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# A Biorefinery from Spent Coffee Grounds: from High-added Value Compounds to Energy by Innovative Processes

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Turning waste into a resource is one of the main aims in circular economy systems. The European Union is strongly promoting innovation in recycling and reuse to reduce waste generation and encouraging the transformation of waste into a major, reliable source of raw materials, to recover energy only from non-recyclable materials, and virtually to eliminate landfilling. In this work, *Coffea canephora* spent coffee grounds were proposed as raw material for a biorefinery involving green processes and innovative solvents, and the effect of pre-treatments on materials destined to energy production was evaluated.

## 1. Introduction

The food and agriculture organization has estimated that about 1.6 billion tons of waste are produced every year by the agri-food sector along the whole value chain. Due to the high amount of organic matter, agri-food industry wastes create problems of disposal and environmental pollution, which accounts for about 6% w/w of global $CO_2$ emissions (Papaioannou et al., 2022). Coffee industry commercializes one of the most traded commodities in the world, with a production of $10.5 \cdot 10^6$ tons in 2020. Despite most of the production of coffee is concentrated in few countries, i.e., Brazil, Vietnam, and Colombia produce together more than 50 % of world's total coffee, its consumption is spread worldwide and in particular in Europe, US, Japan, and Russia Federation (ICO, 2022). Spent coffee grounds (SCG) are obtained after the brewing process and about 650 kg of SCG are estimated to be produced for each ton of green coffee beans (Mata et al., 2018). SCG have not any commercial value and usually are sent to compost facilities or discarded as solid waste, implying soil and groundwater contamination potential due to the content of caffeine, tannins an polyphenols (Mata et al., 2018). SCG can be toxic for several plants, can inhibit plant growth, and may induce mutagenicity in different strains when disposed in landfills. On the other hand, SCG contains antioxidants, lipids, and carbohydrates which can be recovered and reused for pharmaceutical, food, cosmetic industries, and biofuels production. Due to the current "perfect storm" driven by energy transition, political instability, and climate change, it is essential to find new sustainable energy sources to replace fossil energy dependence and more environmentally friendly resources to reduce greenhouse gases emissions and environmental pollution, developing processes able to provide co-products instead of waste. The chemico-physical features of SCG led to several proposals for spent coffee grounds reusing. Sometimes, SCG are directly used in the coffee industry plants, because of the high calorific value. Combined with other biomasses, SCG are able to contribute to the calorific value of pellets, due to the high content of C, H, and oils. Nevertheless, pure SCG pellet implied incomplete incombustion, with an increase in particle and gas emissions. Moisture (<20%), pressure applied, and die height are the main parameters relevant for pellet mechanical properties (Lisowski et al., 2019). The SCG high calorific value allows their direct use for bio-syngas production, as reported by Ramos et al. (2016), who demonstrated the feasibility of their steam gasification, performed at 1 bar, temperatures between 650 and 850 °C and steam partial pressure between 0.05 and 0.3 bar. Additionally, waste-to-energy via $CO_2$/steam gasification of SCG was proposed by Rodrigues et al. (2022), who focused on hydrogen production as a response to the increasing demand of clean energy vectors. Bio-oil suitable for biodiesel production was also obtained by pyrolysis of SCG (Li et al., 2014). The thermal process can provide fuel gas, a liquid bio-oil and a solid char, whose ratios are function of adopted operating conditions. Since the

