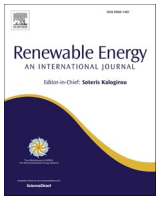
Renewable Energy 220 (2024) 119630

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene



# Platform chemicals recovery from spent coffee grounds aqueous-phase pyrolysis oil

L. Bartolucci [a], S. Cordiner [a], A. Di Carlo [b], A. Gallifuoco [b], P. Mele [a,*], V. Mulone [a]

[a] Department of Industrial Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1, 00133, Rome, Italy
[b] Department of Industrial and Information Engineering & Economics, University of L'Aquila, Piazzale Ernesto Pontieri 1, Monteluco di Roio, 67100, L'Aquila, Italy

ARTICLE INFO

*Keywords:*
Spent coffee grounds
Fast pyrolysis
Solvent extraction
Quinones
Biorefinery
Acetic acid

ABSTRACT

Spent coffee grounds (SCG) are a valuable biogenic waste diffused on a global scale, containing a significant amount of extractives. The aim of this study is to characterize the pyrolysis oil fractions, under various process conditions, targeting their potential applications as biofuels and source of valuable chemicals. Pyrolysis tests were carried out in the range of 400–550 °C with a laboratory-scale screw reactor and a two-step solvent extraction process, was conducted for the aqueous bio-oil phase. The results showed that heavy organic bio-oil resulted in a carbon rich biofuel, with a carbon content of up to 63 % (w/w) and HHV up to 34.8 MJ/kg. Chloroform was selective in extracting xantines (68–74 % of the peak area), furans, phenols, and fatty acids from the aqueous phase, while the ethyl acetate extract was abundant in p-benzoquinone (70–83 % of the peak area), a key-player chemical for the petrochemical industry. The residual unextracted water phase is very rich in organic acids i.e. acetic, propionic, and formic-whose concentration is in the range 47 g/L and 87.9 g/L. The results of this study outline how solvent extraction is a promising technique for extracting valuable chemicals to improve the economic potential of spent coffee grounds pyrolysis-based biorefinery.

## 1. Introduction

The shift to a circular economy has recently been supported by an increase in environmental consciousness and international collaboration for the sustainable use of natural resources [1]. With a focus on waste reduction and the selection of efficient disposal techniques, EU economic policies aim at reducing the environmental impact of manufacturing processes [2]. Recycling waste is a crucial aspect of the energy transition, as it lowers energy demand and related greenhouse gas emissions. Food sector wastes and residues can be used as carbon-based feedstock for biochemical and thermochemical processes to produce platform chemicals and bioenergy carriers [3–5]. [5].

Coffee is among the most consumed beverages in the world, with production exceeding 10 Tg/y and rising demand [1,5–7]. Cherry-containing coffee beans are produced by coffee plants; the production process for coffee involves a number of sub-processes, from harvesting down to the creation of soluble coffee powders, generating a massive amount of wastes, including coffee silverkin [8,9]. Spent coffee grounds (SCG), the ultimate by-products of the brewing process, are very desirable as biomass feedstock for the production of biofuels and chemicals [10,11]. SCG in fact contain typically useful classes of molecules such as lipids, which are more than 10 % of the dry feedstock's weight, and include linoleic, palmitic, oleic, and stearic acid, primarily-polyphenols, which include tannins and chlorogenic acids and are powerful antioxidants also to provide a variety of positive health effects [3,12,13]. Currently, SCG are disposed of in a variety of ways; studies have already demonstrated that incineration and landfilling should be avoided to reduce environmental risks and encourage mass recovery [9,14]. According to Limousy et al. [14], the combustion of SCG in boilers presents low efficiency and produces larger particulate matter emissions than wood pellets (a crucial problem of biomass combustion in general). Fernandes et al. [15] investigated the impact of spent coffee grounds on human and environmental health, coming to the conclusion that landfilling cannot be regarded as a safe disposal method.

