	High antioxidant hydrolysate	TPC = 33.1–51.2 mg_{GAE} $g^{-1}_{extract}$ TFC = 15.1–25.5 mg_{CE} $g^{-1}_{extract}$ RSs = 8.9–39.9 g_{GLU} per 100 $g_{extract}$ DPPH = 400–500 μmol_{TE} $g^{-1}_{extract}$ ABTS = 400–800 μmol_{TE} $g^{-1}_{extract}$ (220 °C)	131
3	Spent coffee grounds	120 °C 20 min 20 mL g^{-1} DM	TPC, TFC, DPPH, FRAP	High antioxidant extract	TPC = 32.9 mg_{GAE} $g^{-1}_{extract}$ TFC = 8.3 mg_{QE} $g^{-1}_{extract}$ DPPH = 70% inhibition	109
4	Coffee silverskin	120 °C 20 min 20 mL g^{-1} DM	TPC, TFC, DPPH, FRAP	High antioxidant extract	TPC = 19.2 mg_{GAE} $g^{-1}_{extract}$ TFC = 2.7 mg_{QE} $g^{-1}_{extract}$ DPPH = 60% inhibition	109
5	Spent coffee grounds	Sampled 140 °C then 220 °C (one extraction) 30 min 3 g 1 mL min^{-1} 90 min	TPC, TSC, HPLC, DPPH, ROS	Bioactive extract (skin anti-aging)	Yield = 15%/40% ($g_{extract}$ per 100 g_{SCG}) TPC = 19.9/5.7 mg_{GAE} $g^{-1}_{extract}$ TSC = 3.8/28.6 (g_{GLU} per 100 $g_{extract}$) EC_{50} = 20.6/132.2 $\mu g_{extract}$ mL^{-1} (DPPH) (140/220 °C)	110
6	Spent coffee grounds	80–160 °C 35–170 bars 5–20 min 0.5–2.5 g 25–75% EtOH %Flush 20–100 11 mL per cell	TPC, HPLC (CAF, 5-CQA), ABTS, DPPH	Antioxidant extract	TPC = 19–26 mg_{GAE} g^{-1}_{SCG} EC_{50} = 16–38 mg_{AAE} g^{-1}_{SCG} (DPPH) EC_{50} = 10–28 mg_{AAE} g^{-1}_{SCG} (ABTS) CAF = 3.2–9.7 mg g^{-1}_{SCG} 5-CQA = 51–201 mg g^{-1}_{SCG} (195 °C, 0.8 g)	113
7	Spent coffee grounds	60–90 °C 5–30 min 0–16% EtOH 20 mL g^{-1} DM Resin purif	TPC, DPPH, ORAC, HPLC (5-HMF)	Polyphenols + reduction 5-HMF	TPC = 14 mg_{GAE} g^{-1}_{SCG} EC_{50} = 52 μmol_{TE} g^{-1}_{SCG} (DPPH) 5-CQA = 30 µg g^{-1}_{SCG} 5-HMF reduction = 95% (90 °C, 16% ethanol)	175
8	Spent coffee grounds	160–200 °C 10–50 min 5–15 mL g^{-1} DM	TPC, TFC, TAA, DPPH, ABTS, FRAP, HPLC (CGA)	Bioactive extract	TPC = 40.4 mg_{GAE} g^{-1}_{SCG} TFC = 1.87 mg_{QE} g^{-1}_{SCG} EC_{50} = 113 μmol_{TE} g^{-1}_{SCG} (DPPH) EC_{50} = 277 μmol_{TE} g^{-1}_{SCG} (ABTS) FRAP = 69.5 mg Fe(II) g^{-1}_{SCG} TAA = 66.2 mg α-TOC g^{-1}_{SCG} CGA = 2.25 mg g^{-1}_{SCG} (200 °C, 15 mL g^{-1}_{SCG}, 50 min)	150
9	Coffee silverskin	25–80 °C (H_2O, 0.1 M HCl, 0.1 M NaOH) – 50 mL g^{-1} DM 180–270 °C 10–53 bars 17–42 min 50 mL g^{-1} DM	HPLC (CAF, 5-CQA, 5-HMF), TSC, RSs, proteins, TPC, DPPH, H-ORAC	High antioxidant extract	Yield = 16/19/29/23% ($g_{extract}$ per 100 g_{CSS}) (25/80/210/270 °C) Yield = 28/44% ($g_{extract}$ per 100 g_{CSS}) (80 °C + 0.1 M HCl/80 °C + 0.1 NaOH) TPC = 36 mg_{GAE} $g^{-1}_{extract}$ (Best TPC, 210 °C) H-ORAC = 262.9 μmol_{TE} $g^{-1}_{extract}$ DPPH = 379.0 μmol_{TE} $g^{-1}_{extract}$ TPC = 28 mg_{GAE} $g^{-1}_{extract}$ (Best AOC, 270 °C) 5-CQA = 9.0 mg $g^{-1}_{extract}$ (Best CQA, 80 °C)	151

Table 4 *(Contd.)*

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
10	Green coffee bean	180–220 °C 30–60 bars 10 min 25 mL g^{-1} DM 5 types of coffee	TPC, TFC, HPLC (CAF, CGA), ABTS, DPPH, MRPs, MIC	Bioactive molecules	TPC = 120.4–144.4 mg_{GAE} g^{-1}_{GCB} TFC = 15–43 mg_{CE} g^{-1}_{GCB} DPPH = 80–88% inhibition CAF = 1.04–2.52 g per 100 g_{GCB} CGA = 46–70 mg g^{-1}_{GCB} (180 °C)	158
11	Green coffee bean	50–300 °C 10–100 bars 20–60 min 1 g min^{-1} 0.8 g	HPLC/UV (CAF, CQA), UPLC/MS (CQA), DPPH, TPC,	Bioactive molecules (degradation 3-CQA)	TPC = 6.7 mg_{GAE} g^{-1}_{GCB} (157 °C, 23 bars, 60 min) DPPH = 73.7 μmol_{TE} g^{-1}_{GCB} (160 °C, 21 bars, 59 min CQAs = 54 mg g^{-1}_{GCB} (212 °C, 20 bars, 55 min)	147
12	Spent coffee grounds	150–220 °C 70 bars 30 min 70 g 10 mL min^{-1}	TPC, TSC, HPLC, DPPH, MIC	Antioxidant extract + carbohydrates	Yield = 55.6% ($g_{extract}$ per 100 g_{SCG}) TPC = 70.3 mg_{GAE} $g^{-1}_{extract}$ TSC = 33.7 g_{GLU} per 100 g_{SCG} EC_{50} = 1.99 $mg_{extract}$ $mg^{-1}_{extract}$ (DPPH) CGA = 0.7–1.5 mg g^{-1}_{SCG} (200 °C)	133
13	Green coffee residues	150–250 °C 225–300 bars 36 min (sample every 2 min) 5 g 10 mL min^{-1} Coffee powder Defatted cake	TPC, TSC, RSs, HPLC (carbohydrates, 5-HMF, furfural)	Polyphenols + polysaccharides	TPC = 26.6 mg_{GAE} g^{-1}_{GCB} (Powder, 200 °C, 22.5 MPa) TSC = 9.0 g_{GLU} per 100 $g_{extract}$ RSs = 6.3 g_{GLU} per 100 $g_{extract}$ (Powder, 150 °C, 30 MPa) TPC = 55.3 mg_{GAE} g^{-1}_{GCB} TSC = 17.2 g_{GLU} per 100 g_{GCB} RSs = 8.8 g_{GLU} per 100 g_{GCB} (Defatted, 175 °C)	176
14	Spent coffee grounds	150–210 °C 20–60 bars 5–15 min 27 mL g^{-1} DM US/MW/SC-CO_2 pretreatment	TPC, TSC, RSs, FT-IR, TGA, SEM, DPPH, ABTS, HPLC (monosaccharides)	Bioactive polysaccharides	Yield = 18% ($g_{extract}$ per 100 g_{SCG}) TPC = 2.2 mg_{GAE} $g^{-1}_{extract}$ TSC = 47.7 g_{GLU} per 100 $g_{extract}$ RSs = 18.8 g_{GLU} per 100 $g_{extract}$ (180 °C, 20 bars, 5 min)	130
15	Spent coffee grounds	160–200 °C 10–50 min 5–15 mL g^{-1} DM	TSC, TPC, RSs, TAA, DPPH, ABTS, FRAP, HPLC, XRD, FT-IR	Bioactive polysaccharides	Yield = 35.9% ($g_{extract}$ per 100 g_{SCG}) TPC = 234 mg_{GAE} $g^{-1}_{extract}$ TSC = 29,3 g_{GLU} per 100 $g_{extract}$ RSs = 9.4 g_{GLU} per 100 $g_{extract}$ EC_{50} = 516 μmol_{TE} $g^{-1}_{extract}$ (DPPH) (160 °C, 15 mL g^{-1}_{SCG}, 10 min)	111
16	Spent coffee grounds	100–180 °C 15–75 min 100–140 mg H_2SO_4 g^{-1} 10–14 mL g^{-1} DM	HPLC	Bioactive polysaccharides	Hydrolysis conversion: Galactan = 100% Mannan = 77.4% Arabinan = 89.5% Hemicellulose = 87.4%	177
17	Green coffee bean	130–170 °C 40–90 min 7–23 mL g^{-1} DM 0–30% EtOH	HPLC (CGA)	Chlorogenic acids	CGA = 50 mg g^{-1}_{GCB} (160 °C, 40 min, 0% eth, 14 mL g^{-1}_{GCB})	178
18	Coffee pulp	65–155 °C 103 bars 15 min	HPLC	Anthocyanin (C-3-R cyanidin-3-rutinoside)	C-3-R = 3 mg g^{-1}_{CP} (120 °C)	159

Table 4 *(Contd.)*

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
19	Spent coffee grounds	200–300 °C	GC-MS, FT-IR, elemental composition, HHV	Bio-crude oil	Yield = 47.3% ($g_{bio\text{-}oil}$ per 100 g_{SCG})	167
		5–25 min 5–20 mL g^{-1} DM N_2 (5–20 bars)			$E_{recovery}$ = 72.6% HHV = 31.0/20.2 MJ kg^{-1} (biocrude oil/biochar) (275 °C, 10 min, 20 mL $g^{-1}{}_{SCG}$)	
20	Spent coffee grounds	225–325 °C	GC-MS, GPC, TGA, viscosity, elemental composition, HHV	Bio-crude oil	Yield → +20% SCG + CS	179
		50–100 bars 10 min 5 mL g^{-1} DM 5% NaOH Co-liquefaction (PF or CS or WPB)			(250 °C, 5% NaOH) HHV = 40.4/31.9/29.5 MJ kg^{-1} Yield = 20.0/25.0/29.5% ($g_{bio\text{-}oil}$ per 100 g_{SCG}) (SCG/SCG + 5% NaOH/mix SCG-CS 1–1 + 5% NaOH)	
21	Spent coffee grounds	180–330 °C	Elemental composition, HHV, FT-IR	Bio-char	$E_{recovery} \simeq$ 95/90/60%	168
		60 min 1 mL g^{-1} DM			HHV = 26.5/27.5/31.3 MJ kg^{-1} (Biocrude oil, 210/240/330 °C)	
22	Coffee husk	150–225 °C	N_2 isotherms, elemental composition, SEM, FT-IR, TGA, pH_{ZPC}, MB adsorption	Hydrochar	S_{BET} = 31.3 m^2 $g^{-1}{}_{hydrochar}$	180
		20–300 min 1–4 mL g^{-1} DM			Methylene blue adorption = 34.9 mg $g^{-1}{}_{hydrochar}$ (210 °C, 243 min, 3.41 mL $g^{-1}{}_{CH}$)	
23	Spent coffee grounds	120–240 °C	(RSM), TGA, CO_2 adsorption	Precursors of activated carbons	CO_2 captured = 2.95%	181
		180–720 min 2–5 mL g^{-1} DM H_2O_2 adding			(180 °C–12 h)	
24	Spent coffee grounds	163 °C	TSC, HPLC, GC (major and minor volatiles)	1^{rst} step: extraction for spirit (drink)	TSC = 3.4 g_{GLU} L^{-1}	182
		45 min 10 mL g^{-1} DM				
25	Spent coffee grounds	160–200 °C	HPLC-RI, TGA	Production of levulinic and formic acid (LA and FA)	Yield (w/w)	183
		180 min 8.3–16.7 mL g^{-1} DM H_2O			LA = 47% FA = 29% (180 °C, 8.3 mL $g^{-1}{}_{SCG}$, 3 h)	

and generated water in a condensed state.[120] HHV is usually expressed in MJ kg^{-1}.