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high moisture represents a problem for agri-food waste storage and thermal treatments, an innovative alternative to recover energy from SCG is based on hydrothermal carbonization, for simultaneous energy and chemicals recovery. This process allowed to obtain high calorific value hydrochar from SCG (64% and a calorific value of 31.6 MJ $kg^{-1}$). Furthermore, SCG are composed by the 10-20 % on dry weight basis of lipids, consisting predominantly of linoleic, palmitic, stearic, oleic arachidic, and linolenic acids. Biodiesel from SCG was obtained by a two-step transesterification process, ultrasound-assisted process (Valderez et al., 2014) in situ extraction, and transesterification with supercritical methanol (Calixto et al., 2011). As reported by Atabani et al. (2018), coffee waste methyl esters exhibit excellent cetane number, higher heating value, and iodine value with poor cold flow properties. Moreover, biogas production by anaerobic digestion of SCG and co-digestion with other waste was studied (Mata et al., 2018). Whereas anaerobic digestion under mesophilic conditions can be sustained, the thermophilic environment provides the accumulation of volatile fatty acids. In addition, long term mono-digestion of SCG lead to inhibitory effects on biogas production (Mahmoud et al., 2022). The composition of SCG is rich in polymeric sugars, in particular hemicellulose and cellulose structures. As reported by Chiyanzy et al., (2015), hemicelluloses in SCG are composed of mannose, galactose, and arabinose, although the whole arrangement is essentially composed of galactomannan, arabinogalactan, and cellulose structure which can be exploited for bioethanol production. Hemicellulose and cellulose fractions of SCG can be converted to monomeric sugars by hydrolytic action of acids or enzymes. However, enzymatic hydrolysis is preferred due to the milder conditions requirements, suitability for food industry application and selectivity. Nevertheless, enzyme accessibility needs to be enhanced by pre-treatments to increase process yields. All the mentioned efforts for waste valorization can provide energy and by-products which can be exploited in several agri and industrial applications. It is worthy observing that SCG contain substantial amounts of high added-value bioactive compounds with antioxidant activity, like melanoidins, caffeine, chlorogenic acid, and polyphenols, which exhibit interesting properties for the food, pharmaceutical and cosmetic sectors (Pettinato et al., 2021). Recovery of such compounds was attempted by innovative processes with the aim of increasing the extraction yields and simultaneously ensuring the preservation of the antioxidant and antimicrobial activities that captured the interest of the industry and defined their value in the market. Starting from a single biomass, is theoretically possible to better exploit its potential by valorization solutions applied according a logic hierarchy. Extraction techniques must be designed to ensure low energy consumption and must use alternative and green solvents to ensure the product safety for consumers and for a low environmental impact. Particularly, the main challenges to achieve efficient extraction of bioactive compounds include the constraint of using solvents generally recognized as safe, potentially implying a reduced affinity towards target compounds compared to conventional solvents. Thus, alternative and more efficient techniques such as supercritical fluid extraction were proposed as green extraction method for added-value compounds recovery, particularly using supercritical $CO_2$ alone or with a polar modifier (e.g. methanol, ethanol, acetone) (Andrade et al., 2012). Furthermore, subcritical water extraction is receiving much attention in the field, as well as microwave-assisted extraction, based on the application of electromagnetic waves, enabling the use of water/ethanol solutions as solvents with remarkable recovery of high-added value compounds (Pettinato et al., 2019). On the other hand, same solvents' extraction efficiency can be enhanced by the mechanical energy of ultrasounds at low temperature, or exploiting high pressures and temperatures in short times (Pettinato et al., 2021). In addition, all the previous stages can serve as pre-treatments of the following stages, to obtain higher yields of the desired product. Approaches to biorefinery concept, were attempted in literature by recovering lipids from SCG to produce biodiesel and reuse defatted SCG for gasification at 900 °C (Tinoco-Caicedo et al., 2021). Similarly, Battista et al., (2021) proposed an integrated process, where defatted SCG were treated by acid and enzymatic hydrolysis, while recovered oil was used for biodiesel production. The used the glycerol co-produced during the previous transesterification stage to obtain sugars, while the residual solids were further treated by anaerobic digestion. A more structured approach was followed in the work of Tongcumpou et al. (2019), where antioxidant recovery from wet SCG using methanol as solvent preceded the stage of in-situ transesterification, while the defatted SCG were exploited to obtain bio-char briquette via a slow pyrolysis process. As often experienced by researchers, several advantages can be obtained by performing cascade operations both in terms of useful by-products and to pre-treat the biomasses. In this work, a SCG-based biorefinery is proposed by adopting a cascade of stages aimed to recover the antioxidant fraction, the coffee oil, polysaccharides, and lignin, using non-conventional processes.