A number of processes must be optimized and integrated due to the high heterogeneity and complexity of the classes [1,3,15] to sustainably recycle coffee grounds in the context of an integrated multiple-output biorefinery. Several authors have investigated about the extraction procedures for obtaining fat and polyphenols, which can then be converted into biodiesel platform chemicals for use in dietary supplements, cosmetics, and food derivatives [1]. However, despite achieving high extraction efficiency, large-scale extraction techniques are typically

* Corresponding author.
*E-mail address:* Pietro.Mele@uniroma2.it (P. Mele).

https://doi.org/10.1016/j.renene.2023.119630
Received 28 February 2023; Received in revised form 30 September 2023; Accepted 12 November 2023
Available online 15 November 2023
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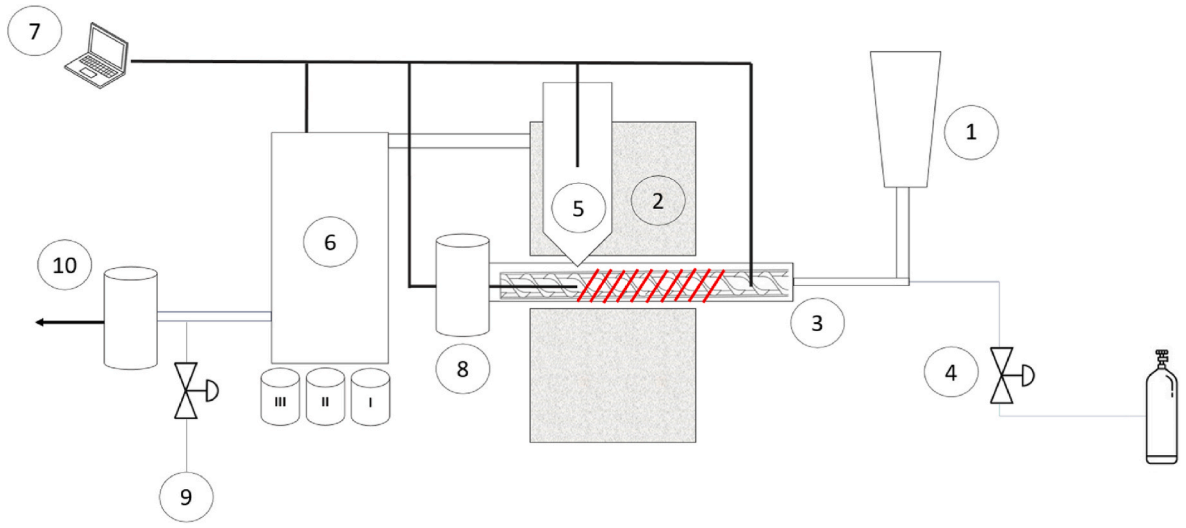


**Fig. 1.** Scheme of the shaftless screw reactor for fast pyrolysis tests, with the following components: 1 Feed Hopper; 2 Electrical-heated oven; 3 Shaftless screw driver; 4 Mass flow controller; 5 Sand filter; 6 Multistage water-glycol cooled condenser; 7 DAQ.

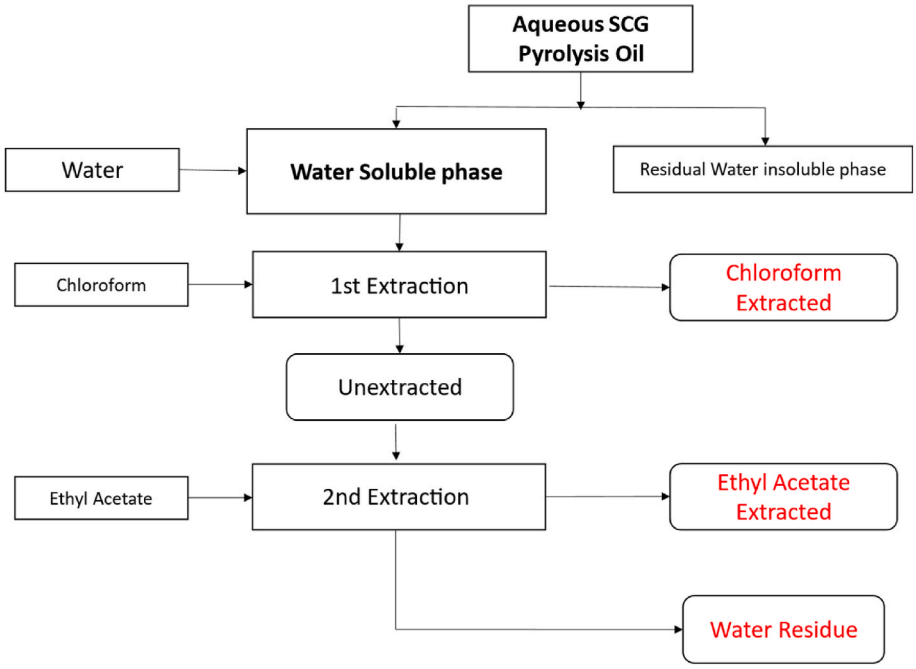


**Fig. 2.** Two-step solvent extraction procedure employed for characterization of SCG aqueous stream of pyrolysis oil.

expensive due to the usage of massive volumes of solvents, which also compromise the process' sustainability [17].