2.4.3.2. Energy yield recovery. The energy yield recovery is defined as the yield of remaining energy after the transformation of the raw material into a biocrude oil or biochar (eqn (2)). This result is as much important as the HHV of the final product.

$$\text{Energy yield recovery} = \frac{\text{HHV fuel} \times \text{fuel mass}}{\text{HHV raw material} \times \text{raw material mass}} \times 100 \quad (2)$$

2.4.4. Lipid extracts

2.4.4.1. Yield of extraction (relative and absolute). The yield of extraction is defined by two different expressions: relative and absolute yields (eqn (3) and (4)).

$$\text{Relative yield} = \frac{\text{oil mass extracted by SC-CO}_2}{\text{oil mass extracted by hexane Soxhlet}} \times 100 \quad (3)$$

$$\text{Absolute yield} = \frac{\text{oil mass extracted by SC-CO}_2}{\text{raw material mass}} \times 100 \quad (4)$$

In the studied literature, SC-CO_2 is considered as an apolar solvent, able to remove exclusively apolar solute *i.e.* the lipidic fraction composed mainly of triglycerides. Hence, for relative yield, the yield of extraction of SC-CO_2 is compared to the yield obtained by hexane with Soxhlet system, considering as a reference method for lipid extraction.[121] The relative yield presents the huge advantage of evaluating and comparing properly the operating conditions of SC-CO_2 described in the literature about same biomass, and this despite the difference of chemical composition.

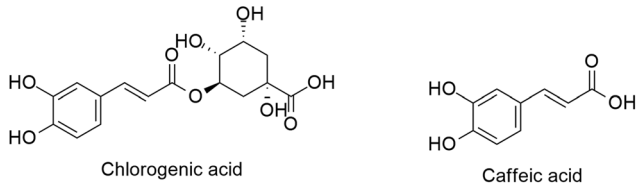

Fig. 2 Main polyphenols in coffee and coffee by-products.

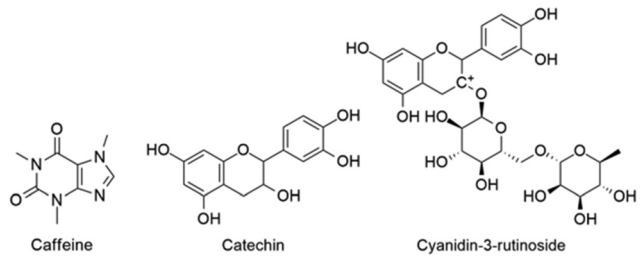

Fig. 3 Main secondary metabolites in coffee and coffee by-products.

The absolute yield remains an interesting measurement to define the quantitative amount of lipid fraction in biomass by hexane Soxhlet extraction or SC-CO_2 extraction. Absolute yield can also be used to compare operation conditions within the same study.

2.4.4.2. Fatty acid composition (FAC). Oleaginous are plant materials including seeds or fruits rich in fats. Those vegetable fats are mainly composed of triglycerides, also called triacylglycerols, which are esters of glycerol bonded to fatty acids. Triglycerides of green coffee beans and spent coffee grounds represent by themselves 75% of the total fats.[122] Fatty acids in spent coffee grounds and green coffee beans have been reported to be mainly palmitic (C16:0) and linoleic (C18:2) acids, followed by stearic (C18:0) and oleic (C18:1) acids (Fig. 4).[122]

The nature and profile of those fatty acids in triglycerides can be determined by Gas Chromatography – Flame Ionization Detector (GC-FID). More precisely, only fatty acid methyl esters (FAME) obtained by transesterification or methanolysis of triglycerides with MeOH and an acid catalyst (HCl, H_2SO_4) are analyzed.[123,124]

2.4.4.3. Terpenoids, sterols and tocopherols. Coming mainly from plant kingdom, the bioactive terpenes and terpenoids are

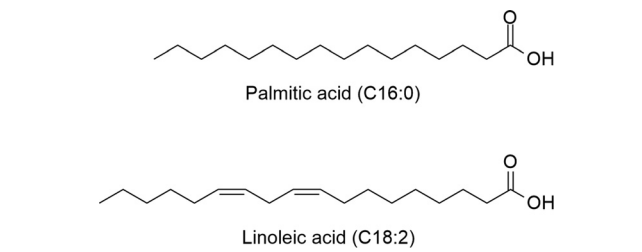

Fig. 4 Main fatty acids pattern of triglycerides in coffee and coffee by-products.

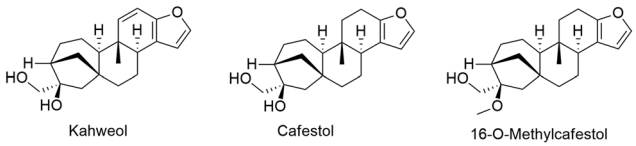

Fig. 5 Main terpenoids in coffee and coffee by-products.

the most important constituents of essential oils. Terpenes are naturally occurring as hydrocarbon based on combinations of the isoprene units. Terpenoids are terpenes that have been denaturated by oxidation, including oxygen functions. Main terpenoids of coffee reported in literature are: kahweol, cafestol, 16-*O*-methylcafestol (Fig. 5).[122]

Phytosterols also called "natural" sterols are a family of sterols found in the fat fraction of plant kingdom. Sterols are lipid molecules composed of a sterane core, with hydroxyl function linked to the third carbon. Main sterols of coffee reported in literature are: campesterol, stigmasterol and β-sitosterol (Fig. 6).[122]

Vitamin E is a vitamin that regroups four forms of tocopherol and four forms of tocotrienol. Tocopherols are lipophilic antioxidant molecules present in abundance in vegetable oils. Tocopherols are composed of chromanol core bonded to a lateral chain of sixteen saturated carbons. Main tocopherols of coffee reported in literature are: α- and β-tocopherol (Fig. 7).[122]

In natural material, terpenes, terpenoids, sterols and tocopherols can be found conjugated to fatty acid or acyl derivatives as esters.[125] Hence, saponification has to be performed before further HPLC-UV or HPLC-DAD analysis.[125]

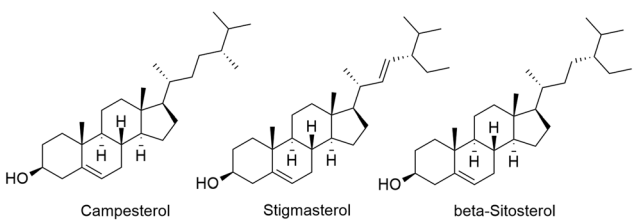

Fig. 6 Main sterols in coffee and coffee by-products.

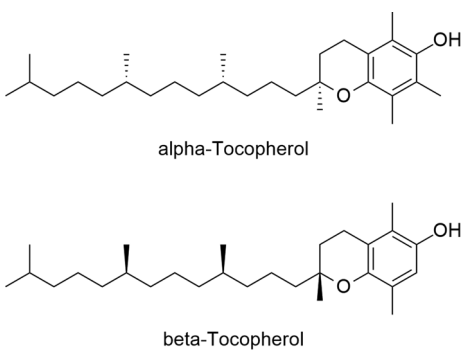

Fig. 7 Main tocopherols in coffee and coffee by-products.

The analysis of terpenoids, sterols and tocopherols in coffee oil is of high order to evaluate oil bioactivity. Indeed, terpenoids have demonstrated antihypertensive, anticancer (Taxol), antifungal and antimicrobial properties.[97,126] This results are reported by more than 2000 patents between 1980–2003 for terpenoids applied in pharmaceutic and cosmetic field.[127]

Strong rates of LDL-cholesterol are responsible for clogging the coronary arteries, leading to cardiovascular disease. Phytosterols have been demonstrated to lowering by 5 to 15% concentration of LDL-cholesterol in human body, resulting in applications in pharmaceutic, cosmetic and nutraceutic fields.[128]

Tocopherols are responsible for protecting membranes against lipids peroxidation, which could slow the aging process in humans or animals.[129] Moreover, tocopherols also exhibit photoprotective properties in cosmetic cream, usefulness to treat Parkinson disease and eye disease or prevent negative effects of ischemia-reperfusion.

3. Pressurized fluids applied to coffee and coffee by-products

This section discusses the different results reported in the literature during the last decades and focused on coffee and coffee by-products valorization using subcritical H_2O and supercritical CO_2. It also highlights the new and future trends and applications of pressurized fluids in this field of research.

3.1. Subcritical water (SCW)

Table 4 reports examples involving the use of SCW for coffee or coffee by-products valorization. The roasted coffee valorization by SCW to prepare coffee beverage, widely investigated at the end of the XXth century,[21,26] has not been reported in this Table 4.

Most of the studies dedicated to the use of subcritical H_2O for coffee and coffee by-products valorization described in the literature report the use of spent coffee grounds as raw material, in 70% of reported cases.

Table 4 shows the wide diversity of compounds that are obtained using SCW for coffee and coffee waste valorization. They can be classified into three groups depending on what they will be intended for: (i) carbohydrate extracts; (ii) antioxidant extracts and (iii) biocrude oils and biochars.

3.1.1. Carbohydrate valorization. Extraction of carbohydrates with subcritical H_2O has been widely investigated. For spent coffee grounds (SCG), Chun *et al.* have reported best Total Sugar Content (TSC) results of 47.7 g_{GLU} per 100 $g_{extract}$ after an ultrasonic pretreatment (20 kHz, 750 W output power), for 5 min of extraction at 180 °C and 20 bars (Table 4, entry 14).[130] Those results can be explained by benefits of hydrothermal extraction combined with ultrasonic pretreatment used. In fact, authors suggest that ultrasonic pretreatment (20 kHz, 750 W output power) facilitates the extraction of carbohydrates by increasing mass transfer from SCG to solvent media. In addition, the pretreatment avoids the use of extreme conditions, responsible of degradation products.