## 2. Theoretical

The recovery of high added value compounds to be used in food, cosmetic and pharmaceutical sectors is the step that can strongly impact on the economic sustainability of processes due to the high commercial value of the products, so it can represent the first stage of a biorefinery which, by consecutive processes, is able to provide products of interest up to energy recovery. But the first stage of a SCG-based hypotetical biorefinery, considering the intended use of recovered compounds, must apply the green chemistry principles (Reverberi et al., 2018). The conceptual biorefinery based on SCG is reported in Figure 1, where the operations cascade is hypothesized under the target of ensuring high quality extracts for food and cosmetic industries and providing raw materials useful for bioenergy production and byproducts of potential exploitation in different sectors. The feasibility of the conceived sequence of main processes was experimentally verified, as detailed in the following. The design of the final processes will foresee the application of an aprioristic approach allowing for a quantitative comparison of different conceptual design solutions that embed the process and preliminary risk analysis (Bassani et al., 2023).

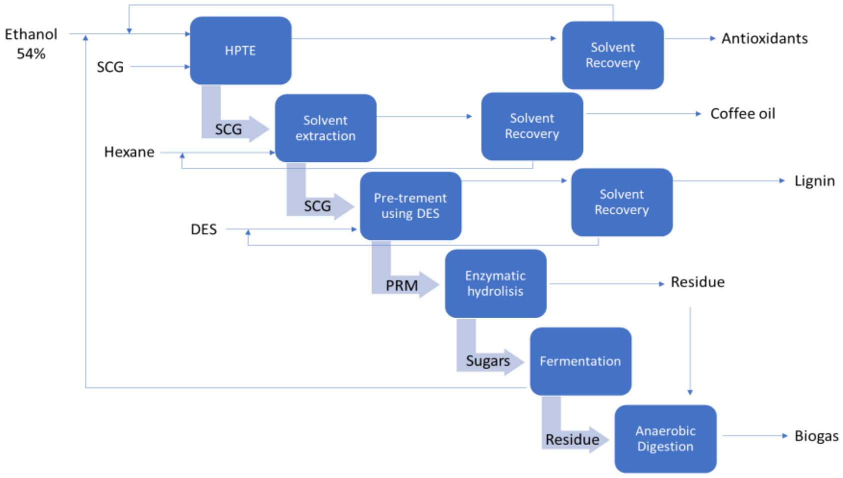

*Figure 1: Scheme of biorefinery based on SCG*.

## 3. Materials and methods

### 3.1 Spent coffee grounds characterization

SCG were collected from vending machines at the University of Genoa, Italy. Biomass characterization in terms of moisture, ash, total extractable materials, polysaccharides were performed according to protocols reported in Sluiter et al. (2011). Calorific value of SCG was determined by a Mahler calorimeter (IKA C200, IKA®-Werke GmbH & Co. KG, Germany).

### 3.2 Antioxidant and lipid extractions

Antioxidants from dry SCG were recovered by high pressure and temperature extraction (HPTE) and quantifies by Folin-Ciocalteu's assay, according to the procedure reported in Pettinato et al. (2021). Coffee oil was extracted by Soxhlet method using hexane for an extraction time of 4 h.

### 3.3 Deep eutectic solvent pretreatment and acid hydrolysis

Fermentable sugars were recovered from SCG by pre-treating the biomass using two deep eutectic solvents, i.e., choline chloride:citric acid (2:1 mol:mol) +9 % w/w of water (DES1) and choline chloride:citric acid (1:1 mol:mol) + 30% w/w of water (DES 2), followed by acid hydrolysis (Sluiter et al., 2011). The latter was also performed on un-pretreated SCG to compare the results. DES were prepared by mixing the components at 60 °C and left under agitation until a homogeneous liquid was obtained. Finally, water was added according to the solvent composition designed and the system was agitated at room temperature on magnetic stirrers for 3 h. SCG pretreatment was carried out at 130 °C for 90 min in a sand bath. Polysaccharides and lignin content were determined according to the protocols reported by Morán-Aguilar et al. (2022). The composition of native and SCG residues after pre-treatments were tested according to National Renewable Energy Laboratory (NREL) Technical Report (Sluiter et al., 2011).The quantification of polysaccharides was carried out by HPLC system (Agilent model 1200, Palo Alto, CA, USA). Total lignin was quantified considering acid soluble lignin (ASL) and Klason lignin (KL). The percentage of lignin removed was calculated according to Eq. (1):