Thermochemical processes, on the other hand, are effective and economical in converting SCG into valuable by-products [3,19]. Fast pyrolysis is a well-established process and a developed technology breaking down biomass into three primary by-products: a solid charcoal, a liquid bio-oil and a non-condensable gaseous fraction, known as syngas. Setting the process temperature in the range between 400 and 700 °C and choosing an appropriate reactor design it is possible to control the relative product yield [17,18]. Different reactor configurations have been used for pyrolysis tests, including fixed bed reactors, fluidized bed reactors (bubbling, circulating, and spouted), ablative reactors (vortex and rotating cone), and auger reactors; all such reactor designs present specific characteristics and are more or less suitable to have high yields and quality of specific pyrolysis products [21]. Characterized by a high energy density, bio-oil is an intriguing product comprising more than 300 species of organic compounds grouped into various chemical classes, including phenols, aldehydes, ketones, acids, furans, esters, and anhydrous sugars [19,20,24]. Many authors reported that bio-oil fractionates into two phases: a viscous organic phase, collected in the bottom layer of bio-oil condensers and a light-brown aqueous phase with a high water content, measured in the range between 36 and 70 % [24]. After fractionation, the top water-soluble layer results rich in carbohydrate-derived compounds, while the bottom layer consists mainly of products from lignin depolymerization [25].

Several studies have focused on the extraction of chemicals from the aqueous fraction of bio-oil pyrolysis, since its use as a fuel is not advantageous [26,27]. Organic acids, sugars, aldehydes, furfural and phenolics are reported in the literature as the main chemical compounds contained in the aqueous phase [24]. Acetic acid is reported to be one of the most important chemicals with a broad spectrum of applications and is the dominant derivate of cellulose, hemicellulose, and lignin

**Table 1**
Feedstock characterization: ultimate and proximate analysis.

| Ultimate Analysis | Results |
|---|---|
| N (% wt.) | 2.13 (0.25) |
| C (% wt.) | 51.34 (0.50) |
| H (% wt.) | 6.91(0.29) |
| S (% wt.) | 0.08 (0.02) |
| O (% wt.)[a] | 39.54 |
| **Proximate Analysis** | |
| Moisture (% wt.) | 4.67 (0.05) |
| Volatile Matter $_{d.b.}$ (% wt.) | 76.73 (0.07) |
| Fixed Carbon $_{d.b}$ (% wt.) | 21.09 (0.08) |
| Ash $_{d.b}$ (% wt.) | 2.19 (0.01) |
| HHV (MJ/kg)[b] | 21.83 |

[a] Calculated by difference.
[b] Calculated using the following correlation the Dulong expression (1).

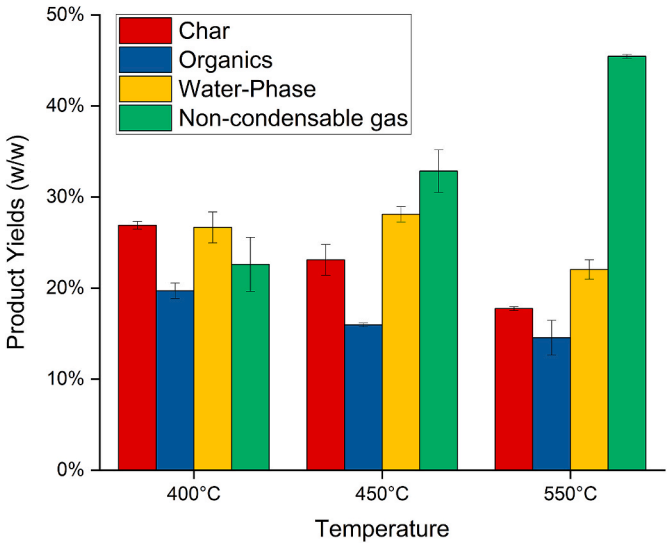


**Fig. 3.** Effect of pyrolysis temperature on spent coffee grounds products yield.

**Table 2**
Effect of pyrolysis temperature on heavy organic and aqueous phases yields (wt. %).

| Pyrolysis Temperature (°C) | Heavy Organic Phase (wt. %) | Aqueous Phase (wt. %) | Aqueous to Organic Ratio | Total Bio-Oil (wt. %) |
|---|---|---|---|---|
| **400°C** | 19.90 % (3.11) | 31.30 % (3.69) | **1.57** | **51.2 % (3.55)** |
| **450°C** | 15.90 % (2.95) | 28.30 % (6.02) | **1.78** | **44.2 % (5.15)** |
| **550°C** | 14.09 % (2.52) | 22.71 % (6.21) | **1.62** | **36.8 % (5.42)** |