Chun *et al.* have reported the use of modifiers such as CO_2 and N_2 with subcritical H_2O for the extraction of carbohydrates (Table 4, entry 2).[131] Maximal RSs (37.91 g per 100 $g_{extract}$) have been observed at 220 °C with N_2. The authors have proposed that the presence of nitrogen in SCW extraction can act as a shield against the reaction with atmosphere. At contrary, at the same 220 °C temperature, subcritical H_2O with CO_2 has resulted in lower RSs. For the authors, the onset of the formation of reducing sugars required a lower residence times due to the faster cleavage of glycosidic bonds due to carbonic acid formation of CO_2 in water. Then, the CO_2/H_2O technology is gaining interest in the field of biomass valorization to improve lignocellulosic fractionation.[132]

Simões and Paiva *et al.* have also reported a semi-continuous extraction (10 mL min^{-1}) during 180 min with a low total sugar content around 3g_{GLU} per 100 g_{SCG} at 150 °C and 30 g_{GLU} per 100 g_{SCG} at 200 °C (Table 4, entry 12).[133] They have shown that SCG has low soluble amount of sugars due to the coffee brewing process. Simões and Paiva *et al.* have suggested that subcritical H_2O at 200 °C acts as reagent performing the depolymerization of lignocellulosic matrix leading to the release of structural carbohydrates. Furthermore, their researches have proved that monosaccharides represent less than 5% of the total carbohydrates, concluding that subcritical H_2O has hydrolyzed the polysaccharides into oligomers, rather than to monomers. However, another hypothesis could be that a larger amount of monosaccharides has been produced and degraded at the same time. Indeed, the main products of degradation of hexoses in subcritical H_2O have been demonstrated to be 5-hydroxymethyl-2-furaldehyde (5-HMF) and furfural (Fig. 8).[134,135]

However, the self-ionization of H_2O into H_3O^+ and HO^- in subcritical H_2O (pH = 5.5 at 250 °C, pH = 7 at 25 °C) is essential to act as catalyst for hydrolysis of hemicellulose and cellulose into monosaccharides.[140] Forster-Carneiro *et al.* has reported that the dielectric constant, the viscosity and the surface tension have been reported to decrease for water above

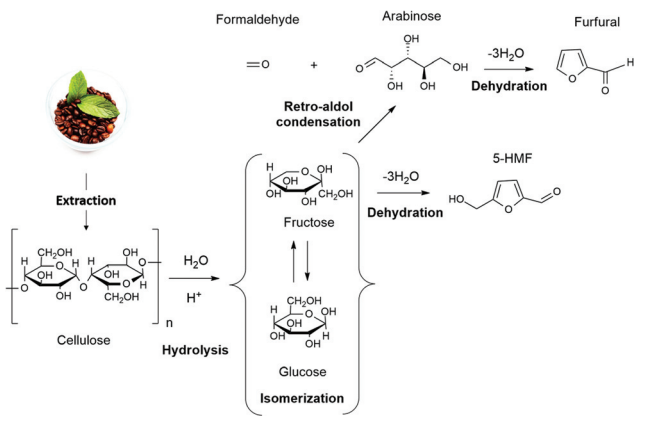

Fig. 8 Extraction and degradation mechanism of cellulose in subcritical H_2O adapted from Banerjee and Goud *et al.*, Aida *et al.*, Lü *et al.*[134,136,137]

100 °C.[138] King *et al.* have observed that the diffusion rate increase under these conditions.[139] In addition, they also have noted that glucose solubility is five-fold times higher in water at 180 °C compared to 100 °C.[139]

Mussatto *et al.* have reported the influence of subcritical H_2O on the distribution of monosaccharides pattern in extracts (Table 4, entry 15).[111] They have found that in every extracts, galactose was the main monosaccharide and arabinose the less representative. Authors have suggested that galactomannan and arabinogalactan are initially present in the SCG. Mussatto *et al.* have also reported the temperature influence on the sugar composition with 48%/32%/10%/10% (160 °C, 30 min) and 47%/17%/28%/8% (180 °C, 30 min) of galactose/mannose/glucose/arabinose in the extracts. The main difference of composition between mannose and glucose has not been explained by the authors. To the best of our knowledge, four hypotheses can be proposed to explain these results obtained at 180 °C: (i) the hydrolysis on cellulose or hemicellulose containing glucose pattern that could be more selective, (ii) the kinetic of the degradation that may be faster for mannose than for glucose, (iii) the isomerization reaction of monosaccharides that may occur; (iv) hypotheses (i), (ii) and (iii) can occur simultaneously. Even if the kinetic of hydrolysis of cellulose has been investigated,[141] no publication reported in the literature can support the hypothesis (i), since no publication reports the comparison of kinetic hydrolysis between galactan, mannan, arabinan and glucan or heteropolymers.[135] In addition, kinetics of polysaccharides hydrolysis have been observed to be different depending on the degree of polymerization.[142] The hypothesis (ii) is documented by the literature demonstrating the difference of kinetic degradation of several monosaccharides such as glucose, galactose and mannose.[135] However, similar rates of degradation for glucose and mannose have been reported at 220 °C.[135] The hypothesis (iii) has been supported by literature. Monosaccharides under subcritical ethanol/water and under SCW lead to an epimerization of glucose/mannose.[134,143]

Subcritical H_2O extractions have been compared to traditional chemical extraction such as alkaline treatment.[144] Mussatto *et al.* have used an alkaline treatment of 4 M NaOH at 25 °C overnight and have obtained interesting TSC results of 39.0 g_{GLU} per 100 $g_{extract}$.[144] The authors have specified that the extraction parameters have not been optimized. Despite significant results (i) the yields are lower than the best result obtained under subcritical H_2O (47.7 g_{GLU} per 100 g) with pretreatment and (ii) the use of NaOH generates a significant amount of salts that makes difficult the valorization of polyphenols after carbohydrates precipitation.

Based on the studies reported in Table 4, supplementary knowledge is required since the system looks like a black box where only the final results are considered. Several phenomena are known to operate at the same time without knowing the specific influence of (i) solubilization at high temperature of soluble carbohydrate in subcritical H_2O without hydrolysis, (ii) hydrolysis of polysaccharides into oligosaccharides, then into monosaccharide, (iii) chemical reactions such as dehydration due to acid subcritical H_2O that act as reagent and (iv) chemical reactions such as decarboxylation due to thermal degradation.

To conclude, the subcritical H_2O appears to be the most suitable, efficient and competitive solution to perform hydrolysis and extraction of carbohydrates from coffee and coffee by-products with high yields and low environmental impact.

3.1.2. Polyphenols valorization

3.1.2.1. Extraction of the main polyphenols. Extraction of polyphenols with subcritical H_2O has been investigated (Table 4, entries 1, 5–12 and 17). Chlorogenic acids (Fig. 2) constitute the most important family of polyphenols, mostly responsible of Total Polyphenol Content (TPC) and AntiOxidant Capacity (AOC) values. Among them, *n*-caffeoylquinic acids (CQA) represent the most studied molecules in coffee and coffee by-products extraction.[145] Clifford fully have investigated chlorogenic acids, a family of molecules composed of a quinic acid core, acylated with one or more caffeoyl groups.[115] Chlorogenic acids such as CQA and di-CQA are predominant, these two compounds are about 120 times more concentrated (43.52 mg g^{-1}) than free caffeic acid in spent coffee grounds extract (0.36 mg g^{-1}).[146]

Simões and Paiva *et al.* have reported a subcritical H_2O semi-continuous extraction of polyphenols (Table 4, entry 12).[133] At 200 and 220 °C, they have recovered more polyphenols in comparison to classical hydroalcoholic extraction as reference method. According to the authors, this improvement may be explained by (i) the release of phenolic compounds entrapped within the SCG matrix and (ii) the potential degradation of lignin into phenolic compounds.

Gao *et al.* have reported that an increase of the temperature leads to an enhancement of the diffusion coefficient of solvent, solubility of solutes, diffusion rate of analytes, and a reduction of solvent viscosity and surface tension.[112] They have also pointed out from literature that the dielectric constant close to methanol may enhance the solubility of phenolic compounds. However, the concentration of *n*-CQA (3, 4 and 5-CQA) drops significantly above 190 °C since high temperature can promote the degradation of phenolic compounds. Indeed, longer extraction at high temperature favors oxidation and degradation of phenolics. The degradation products of *n*-CQA have not been analyzed in this work. This information is crucial, even more since the ratio *n*-CQA/TPC is way lower above 190 °C (*n*-CQA/TPC = 0.070–0.095 at 110–170 °C, *n*-CQA/TPC = 0.038 at 190 °C). This suggests that above 190 °C, another source of polyphenols than *n*-CaffeoylQuinic Acid (*n*-CQA) impacts the result of the Total Polyphenol Content (TPC) and AntiOxidant Capacity (AOC) of the spent coffee grounds (SCG) extract.

Literature about fundamental research has been investigated to understand polyphenols behavior including *n*-CQA and role of degradation products as new antioxidants in subcritical H_2O. Sato *et al.* have reported the hydrolysis phenomenon of 3-caffeoylquinic acid into caffeic acid and quinic acid.[147] Khuwijitjaru *et al.* have highlighted that caffeic acid has a higher antioxidant capacity (2.37 g_{AAEAC} $g^{-1}_{caffeic\ acid}$)

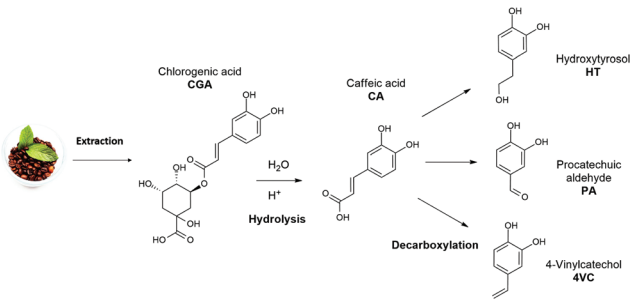

Fig. 9 Extraction and degradation mechanism of chlorogenic acid and caffeic acid in subcritical H_2O adapted from Khuwijitjaru *et al.*[149]

than chlorogenic acid (1.39 g_{AAEAC} $g^{-1}_{chlorogenic\ acid}$).[148] Unfortunately, they also have shown that degradation kinetic is faster for caffeic acid than chlorogenic acid. The products resulting from caffeic acid degradation in subcritical water have also been studied (Fig. 9).[149]

Chun *et al.* (220 °C, 10 min) and Mussatto *et al.* (200 °C, 50 min) have reported different temperature with different time of extraction under optimal conditions for polyphenols recovery. This suggests that the combination temperature/time of extraction is one of the most important factor to take into account.[131,150]

Inouye *et al.* have reported the use of subcritical H_2O for the production of antioxidant extract from coffee silverskin (CSS, Table 4, entry 9).[151] They have observed a larger amount of 5-CQA at 80 °C (1.7 mg $g^{-1}_{extract}$) than at 180 °C (1.5 mg $g^{-1}_{extract}$) and even their absence at 210 °C (not detected) after 10 min. However, TPC have been reported to inversely increase from 180 °C (22 mg $g^{-1}_{extract}$) to 210 °C (36 mg $g^{-1}_{extract}$), contradicting the conclusion with SCG. The authors have supported the hypothesis that hydrolysis or degradation of lignin and lignan generate smaller and soluble phenolic compounds, without further investigations.