$$\text{Delignification (\%)}= \left[1-\frac{\text{total lignin in pretreated SCG}}{\text{total lignin in native SCG}}\cdot S\right]\cdot 100 \qquad (1)$$

where S (-) is the mass of solid recovered after treatment/ mass of treated SCG.

## 4. Results and discussion

### 4.1 SCG characterization

SCG were collected from vending machines (moisture 53.8±0.2 $\%_{\text{wet based}}$) and immediately dried at 45 °C up to constant weight. Biomass after drying was stored at room temperature. In Table 1 the results of characterization are reported.

*Table 1: SCG characterization*

| Parameter | Units | Value |
|---|---|---|
| Moisture | % wet based | 2.09±0.02 |
| Ashes | % dry based | 1.88±0.05 |
| Calorific value | $J/g_{\text{dry SCG}}$ | 20888±135 |
| Total extractable compounds | g/g dry biomass | 0.29±0.01 |
| Glucans | g/g dry biomass | 0.09±0.02 |
| Galactans+Mannans | g/g dry biomass | 0.43±0.02 |
| Arabinan | g/g dry biomass | 0.07±0.02 |
| Soluble lignin | g/g dry biomass | 0.02±0.00 |
| Insoluble lignin | g/g dry biomass | 0.18±0.01 |

### 4.2 Extraction of antioxidants and lipids

To extract antioxidants from SCG, ethanol 54% was selected as solvent according to previously optimized conditions (150 °C, 1 h as extraction time and liquid-to-solid ratio of 10 mL/g, 7.2 bar) but without using an inert atmosphere inside the extraction vessel. Presence of oxygen provided a lower yield of polyphenols compared to previous studies (Pettinato et al., 2021) due to the partial occurrence of degradation reactions, otherwise prevented by the inert gas. To evaluate the hierarchy of operations, two stages of extraction were performed on dried SCG (Figure 2) and on defatted SCG after Soxhlet extraction. Defatting process enabled better availability of compounds to be extracted, resulting in a 17% higher extraction yield in the first stage of extraction, while no significant differences were observed between results of the second stage of HPTE.

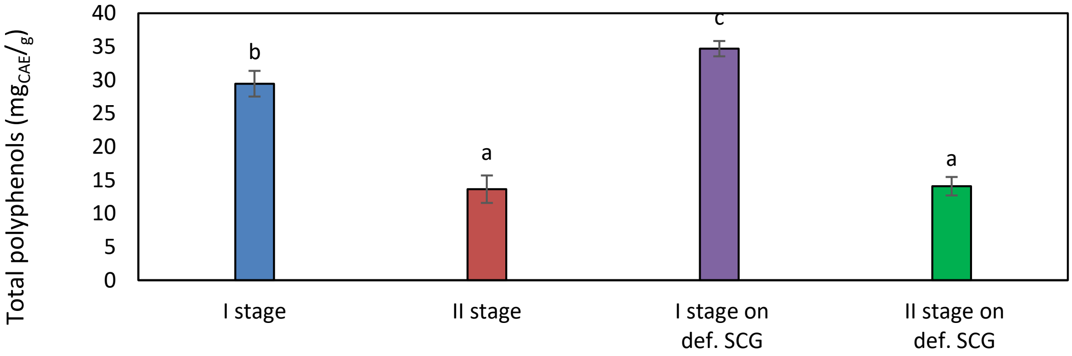

*Figure 2: Polyphenols extraction in ethanol 54% from SCG (*150 °C, 1 h as extraction time, and liquid-to-solid ratio of 10 mL/g, 7.2 bar) before and after defatting.