Sato *et al.* have investigated the subcritical H_2O semi-continuous extraction from green coffee beans at 1 g min^{-1} during 20–60 min (Table 4, entry 11).[147] They have reported three different ranges of temperature of extraction: (i) 70 to 140 °C with elevation of Antioxidant Capacity (AOC), (ii) 140 to 200 °C with reduction of AOC and (iii) 200 to 300 °C with significant raise of AOC. The authors have described that the structural distribution of CaffeoylQuinic Acid (CQA) in natural plants is typically composed of oligomeric structures like glycosides. Hence, in first range (70–140 °C) recover of CQA requires lignocellulose hydrolysis that is enhanced by increasing temperature. For the second range (140–200 °C), AntiOxidant Capacity (AOC) and CaffeoylQuinic Acid (CQA) have been reported to decrease simultaneously. The authors have reported that the increase of the temperature leads to the water density decrease and its ionic product increase. Then, the solvation structure and protonation of CaffeoylQuinic Acid (CQA) might be more sensitive resulting in CQA degradation by hydrolysis. Finally, for the third range, AntiOxidant Capacity (AOC) and melanoidins index have been observed to rise simultaneously. Coffee melanoidins have been reported in literature to exhibit antioxidant activity.[152,153] Farah *et al.* have studied the contribution of high molecular weight melanoidins, which is up to 36% of the total Trolox Equivalent Antioxidant Capacity (TEAC) in coffee brews. Moreover, the authors have pointed out that chlorogenic acids are up to 39% covalently bounded to melanoidins (220 °C, 15 min), which can be partially responsible of the antioxidant activity of melanoidins.[153]

Coimbra *et al.* have shown that during roasting process the polysaccharides depolymerize then repolymerize, forming new polymers through non-enzymatic transglycosylation reactions with phenolic compounds (Fig. 10).[154] In addition, for non-roasted material such as algae biomass, Herrero *et al.* have suggested that Maillard, caramelization and thermoxidation reactions affect the overall antioxidant capacity of subcritical H_2O extracts depending on the nature of the sample.[155]

3.1.2.2. Extraction of secondary antioxidant metabolites. Caffeine, with its antioxidant properties,[156] is the only molecule from the methylxanthines that is present in large amount in coffee and coffee by-products (Fig. 3). Inouye *et al.* have reported the extraction of caffeine in coffee silverskin with subcritical H_2O (Table 4, entry 9).[151] Caffeine concentration with water extraction at high temperature (270 °C, $23\%_{yield}$, 4.1 mg $g^{-1}_{extract}$) has been proven to be as efficient than ambient water extraction (25 °C, $16\%_{yield}$, 4.1 mg $g^{-1}_{extract}$), showing the high thermal and chemical stability of caffeine.[151,157]

Sato *et al.* have reported the subcritical H_2O extraction of caffeine in green coffee beans (Table 4, entry 11).[147] Caffeine concentration for extraction that have been performed at 280 °C (60 mg g^{-1}_{GCB}) are more efficient than at 230 °C (18 mg g^{-1}_{GCB}). The authors have also proposed that higher yield can be correlated to better hydrolysis of cellulosic walls at higher temperature, thus, the trapped caffeine inside the matrix being released. However, these results have to be interpreted carefully since the 60 mg g^{-1}_{GCB} (6% w/w) reported by Sato *et al.* exceeds the caffeine content value in coffee generally reported in the literature.

Chun *et al.* have reported results of Total Flavonoid Content (TFC) and catechin, the main flavonoid in coffee and coffee by-products during the extraction of green coffee beans (Table 4, entry 10).[158] The authors have obtained better results at 180 °C

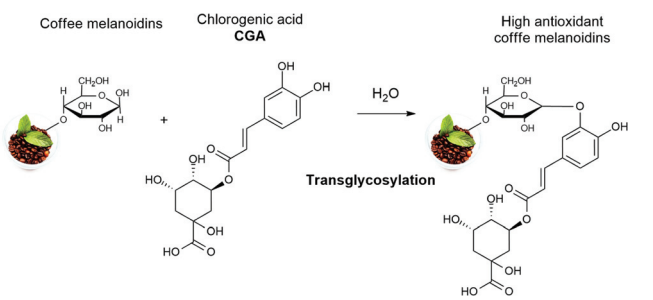

Fig. 10 Formation of new antioxidant compounds through transglycosylation of melanoidins with phenolic compounds during roasting step adapted from Coimbra *et al.*[154]

(43 mg g^{-1}_{GCB}) than 220 °C (15 mg g^{-1}_{GCB}). They have proposed the hypothesis that phenolic compounds and flavonoids have been decomposed in very hot water, with a slower rate of decomposition for flavonoids.

Punbusayakul *et al.* have investigated anthocyanins extraction (15 min, 65–155 °C) from coffee pulp by subcritical water acidified with 7% v/v acetic acid (Table 4, entry 18).[159] Major anthocyanin in coffee pulp is the cyanidin-3-rutinoside (C-3-R, Fig. 3). The authors have ascribed that to the dielectric constant of subcritical water at 120 °C close to those of methanol and ethanol. In addition, it has been reported that anthocyanins have high solubility in methanol. The authors have also suggested that temperature higher than 120 °C can lead to degradation of the C-3-R linkage.

3.1.2.3. Use of non-conventional methods and solvents. The subcritical H_2O has been demonstrated to be an eco-compatible solvent of extraction for biomass valorization. Hence, polyphenols extraction has been compared from subcritical H_2O, non-conventional (ultrasound (US), microwave (MW), Deep Eutectic Solvent (DES), ...) and traditional methods of extraction to evaluate the competitiveness of subcritical H_2O. The following results have to be interpreted with cautious since the raw material of each publication is different and the corresponding conclusions can be slightly biased.

For Ultrasound Assisted Extraction (UAE), Ponmurugan *et al.* have performed ethanol extraction under different conditions of temperature (30–50 °C), time (5–45 min), liquid/solid ratio (5–30 mL g^{-1}) and ultrasonic power output (100–300 W) with TPC range of 32.81–36.23 mg_{GAE} g^{-1}_{SCG}.[160] The reported results are higher than traditional one, but no blank under silent conditions has been carried out. Hence, the authors have suggested that during ultrasonic irradiation from 100 to 250 W, the SCG cell is exposed to shock waves and liquid jets, resulting in higher yield. In any case, reported results are still considered as lower than the one of subcritical H_2O. However, UAE can be implemented as pre- or post-treatment of subcritical H_2O extraction of coffee and coffee by-products, as reported by Chun *et al.* and Arauzo *et al.*[130,161]

For Microwave Assisted Extraction (MAE), Casazza *et al.* have conducted hydroalcoholic (EtOH 54% v/v) extraction under different conditions of temperature (120, 135 and 150 °C) and heating time (1, 10 and 20 min).[162] Highest extraction yield of polyphenols (3.9 mg_{CAE} $mL^{-1}_{extract}$) have been reported at 150 °C for 10 min. Those results are two times higher than the blank (room temperature, 24 h) with hydroalcoholic (EtOH 54% v/v, 2.0 mg_{CAE} g^{-1}), water (1.4 mg_{CAE} g^{-1}) or ethanol (0.67 mg_{CAE} g^{-1}), despite differences of experimental conditions. The authors have suggested that more intense microwave irradiation power promotes a faster heating with (i) more intense wall-cell rupture and (ii) faster analytes release.

For Deep Eutectic Solvents (DES), Lee *et al.* have tested 13 choline-chloride based DES.[163] In similar experimental conditions (room temperature, 45 min, UAE), the HeCh DES (15 mg_{GAE} g^{-1}_{SCG}) has showed better TPC results than hydroalcoholic solution (EtOH 20% v/v, 9 mg_{GAE} g^{-1}_{SCG}) and water (6 mg_{GAE} g^{-1}_{SCG}) used as reference. The authors have observed that the nature of DES is a significant parameter for polyphenols extraction. But no explanation has been proposed to justify the better results observed with HeCh. The authors have also pointed out the necessity to perform an extra-step with elution column to separate polyphenols up to 79% from DES.

Globally, subcritical H_2O has offered higher results for polyphenols recovery than other physical assisted methods of extraction. However, the comparison is limited since no reference extraction method has been defined yet. The subcritical H_2O is the greenest and most competitive solvent reported for the polyphenols extraction of coffee and coffee by-products.

3.1.3. Biocrude oil and biochar production. Biomass can be converted into energy *via* the production of bio-oil or biocrude oil, a liquid fuel that could replace petroleum. Biocrude oil is obtained *via* two main methods described in the literature, which are, fast or flash pyrolysis and hydrothermal liquefaction (HTL). Pyrolysis pathway consists in a thermal decomposition without oxygen. Conventional pyrolysis is performed from 280 to 680 °C at 0.1–1 °C min^{-1}. Rapid pyrolysis is performed from 580 to 980 °C at a 10–200 °C min^{-1} increase of temperature. Flash pyrolysis is performed from 780 to 1030 °C with ramp >1000 °C min^{-1}.[164] Flash pyrolysis is the most common method employed at industrial scale. The HTL pathway consists in a reaction between biomass and water at temperatures over 100 °C.[165] Hydrochar can be used as solid fuel because of both its higher HHV and lower volatile matter/ashes ratio than those of raw material.[166]

Hydrothermal liquefaction (HTL) is the most suitable method for wet biomass. For this reason, spent coffee grounds with its high moisture content has been studied for the production of biocrude oil and biochar.

Xu and He *et al.* have investigated the influence of retention time (5–25 min), reaction temperature (200–300 °C), water/feedstock mass ratio (5–20 mL g^{-1}) and pressure (5–20 bars) during the HTL of spent coffee grounds (Table 4, entry 19).[167] Under optimal conditions, the HHV has been significantly increased from the raw material (20.2 MJ kg^{-1}) to biocrude oil (31.0 MJ kg^{-1}). To obtained higher yields, a shorter time (10 min) is preferable to a longer time (30 min) under the experimental conditions described (300 °C, 5 mL g^{-1}).[167] Xu and He *et al.* have explained that a longer time generates smaller and lighter products and gases. In addition, solid residues have shown a slight increase after 30 min that might be caused by the repolymerization of biocrude oil into biochars, reducing then the biocrude oil yield.

In addition, the yield of biocrude oil continuously raises with feedstock/water mass ratio (35.29% for 5 mL g^{-1}, 47.28% for 20 mL g^{-1}).[167] The authors explained that the lower yields obtained with a lower biomass/solvent ratio are the result of insufficient mixing of reagents. More specifically, these conditions have led to unfavorable heat/mass transfer conditions and to slow down the liquefaction and solvolysis processes, generating less biocrude oil and more solid residues.

Park *et al.* have characterized a biochar formed during the hydrothermal carbonization (HTC) at different temperatures (180–330 °C).[168] The calorific value of raw material (21.8 MJ kg^{-1}) continuously increases with the temperature from 180 °C (22.9 MJ kg^{-1}) to 330 °C (31.3 MJ kg^{-1}). At contrary, the biochar product yield continuously decreases by increasing the temperature. The authors explained these results by the dehydration and decarboxylation reactions leading to CO_2 releases. Hence, the optimal energy yield recovery (ERE) is obtained at a temperature between 210 °C (94%) and 240 °C (90%).

No author has experimentally compared inside the same paper the differences between pyrolysis and hydrothermal processes with the same coffee by-product. Hence, Choi *et al.* have reported the interesting results with an oil yield of 54.85% obtained after a spent coffee grounds pyrolysis.[169] Unfortunately, due to high moisture content (50–60% w/w) of spent coffee grounds, a pre-drying step is required to perform the pyrolysis, leading to an important energy consumption limiting the economic viability of the overall process.

As a global conclusion, subcritical H_2O can act as super solvent, reagent and catalyst able to solubilize, hydrolyze and decarboxylate molecular matrix allowing recovering a wide range of molecules such as low weight carbohydrates and high value polyphenols. Hence, the green subcritical H_2O can cover almost all the pre-existing applications of coffee and coffee by-products valorization that is typically achieved with traditional solvents or methods. In addition, subcritical H_2O is more efficient than the physical activation methods of coffee and coffee by-product valorization.

3.2. Supercritical carbon dioxide (SC-CO_2)

Table 5 reports examples involving the use of supercritical carbon dioxide (SC-CO_2) for coffee or coffee by-products valorization. This Table 5 does not present the examples from decaffeination process by SC-CO_2 that has been widely investigated and described in several papers and patents.[170–173] Table 5 shows that a wide range of final products is obtained using SC-CO_2 extraction under different experimental conditions, essentially from the extraction or fractionation of the lipophilic fractions. These final products can be classified by field of application: (i) bioactive oil extracts including sterols, caffeine, polyphenols used in pharmaceutical, cosmetic or nutraceutical fields; (ii) triglycerides oil for biodiesel production.

3.2.1. Yield of extraction. Simões *et al.* have investigated the influence of pressure (150–300 bars) and temperature (40–55 °C) on the supercritical CO_2 (SC-CO_2) extraction of spent coffee grounds (Table 5, entry 3).[174] A maximum SC-CO_2 extraction yield of 85% has been reached after 3 h under 250 bars at 50 °C and 300 bars at 55 °C. Experimental results have pointed out an increase of extraction yield with pressure. According to the authors, the increase of pressure leads to an increase of density of CO_2, resulting in higher yield. The extraction curve has also been observed to be splitted in two distinct parts: (i) the extraction of available oil at the solid surface and (ii) the extraction of oil inside the matrix. Along all this process, extraction rate has been dominated by (i) external mass transfer resistance and (ii) diffusional and internal mass transfer. The temperature influence is balanced between two opposite effects. Increasing the temperature decreases the density of the supercritical fluid and thus its solvation capacity. On the other hand, it increases the vapor pressure of the solutes, therefore increasing their solubility in the supercritical solvent.

Mazzafera *et al.* have explained that the addition of the co-solvent such as isopropyl alcohol and ethanol enhances solvent density and modifies physical and chemical intermolecular interaction forces in the system (Table 5, entry 15).[184] More precisely, it increases the local density around the solute molecule, by increasing the physical interactions that are short range forces. In addition, the co-solvent can also lead to hydrogen bonding interaction.[185] However, since the addition of polar co-solvent targets phenolic and other polar compounds that are usually not extracted during pure SC-CO_2, the measure of oil yield with SC-CO_2 associated to a co-solvent is probably overestimated.

More globally, several parameters such as (i) pressure, (ii) temperature and (iii) co-solvent influence have been pointed out to be the controlled parameters that influence the yield of supercritical CO_2 (SC-CO_2) extraction.[186] In particular, pressure is the key parameter to significantly improve extraction yield. In addition, the reported results of yield are often competitive with the one obtained by the use of hexane with Soxhlet. The real challenge for researchers is to obtain the maximum extraction yield with the minimum amount of CO_2 used per g of raw material.

3.2.2. Fatty acid content (FAC) and triglycerides content. The fatty acid content (FAC) has been investigated for supercritical CO_2 (SC-CO_2) extraction of coffee and coffee by-products. Banchero *et al.* have reported the FAC of spent coffee grounds extract obtained with SC-CO_2 (Table 5, entry 2).[187] The SC-CO_2 extract is composed of 45.0, 23.0, 19.6 and 12.3% (w/w) of palmitic (C16:0), linoleic (C18:2), stearic (C18:0) and oleic acid (C18:1). The FAC has been demonstrated to be similar in proportion in comparison to the extract obtained with hexane Soxhlet.

Simões *et al.* have analyzed the Fatty Acid Content (FAC) of SC-CO_2 extract from spent coffee grounds (SCG) at different pressure (150–300 bars) and temperature (40–55 °C), but no significant difference in FAC has been observed due to these different modifications (Table 5, entry 3).[174] More generally, Zaidu *et al.* have demonstrated that modifying pressure of SC-CO_2 can influence the nature of fatty acids, depending of the number of carbons. Here, the main fatty acids in spent coffee grounds have almost the same number of carbon (C16:0, C18:0, C18:1 and C18:2), making them difficult to be selectively extracted.

In conclusion, the Fatty Acid Content (FAC) is ascribable to raw material nature that shows differences in terms of species origin, cultivation process, location of the coffee plants, *etc.*

Table 5 SC-CO_2 applied to coffee and coffee by-products valorization

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
1	Spent coffee grounds	40–55 °C 190 bars 0–450 min 60 g 12 g min^{-1}	GC-FID (FAC)	Lipids	AbsYield = 11.5% RelYield = 75% (190 bars, 40 °C, 400 min) FAC: C18:2 → 44.5% C16:0 → 37.5%	197
2	Spent coffee grounds	40–60 °C 350–500 bars 0–500 min 16 g 1 g min^{-1}	GC (FAC)	Lipids	AbsYield = 4.8% RelYield = 85% (500 bars, 60 °C, 350 min)	187
3	Spent coffee grounds	40–60 °C 150–300 bars 180 min (sample each 15 min × 4 + 60 min × 2) 20 g 10 g min^{-1} CO_2 0.7 g min^{-1} EtOH	GC (FAC)	Lipids	AbsYield = 15.4% (55 °C, 300 bars) AbsYield = 19.4% (40 °C, 200 bars, EtOH) FAC: C18:2 → 35% C16:0 → 35%	174
4	Spent coffee grounds	40–70 °C 140–190 bars 60 g 12 g min^{-1} 0–5% EtOH	HPLC-UV (kahweol, cafestol, 16-O-Methylcafestol),	Lipids + terpenoids	AbsYield = 12.0% (55 °C, 190 bars, 5% EtOH) Terpenes = 107.4 mg g^{-1} (55 °C, 140 bars, 0% EtOH)	188
5	Spent coffee grounds	40–80 °C 100–200 bars 0–300 min Static extraction (10–90 min) Dynamic 2.0 mL min^{-1} EtOH/SCG (0.25/1 to 2/1)	GC (FAC), IV, SV, TPC, ABTS, DPPH, polyphenols, CAF	Lipids + polyphenols	AbsYield = 15.9% RelYield = 109.5% (SC-CO_2/EtOH 2/1, 80 °C, 200 bars, 30 min static, 20 min dynamic) FAC: C18:2 → 45.4% C16:0 → 33.0% TPC = 64–411 mg_{GAE} g^{-1}_{oil} ABTS = 397–4610 μmol_{TEAC} per 100 g_{oil} DPPH = 345–3215 μmol_{TEAC} per 100 g_{oil} CAF = 64–711 mg per 100 g_{oil}	192
6	Spent coffee grounds	40–60 °C 300–400 bars 0–220 min 15 g 1.8 g min^{-1} 0–10% EtOH	DPPH, ^{1}H NMR, terpenes	Lipids	AbsYield = 9.5–10.7% RelYield = 91.3–102.9% (Pure SC-CO_2) AbsYield = 12.0% RelYield = 115.4% EC_{50} = 96.2/12.4 $mg_{extract}$ mL^{-1} (DPPH) CAF = 0.13/1.45%$_{mol\ extract}$ Cafestol = 5.30/2.26%$_{mol\ extract}$ 16-*O*-Methylcafestol = 3.70/2.00%$_{mol\ extract}$ Kahweol = 0.86/1.20%$_{mol\ extract}$ (SC-CO_2/SC-CO_2 + EtOH)	194
7	Spent coffee grounds	40–80 °C 98–379 bars 60 min 12 g	GC (FAC), OSI, PV, HPLC (kahweol, cafestol), LC-MS-MS (polyphenols), TPC, DPPH	Lipids + polyphenols	FAC: (Classic, Soxhlet, SC-CO_2) C18:2 → 45/45/46% C16:0 → 30/32/36% Kahweol = 214/164/34/11–43 mg per 100 g_{SCG}	189