These findings indicated an effect of HPTE operating conditions in providing partial destruction of the initial biomass. This hypothesis was confirmed by tests on coffee oil extraction, which were carried out on SCG before and after HPTE. In particular, coffee oil yields of 9.14±0.07 % and 12.06±0.16% were obtained for the extractions from SCG and from solid residue after HPTE, respectively. Obtained results are in agreement with literature (Kondamudi et al., 2008). Albeit both antioxidant and lipid extractions provided better performances after the related pre-treatment, i.e., defatting for HPTE and hydrophilic compounds extraction for lipid recovery, the hierarchy of operations should consider the end use of obtained products. Due to the intended product use as antioxidants for food, pharmaceutical and cosmetic industry and to comply with green chemistry principles (Reverberi et al., 2018), the first stage of the biorefinery based on SCG should consist in antioxidant extraction, followed by lipid extraction. In addition, this sequence of operations ensured a higher difference in lipid yield (33% more) than the alternative in terms of gain in antioxidant yield (about 17%).

### 4.3 Effects of DES pre-treatment

Table 2 shows the results of SCG treatment with two different compositions of DES made by citric acid (CA) as hydrogen bond acceptor and choline chloride (ChCl) as hydrogen bond donor. The addition of water is mainly needed to reduce solvent viscosity. Nevertheless, when added in small percentages, water can work as component of a ternary DES more than as a diluting agent, enabling formation of a higher ordered hydrogen-bonding network (Liu et al., 2018).

*Table 2: Effects of SCG treatment by DES 1 (ChCl:CA 2:1, mol:mol + water 9 %, w/w) and DES 2 (ChCl:CA 1:1, mol:mol + water 30 %, w/w)*

| Parameter | DES1 | DES2 |
|---|---|---|
| PRM*/SCG (g/g) | 0.408±0.009 | 0.410±0.072 |
| Delignification (%) | 27±5 | 34±7 |
| Glucans (g/g PRM) | 0.38±0.14 | 0.35±0.10 |
| Galactans+Mannans (g/g PRM*) | 0.23±0.11 | 0.34±0.0.07 |
| Arabinan in PRM (g/g PRM*) | n.d.** | n.d.** |
| Lignin recovered (g/g SCG) | 0.050±0.006 | 0.033±0.002 |

*PRM: solid polysaccharide-rich material recovered after DES treatment.
** n.d.: not detected.

Comparing the performances of the two tested DESs, a higher degree of delignification was obtained by DES 2, which can be traced back in the lower viscosity of the solvent and in the swelling action of water, which allowed a better penetration in the matrix. The solid after the pretreatment by both DESs resulted in highest yields of glucose after acid hydrolysis, making the compounds available to produce bioethanol, which, in the specific case, can be exploited also as biosolvent in the previous stage related to the antioxidant extraction. Lignin represents the by-product of the pre-treatment, and it can be further exploited for production of chemicals and biofuels. The lower amount of lignin separated from DES 2 compared to DES 1, despite the higher degree of delignification of the PRM, can be ascribed to the downstream operations and solvent properties, which implied losses of the lignin separated from SCG within the solvent. It is noteworthy noting that obtained results are in full agreement with the required targets of the conceptual biorefinery scheme anticipated in Figure 1.

## 5. Conclusions

In this preliminary work, a biorefinery based on SCG was proposed, analysing hierarchy of operations based on renewable and innovative solvents. SCG can be valorised by recovering high-added value compounds that can find applications in food, pharmaceutical and cosmetic industries by exploiting a GRAS and renewable solvents (ethanol 54%). The extraction residue can be further defatted providing coffee oil, which can used in the cosmetic sector or for energy production by transesterification. Bioethanol production can be the following destination of the extraction residue, and pre-treatment by DES allowed to increase the accessibility to cellulose and hemicellulose through delignification, enabling the possibility to replace acid hydrolysis with the more environmentally friendly enzymatic process. Albeit glucose, mannose, and galactose can be exploited in different processes, here bioethanol production was proposed due to the double role of the bio-solvent in HPTE process and as renewable energy vector in line with UN SDG 7 target.

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