Table 5 *(Contd.)*

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
					Cafestol = 467/249/42/21–83 mg per 100 g_{SCG} (Saponification, Classic, Soxhlet, SC-CO_2)	
8	Spent coffee grounds	33–67 °C 116–284 bars 19–221 min 24 mL min^{-1}	GC (FAC, sterols, tocopherols)	Lipids + sterols + tocopherols	FAC: (Soxhlet/SC-CO_2) C18:2 = 24.5/27.2% C16:0 = 48.4/49.0% Tocopherols SCG1 = 0.90/1.51%$_{oil}$ Tocopherols SCG2 = 2.34/2.12%$_{oil}$ Sterols SCG1 = 8.85/12.21%$_{oil}$ Sterols SCG2 = 8.76/15.60%$_{oil}$	191
9	Spent coffee grounds	200–300 °C 100–200 bars 40–50 min CO_2/MeOH = 0.11–0.30 (mol mol^{-1}) *In situ* transesterification	GC (FAC, FAME)	Lipids (biodiesel)	FAME yield = 84.9% (330 °C, 300 bars, SC-MeOH) FAME yield = 93.4% (300 °C, 100 bars, SC-CO_2/MeOH = 0.11 mol mol^{-1})	198
10	Green coffee bean	60–90 °C 235–380 bars 25 min 0.2 g 1.5 mL min^{-1}	HPLC (kahweol, cafestol)	Lipids + terpenoids	GCB (Soxhlet/SC-CO_2 70 °C/327 bars) Terpenes = 860/491 mg per 100 g_{oil}	190
11	Roasted coffee bean	60–90 °C 235–380 bars 25 min 0.2 g 1.5 mL min^{-1}	HPLC (kahweol, cafestol)	Lipids + terpenoids	RC (Soxhlet/SC-CO_2 80 °C/379 bars) Terpenes = 726/288 mg per 100 g_{oil}	190
12	Spent coffee grounds	40–60 °C 100 bars 150 min 15 g 6.6–16.6 g min^{-1} SC-CO_2 4–15% EtOH	DPPH, ABTS, TPC, HPLC (polyphenols)	High antioxidant extract	(SC-CO_2 pure) RelYield = 10.5% (40 °C, 300 bars) (SC-CO_2 + EtOH) AbsYield = 14% (60 °C, 100 bars, 15% CoSolv) (SC-CO_2/Soxhlet/US) TPC = 57/120/587 mg_{GAE} g^{-1}_{oil} (SC-CO_2, 40 °C, 200 bars, 4% EtOH)	199
13	Coffee husk	40–60 °C 100–300 bars 270 min 4–8% EtOH 15 g 6.6–16.6 g min^{-1} SC-CO_2	DPPH, ABTS, TPC, HPLC (polyphenols)	High antioxidant extract	(SC-CO_2 pure) RelYield = 2.0% (50 °C, 300 bars) (SC-CO_2 + EtOH) AbsYield = 2.2% (50 °C, 200 bars, 8% CoSolv) (SC-CO_2/Soxhlet/US) TPC = 36/151/133 mg_{GAE} g^{-1}_{oil} (SC-CO_2, 50 °C, 200 bars, 8% EtOH)	199
14	Green coffee bean	50–70 °C 152–352 bars 100 min 15 g 1.8 g min^{-1}	HPLC (FAC, CAF)	Lipids + CAF	AbsYield = 15.1% YieldCAF = 92.2% (SC-CO_2, 152 bars, 70 °C)	200
15	Green coffee bean	50–60 °C 152–352 bars 15 g 1.8 g min^{-1} Pure or 5% IPA or EtOH	HPLC (CAF, CGA)	Lipids + CAF + CGA	SC-CO_2 + none/IPA/EtOH RelYield = 70/93/99% CAF = 1.7/2/17 g per 100 g_{oil} of solvent CGA = 0/traces/0 (60 °C, 352 bars)	184
16	Green coffee bean	40–60 °C 150–300 bars 360 min 4–25 g 3–5 mL min^{-1} CO_2 1 mL min^{-1} H_2O	HPLC (CAF, CLA)	CAF + CGA	Most influent: pressure	201

Table 5 *(Contd.)*

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
17	Coffee husk	40–100 °C 60–300 bars 100–300 min Humidity	HPLC (CAF)	CAF	CAF = 84% (197 g CO_2 g^{-1}_{CH}) CAF = 78% (58 g CO_2 g^{-1}_{CH}) (SC-CO_2, 100 °C, 300 bars, 32% humidity)	202
18	Spent coffee grounds	50 °C 250 bars 180 min 1.9–5.3 g min^{-1}	FAC, MDTC	Lipids (PHA)	RelYield = 90% AbsYield = 12.6% FAC: C18:2 → 38.4% C16:2 → 39.7%	203
19	Spent coffee grounds	40–60 °C 200–300 bars 0–18 mL per 100 g CO_2 + (H_2O, ethanol or hexane) + MW, US	GC (FAC)	Lipids	AbsYield = 15.1% RelYield = 90.6% (60 °C, 300 bars) AbsYield = 16.4% RelYield = 98.1% (40 °C, 250 bars, 18 mL EtOH) FAC: C18:2 → 25.8–44.1% C16:0 → 33.6–36.9%	204
20	Spent coffee grounds	55 °C 250 bars 60 min 500 g 4.2 g min^{-1}	FFA, UPL, GC (FAC)	Lipids (cosmetic)	AbsYield = 12.1% FAC: C18:2 = 44.7% C16:0 = 33.1%	205
21	Spent coffee grounds	50 °C 200 bars 120 min 45 mL min^{-1} 1000 g 10% EtOH	GC (FAC), biological assays	High value extract	FAC: C18:2 → 43.3% C16:0 → 35.2%	206
22	Spent coffee grounds	40–60 °C 175–250 bars 60–300 min 1500 g 1833–2833 mL min^{-1}	GC (FAC), FFA, AV, IV, PV, TBARS	Lipids	AbsYield = 12.1% RelYield = 79% (50 °C, 200 bars, 120 min) FAC: C18:2 → 35–43% C16:0 → 33–42%	207
23	Green coffee bean	66–94 °C 179–325 bars 20 min static 360 min dynamic 5 g min^{-1}	GC-MS (terpenoids, CAF, FAC), TPC	Lipids, terpenoids, CAF	AbsYield = 6.5% CAF max = 1.6% (300 bars, 90 °C) TPC = 16.6 mg_{GAE} per 100 g_{GCB} TPC = 2.62 mg_{GAE} g^{-1}_{oil} (200 bars, 90 °C) Terpenes = 114/21 mg g^{-1}_{oil} (SC-CO_2, 200 bars, 90 °C/manual pressing)	208
24	Spent coffee grounds	60 °C 400 bars 25 g 15 g min^{-1} SC-CO_2 15/1.7 g min^{-1} SC-CO_2/EtOH 7.8 g min^{-1} EtOH 4 separators (300, 200, 100 and 1 bars)	TPC, GC-FID (FAC)	Lipids, polyphenols	AbsYield = 25% TPC = 4.56 mg_{GAE} $g^{-1}_{extract}$ (EtOH) Extract enriched 4 times in TPC with separators TPC = 24.1–56.7 mg_{GAE} $g^{-1}_{extract}$ (SC-CO_2) TPC = 42–57 mg_{GAE} $g^{-1}_{extract}$ (SC-CO_2/EtOH)	196
25	Spent coffee grounds	40–60 °C 500 bars (max) SC-CO_2 + isopropanol, EtOH or ethyl lactate	NMR, GC-FID (FAC), DPPH	Lipids, antioxidant activity	C16:0 + C18:2 = 76% oil FAC CAF = 0.56–3.96 g per 100 g_{oil} DPPH increased 12.5 times with co-solvent	193

Table 5 *(Contd.)*

Entry	Raw material	Parameters	Analysis	Final products	Main results	Ref.
26	Green coffee bean	20–75 °C 70–250 bars SC-CO_2 + US	UPLC-MS/MS	CAF	%Decaffeination =8.86% (SC-CO_2, 75 °C, 250 bars, 1 h) =18.19% (SC-CO_2 + US, 75 °C, 250 bars, 1 h) =63.10% (SC-CO_2 + US, 75 °C, 250 bars, 4 h)	209

3.2.3. Bioactive molecules

3.2.3.1. Terpenoids. Main terpenoids in SC-CO_2 extract of coffee has been observed to be kahweol, cafestol and 16-*O*-methylcafestol (Fig. 5, Table 5, entries 4, 6, 7, 10 and 11).[188–190]

Acevedo *et al.* have compared simple, Soxhlet, direct saponification and SC-CO_2 extraction of cafestol (CFT) and kahweol (KW, Table 5, entry 7).[189] Best results have been obtained by direct saponification (CFT = 214.3 mg per 100 g_{SCG}, KW = 466.6 mg per 100 g_{SCG}), followed by Soxhlet (CFT = 164.1 mg per 100 g_{SCG}, KW = 249.0 mg per 100 g_{SCG}), classical (CFT = 34.4 mg per 100 g_{SCG}, KW = 42.4 mg per 100 g_{SCG}) and SC-CO_2 extraction (CFT = 11.4–42.5 mg per 100 g_{SCG}, KW = 20.7–82.8 mg per 100 g_{SCG}). According to the authors, kahweol and cafestol are highly unstable molecules that easily form oxides. Hence, direct saponification has been described in literature as an efficient alternative to extract the unsaponifiable fraction of green coffee beans, avoiding diterpene oxidation. The other procedures (classical, Soxhlet, SC-CO_2) produce extracts that are going through a further saponification process after extraction, but exposing diterpenes to a possible higher oxidation rate.

In conclusion, supercritical CO_2 is not the most efficient solvent for terpenoids extraction. Hence, supercritical CO_2 offers a greater selectivity to produce high value oil enriched in terpenoids.

3.2.3.2. Sterols and tocopherols. Akgün *et al.* have identified campesterol, stigmasterol, sitosterol, α-tocopherol, β-tocopherol but also the absence of γ-tocopherol and δ-tocopherol in the SC-CO_2 extract in SCG (Table 5, entry 8).[191] The authors, through a response surface methodology (RSM), have estimated that moderate pressures (>200 bars), near-critical temperatures (40 °C) and with long extraction times (4 h) are required for efficient extraction of sterols and tocopherols. Moreover, they have demonstrated that SC-CO_2 extract is richer in sterols (12.21–15.60%$_{oil}$) and tocopherol (1.51–2.12%$_{oil}$) with global yield of 10.62–11.41% compared to hexane Soxhlet (8.76–8.85%$_{oil}$ of sterols and 0.90–2.34%$_{oil}$ of tocopherol; global yield = 12.29–14.97%).

More generally, sterols and tocopherols have not been enough investigated to draw accurate conclusions, but SC-CO_2 has been shown to be efficient and can more selectively extract those compounds compare to hexane Soxhlet.

3.2.3.3. Caffeine. Caffeine identification and quantification have been investigated for supercritical CO_2 (SC-CO_2) extraction of spent coffee grounds (SCG) and green coffee beans (GCB, Table 5, entries 5 and 15).[184,192] Mazzafera *et al.* have investigated the influence of pressure (152–352 bars), temperature (50–60 °C) and co-solvent (ethanol, isopropyl alcohol) on the SC-CO_2 extraction of caffeine in GCB (Table 5, entry 15).[184] The most efficient SC-CO_2 extraction (17 $g_{caffeine}$ $g^{-1}_{solvent}$) has been reported to be the combination of high pressure (352 bars) and the addition of a co-solvent (EtOH 5% w/w). Without the co-solvent, the yield is ten times lower (1.7 $g_{caffeine}$ $g^{-1}_{solvent}$). According to the authors, that might be due to caffeine molecules in GCB that are complexed by chlorogenic acids, and then hydrogen bonds between caffeine and chlorogenic acid molecules have to be broken. The addition of EtOH allows the solvation of caffeine and intermolecular interaction between EtOH and caffeine such as hydrogen bonding, resulting in higher yield.

In conclusion, contrary to one might think due to supercritical CO_2 decaffeination, SC-CO_2 is not the most appropriate solvent to remove caffeine. Hence, it is the most suitable solution to enrich selectively coffee oil in caffeine.

3.2.3.4. Polyphenols. Polyphenols and antioxidant activity have been investigated for supercritical CO_2 (SC-CO_2) extraction of spent coffee grounds (SCG, Table 5, entry 25).[193] Coelho *et al.* have performed 2,2-diphenyl-1-picrylhydrazyl (DPPH) analysis of SCG extract obtained by SC-CO_2 extraction at different pressure (300–400 bars), temperature (40–60 °C) and co-solvent (EtOH).[194] The most antioxidant extract (Inhibition Concentration IC_{50} = 12.39 $mg_{extract}$ mL^{-1}_{DPPH}) has been observed at 300 bars, 60 °C with 10% EtOH. The SC-CO_2 extractions without EtOH (IC_{50} = 96.23–163.1 $mg_{extract}$ mL^{-1}_{DPPH}) have been reported to be four to six times less efficient than hexane Soxhlet (IC_{50} = 25.07 $mg_{extract}$ mL^{-1}_{DPPH}). Hence, co-solvent is the most influent parameter compared to pressure and temperature, during a SC-CO_2 extraction of antioxidants molecules. According to the authors, the addition of EtOH is necessary to increase the solvent polarity that is essential for extraction of polar molecules, responsible for the antioxidant capacity.

In conclusion, SC-CO_2 is not suitable solvent for polyphenols extraction. Hence, the addition of EtOH co-solvent is an interesting opportunity for enrichment of oil in polyphenols.

To conclude, SC-CO_2 and SC-CO_2/EtOH are not the most efficient solvents for bioactive molecules recovery in term of quantity, but are more selective than hexane Soxhlet. It is poss-

ible to obtain dual enrichment into lipophilic and hydrophilic compounds, by performing sequential extraction with pure SC-CO_2 followed by SC-CO_2/EtOH extraction, both at low pressure.

3.2.4. Fractionation. Fractionation with SC-CO_2 is a more rarely investigated step for the valorization of coffee and coffee by-products. This is mainly due to the necessity for the operators to possess a supercritical system with at least two or more separators. Hence, it represents another alternative to (i) enrich an extract selectively in specific compounds or (ii) to completely recover expected compounds or removing unwanted compounds as described in by Reverchon *et al.*[195]

Bitencourt *et al.* have reported the use of supercritical CO_2/EtOH (SC-CO_2/EtOH, 90.6/9.4 w/w) followed by fractionation into 4 separators (Table 5, entry 4).[196] Pressurization of the separators have been performed with SC-CO_2/EtOH (90.6/9.4 w/w, condition A) and with pure SC-CO_2 (condition B) at 300, 200, 100 bars and P_{atm}, respectively called F1, F2, F3 and F4 (Fig. 11). Results have shown that nearly the entire extract precipitates in F3 and F4. According to the authors, the spent coffee grounds (SCG) extract is mainly composed of a lipid portion that is highly soluble in SC-CO_2/EtOH, even at 300 and 200 bars. More specifically, the extract precipitation in separators F3 and F4 can also be explained by the observations of phase equilibrium behavior for CO_2/EtOH system. Under condition A, the Total polyphenol content (TPC) of the extract obtained from F1 (TPC 3.2 = mg_{GAE} $g^{-1}_{extract}$) is four times more concentrated than the original SC-CO_2/EtOH extract without fractionation (TPC = 0.8 mg_{GAE} $g^{-1}_{extract}$). The drop of pressure from 400 to 300 bars induces a more selective precipitation of polyphenols than other compounds. Yet, the results have to be interpreted with cautious; the F1 extract is the most enriched in polyphenols but is not the fraction with the largest amount of polyphenols, representing only 9.55% of the polyphenols extracted from SCG (for examples, TPC_{SCG} = 0.01952 mg_{GAE} g^{-1}_{SCG} in F1 extract, TPC_{SCG} = 0.2043 mg_{GAE} g^{-1}_{SCG} in total extract). Under condition B, the use of pure SC-CO_2 to pressurize the separators have been performed to reduce drastically the EtOH concentration, thus, decreasing polarity of solvent to expect a higher polyphenols precipitation in F1. The TPC measured in F1, condition B (TPC = 3.4 mg_{GAE} $g^{-1}_{extract}$) is slightly better than the one in F1, condition A (TPC = 3.2 mg_{GAE} $g^{-1}_{extract}$), but the improvement is not significant and is in the uncertainties interval. By the way, a more significant precipitation of extract has been reported under F3 (100 bars) of condition B (yield = 13.6%) than F3 under condition A (yield = 8.6%). According to the authors, this might be due to the decrease of ethanol content in the solvent mixture (condition B) that significantly decreases the solubility of coffee lipids and phenolic compounds at 100 bars.

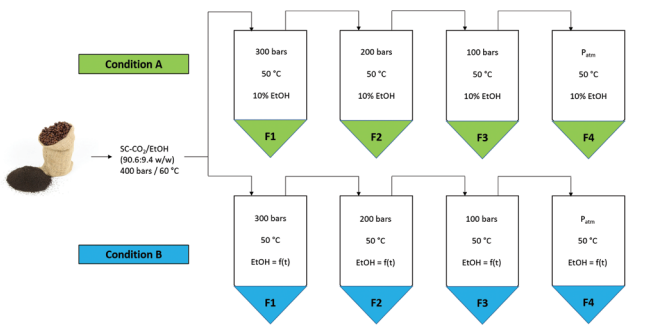

Fig. 11 Fractionation process of SC-CO_2 extraction of SCG for production of extracts enriched in phenolic compounds, adapted from Bitencourt *et al.*[196]

Fractionation represents an interesting but underdeveloped process for the valorization of coffee and coffee by-products. In theory, it could allow industrials to realize a single extraction with separation of final products such as phenolic, triglycerides and essential oil extracts for example. Hence, the use of multiple separators at different pressures allows the selective recovery of fatty acids, based on their number of carbons or higher added value compounds with different volatility or affinity with the supercritical CO_2.[210]

To conclude, the supercritical CO_2 is a true chameleon. By its astonishing capacity to modify its own properties in function of pressure, temperature and co-solvent, the supercritical CO_2 allows to selectively enrich or recover high value molecules such as terpenoids or polyphenols in extracts. Moreover, it is a solvent able to mimicry the efficiency of organic solvents for oil recovery in term of quantity (yield) and quality (Fatty Acid Content FAC) of oil recovered, without the major toxic drawbacks.

3.3. Major trends, comparison and sequential combination of SCW and SC-CO_2 applied to coffee and coffee by-products valorization

Table 6 compares subcritical water (SCW) and supercritical CO_2 (SC-CO_2) extraction used for coffee products and by-pro-

Table 6 SCW and SC-CO_2 major trends of operating parameters, carried analyses and obtained final products

	Subcritical H_2O	Supercritical CO_2
Parameters	100–250 °C 20–50 bars 10–50 mL g^{-1} Static or dynamic Modifiers: N_2, CO_2 Pretreatment: US, MW, SC-CO_2	40–80 °C 100–400 bars Dynamic Cosolvent: EtOH
Analyses	TPC (polyphenols) TFC (flavonoids) TSC, RSs (sugars) DPPH, ABTS, FRAP, ORAC (antioxidant capacity) HPLC (chlorogenic acids, caffeine, oligosaccharides, monosaccharides)	Yield (oil) GC and HPLC (fatty acids composition, (terpenoids, sterols, tocopherols, caffeine) TPC (polyphenols) DPPH (antioxidant capacity)
Final products	Bioactive molecules (ingredient) Bio-crude oil (energy)	Bioactive oil (ingredient) Biodiesel (energy)

ducts valorization. The two pressurized technics are very different. Indeed, physico-chemical properties of H_2O and CO_2 are initially different. Water remains a polar solvent, even in subcritical conditions. At contrary, carbon dioxide is an apolar solvent. Hence, the obtained final products are also very various, favoring sugars extraction using SCW and lipids extraction using SC-CO_2.

By using them in a sequential manner, these complementary processes could contribute to maximize the recovery of high value molecules from a same raw material obtained from coffee and/or coffee by-products.[211] Thus, multiple-ways of valorizations of coffee by-products, such as spent coffee grounds, have already been published in reviews and/or investigated on the basis of experimental results obtained using traditional methods, from coffee by-products,[10,212] spent coffee grounds[213–215] or coffee silverskin.[44] These researches have suggested the concept of biorefinery to generate phenolic compounds, biofuels and/or biocomposites.[46,216] The biorefinery concept is in agreement with the long term goal of European Commission of building a sustainable bio-based economy.[217]

Hence, experiments have been performed on combination of double or triple ways of valorization. For example, spent coffee grounds have been tested for production of polyhydroxyalkanoates (PHA) and carotenoids.[89] It has also been used to generate phenolic compounds and bioenergy.[218] Finally, SCG has been proposed for production of biodiesel, biocrude oil and biochar.[88]

In agreement with the results of the literature of the last twenty years, Green Solvent Bio-Refinery concept (GreSBiR) using subcritical H_2O and supercritical CO_2 for the full valorization of coffee and coffee by-products can be proposed (Fig. 12). SC-CO_2 under different pressures with or without co-solvent allows producing sequentially, multiple oils with different properties. Otherwise, an extraction at high pressure with co-solvent can be followed by fractionation at different pressure and solvent composition. SCW at different time and temperatures of exposition allows producing sequentially, bioactive extracts, bioactive sugars, bioethanol, biocrude oil and/or biochar.

This biorefinery could be able transforming coffee and coffee by-products into various products with higher value

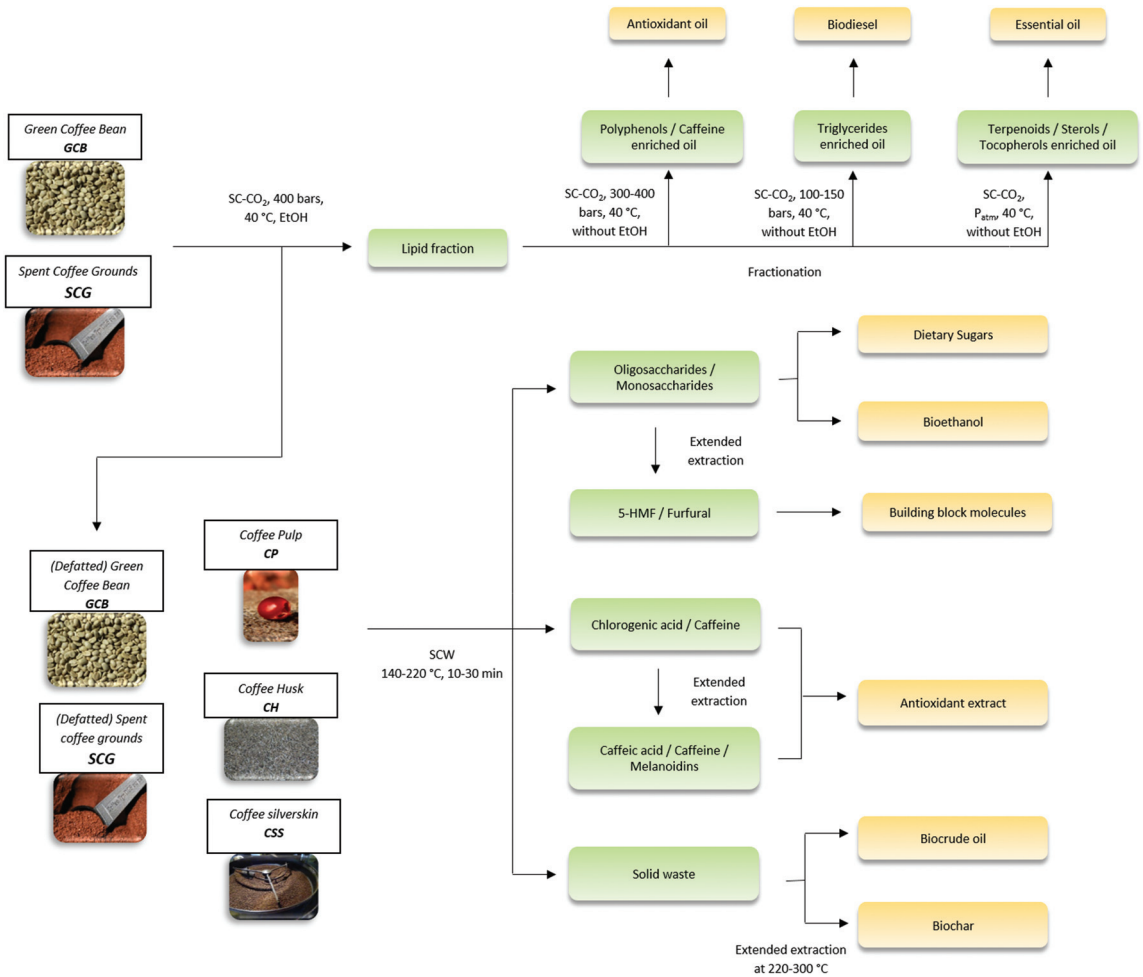

Fig. 12 Green solvent bio-refinery (GreSBiR) with subcritical water (SCW) and supercritical carbon dioxide (SC-CO_2) applied to coffee and coffee by-products.

owing their applications in energy, cosmetic, nutraceutical or pharmaceutical fields. Nevertheless, life cycle assessment (LCA) and economic analysis are required to estimate the industrial interest of such biorefinery.[219]

4. Conclusions and perspectives

The current review reports the great interest of subcritical water and supercritical carbon dioxide used for coffee and coffee by-products and reports the following advantages: (i) similar or better amount and quality of extracts produced by SCW and SC-CO_2 in comparison with traditional methods; (ii) customized properties of SC-CO_2 to selectively extract high value molecules; (iii) triple action of SCW as solvent, reagent and catalyst; (iv) wide range of final products covered by the two technologies (SCW and SC-CO_2) and (v) the reduction of environmental impact by limiting toxic solvents and/or required catalyst with the use of SCW and SC-CO_2.

For subcritical H_2O, the prime influent parameter is the combination of temperature/time. Carbohydrates and polyphenols recovery has been performed with SCW at moderate temperature (150–220 °C) with shorter time of extraction (10–30 min). Biocrude oil and biochar production have been performed with SCW at high temperature (220–300 °C). The reported results for carbohydrates and polyphenols under those conditions have been demonstrated to be more efficient than any other traditional or non-conventional technologies.

Perspectives could be a step back to reinforce the fundamental knowledge about the black box phenomena that occurred during SCW applied to biomass. More specifically, deeper studies are required on (i) the solubilization under the chosen conditions; (ii) the kinetic of the hydrolysis of polysaccharides and oligosaccharides; (iii) the kinetic of degradation of monosaccharides.

For the SCW solubilization of oligosaccharides of different molecular weights, no experiment has been carried out to measure the unique solubilization part without SCW hydrolysis and corresponding solubilization of lower weight degradation products. The addition of a hydrolysis inhibitor could allow assessing the influence of the solubilization properties of oligosaccharides in SCW at different temperatures.

For kinetic of hydrolysis, it could be interesting to quantify the different poly- or oligo-saccharides as a function of time to determine if a monosaccharide pattern (galactose *vs.* mannose) is more selectively hydrolyzed. The influence of the nature of glycosidic binding on the hydrolysis rate should be also evaluated.

The measurement of kinetic of degradation is essential too. Hence, a comparison between kinetic of hydrolysis and kinetic of degradation could help the researchers anticipating their results instead of taking an empirical approach. For example, if the kinetic of degradation is ten times faster than the one of hydrolysis, there is no chance to recover some high value molecules, despite their production after hydrolysis.

The lack of control during SCW applied to coffee and coffee by-products makes the production of monosaccharides difficult. It results in several limitations such as low yield in SCW at low temperature and high degradation in SCW at high temperatures. With a selective and reversible protective agent of monosaccharides, higher temperature or longer time of extraction could be further used to get extremely high yield. No research has been carried out yet, hence, the acetylation of monosaccharides could be the solution.[220]

For supercritical CO_2, the studied literature dealing with coffee and coffee by-products has highlighted a chameleon technology with unlimited tunability to selectively extract solutes for biomass valorization. The prime influent parameters are reporting the pressure and the co-solvent addition. Supercritical carbon dioxide has been used at relatively high pressure (300–400 bars) for lipids extraction and with EtOH addition as modifier for phenolic compounds recovery. The reported results with SC-CO_2 have been demonstrated the same efficiency in term of amount and quality of oil but present a better selectivity of high value molecules such as terpenoids sterols, tocopherols, caffeine, polyphenols in comparison with the use of hexane Soxhlet method.

Volatile lipophilic compounds such as terpenoids, sterols and tocopherols can be extracted more selectively at low pressure (100–200 bars). Triglycerides and volatile compounds are both extracted at high pressure (300–400 bars). Volatile, triglycerides and phenolic compounds are all extracted under high pressure (300–400 bars) with addition of EtOH.

The influence of the residual water in the dry coffee by-products used under supercritical CO_2 is rarely reported in the literature. Hence, Dunford *et al.* have observed that majority of water moisture remains in the material, but, a small part is extracted from the media.[221] In addition, after deduction of the extracted mass of water, significant differences of yield (5.5–7.1 g) have been reported at different moisture levels (12.7–37.8% w/w) at 75 °C, 600 bars for examples. Since the pressure and temperature of critical point depend of the proportion of CO_2/H_2O the mixture, it is possible than residual water play a significant part to influence the extraction and nature of extracts.[222] More specifically, the residual subcritical or supercritical H_2O in presence of CO_2 becomes a strong acid able to hydrolyze lignocellulosic materials such as cellulose, hemicellulose, lignin as suggested by Morais *et al.*[132]

Perspectives of SC-CO_2 applied to coffee and coffee by-products could focus on (i) the improvement of extraction and (ii) the development of novel technologies of fractionation.

Yield of extraction, selectivity and CO_2 consumption can be improved with pretreatment such as ultrasound (US) or microwave (MW) or ionic liquid (IL) or deep eutectic solvent (DES).[209,223]

Polarity modification during SC-CO_2 extraction has already been performed by the addition of water or alcohols such as ethanol or isopropyalcohol. Hence, the addition of novel hydrophilic solvent such as DES during SC-CO_2 has never been performed. Moreover, DES is not soluble in SC-CO_2 but SC-CO_2 is slightly soluble in DES. Hence, the addition of DES could be used in static mode without be totally consumed with

dynamic extraction by SC-CO_2, resulting DES-free extract enriched in polar compounds.

Hemi-synthesis is an understudied field in SC-CO_2 for coffee and coffee by-products valorization. The co-solvent could become reagent introduced simultaneously with SC-CO_2 to extract and functionalize triglycerides. For example, unsaturated fatty acids could be oxidized to form higher value products than the biodiesel obtained through transesterification reactions. Such possibility has been studied for the oxidation of oleic acid into pelargonic and azelaic acids, with ozone or potassium permanganate under supercritical CO_2.[224]

The fractionation through the use of SC-CO_2 technology should be more investigated. The pressurization with a more apolar solvent than CO_2 could allow selectively precipitating polar compounds in separators. Otherwise, the addition of a resin or adsorbent inside the separator could trap phenolic compounds, despite an extra step to desorb the high value compounds.

To conclude, subcritical H_2O and supercritical CO_2 are greener, more efficient and more selective than traditional methods for the valorization of coffee and coffee by-products. Moreover, the two technologies are complementary. Used sequentially, the subcritical H_2O and supercritical CO_2 unable covering almost all the possibilities of valorization of coffee and coffee by-products. Hence, the knowledge and way to use those technologies have to be further investigated to ensure the rightful place of subcritical H_2O and supercritical CO_2 in the field of biomass valorization, including coffee and coffee by-products.

List of abbreviations

AAE	Ascorbic acid equivalent
AbsYield	Absolute yield
ABTS	2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)
AOC	Antioxydant capacity
AV	Acid value
C16:0	Palmitic acid
C18:2	Linoleic acid
C-3-R	Cyanidin-3-rutinoside
CAF	Caffeine
CE	Catechin equivalent
CGA	Chlorogenic acids
CH	Coffee husk
CP	Coffee pulp
CQA	Caffeoylquinic acid
CSS	Coffee silverSkin
DAG	Diacylglycerol (=Diglyceride)
DES	Deep eutectic solvent
DM	Dry matter
DMC	Dimethyl carbonate
DPPH	2,2-Diphenyl-1-picrylhydrazyl
EC50	Half effective concentration
FAC	Fatty acids composition
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FRAP	Ferric ion reducing antioxidant power
FT-IR	Fourier transform – infraRed spectroscopy
GAE	Gallic acid equivalent
GC	Gas chromatography
GCB	Green coffee bean
GLU	Glucose equivalent
GPC	Gel permeation chromatography
GReSBiR	Green solvent bio-refinery
HHV	Higher heating value
5-HMF	5-(Hydroxymethyl)-2-furaldehyde
HPLC	High performance liquid chromatography
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquefaction
IC_{50}	Inhibition concentration
IPA	Isopropyl alcohol
IV	Iodine value
LCA	Life cycle assessment
MAE	Microwave assisted extraction
MB	Methylene blue
MIC	Minimum inhibitory concentration
MRPS	Maillard reaction products
MS	Mass spectrometer
MW	Microwave
NMR	Nuclear magnetic resonance
ORAC	Oxygen radical absorbance capacity
OSI	Oxidative stability index
PHA	Polyhydroxyalkanoate
PV	Peroxide value
QE	Quercetin equivalent
RelYield	Relative yield
RESS	Rapid expansion of supercritical solution
ROS	Reactive oxygen species
RSs	Reducing sugars
SC-CO_2	Supercritical carbon dioxide
SCG	Spent coffee grounds grounds
SEM	Scanning electron microscopy
SCW	Subcritical water
TAA	Total antioxydant activity
TAG	Triacylglycerol (=Triglyceride)
TBARS	Thiobarbituric acid reactive substances
TEAC	Trolox equivalent antioxidant capacity
TFC	Total flavonoid content
TGA	Thermogravimetric analysis
TPC	Total polyphenol content
TSC	Total sugar content
UAE	Ultrasound assisted extraction
UPLC	Ultra performance liquid chromatography
US	Ultrasound
XRD	X-Ray diffraction

Conflicts of interest

There are no conflicts to declare.

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