degradation [28–30]. Different studies quantified acetic acid in the aqueous phase of bio-oil in the range between 76 g/L and 156 g/L, highlighting how an extraction procedure appears to be cost-effective [31]. Functionalized phenolics, the main products of lignin degradation, are reported in the literature [32,33]. Quinones, in particular hydroquinone and benzoquinone, are two widely used chemicals in industrial activities as electrochemical mediator in enzymatic and non-enzymatic processes, inhibitors, intermediates for the synthesis of dyes, cosmetics and medical preparations [34,35]. Catechol (benzene-1, 2-diol) is a diffused chemical platform used in the industry of pesticides and pharmaceuticals.

The pyrolysis of SCG has already been investigated by different authors, who evaluated the impact of the process temperature and the residence time on product yield and composition [13,21]. However, there are no studies available in the current literature on SCG pyrolysis oil fractionation and characterization targeted both to energy utilization and biorefinery applications. The aim of this study is then to identify the most advantageous strategies for the sustainable use of the organic and aqueous fractions of the SCG pyrolysis oil, such as liquid biofuels and sources of platform chemicals for industrial applications. To demonstrate this, the spent coffee grounds were first pyrolyzed in a lab-scale screw reactor in the temperature range between 400 and 550 °C and the bio-oils were fractionated into heavy-organic and aqueous phases. A sequential liquid extraction procedure was then applied to the aqueous phase of the bio-oil samples to understand the affinity of the main organic compounds to various solvents (chloroform and ethyl acetate), assessing the potential recovery of specific chemicals. Finally, the chemical composition of the condensates was determined through gas chromatography-mass spectroscopy analysis for the solvent extracts and HPLC analysis for the unextracted water phase.

## 2. Materials and methods

### 2.1. Materials

Chloroform (HPLC Grade; 99.5 %, stabilized with amylene) ethanol (99.8 % with 1 % MEK) and ethyl acetate were purchased from Merck (Darmstadt, Germany). SCG were collected from the coffee shop of the school of engineering at the University of Rome 'Tor Vergata'. The feedstock was dried for 12 h in a static oven at 105 ∓ 1 °C before testing, sieved to obtain a uniform particle size with a mesh between 500 and 850 μm diameter.

### 2.2. Reactor and pyrolysis experiment

A lab-scale screw reactor was employed to perform the fast pyrolysis experiment on SCG (Fig. 1). A feed-hopper feeds the system with an adjustable mass flow rate in the range between 100 and 500 g/h. The reactor is a horizontal tube with external diameter of 20 mm, thickness of 1 mm and length of 500 mm made of stainless steel AISI 304, while the reaction zone is 150 mm long. The screw conveyor, made of AISI 304 as well, is shaftless to control the gaseous residence time while improving the bio-oil yield at the same time. A variable speed motor controls the rotation rate of the screw and in turn the nominal residence time of the solid biomass into the reactor. Heat is provided through a 1.4 kW NiCr mini-tubular electrical resistor supplied by BL Sistemi s.r.l ® (Italy). The solid residue of the process, char, is conveyed to a collector bucket, while the volatiles pass through a silica bed filter, maintained at the temperature of 400 °C to avoid tar condensation. A three-stage quenching system is included in the setup for fractional condensation and collection of the bio-oils. The temperature of the condensation stage is kept constant by a cooling system based on water and ethyl alcohol solution (50:50) kept at −10 °C, flowing counter-current to the vapours. The flow rate of the cooling solution is set in such a way that the volatiles in the first stage condense between 280 and 90 °C, in the second one between 90 °C and 35 °C, while in the last stage between 35 °C and room temperature. Finally, the residual fraction of non-condensable gas is burned in a torch. Other technical specification on reactor designare available in previous works [37]. Before each test, the system is heated up to the target process temperature. A nitrogen flow rate of 0.5 NL/min is measured by an Aalborg GFC mass flow controller and kept constant throughout the duration of the test. The reactor was operated to have a nominal residence time of the solid biomass in the reaction zone of 5s,

**Table 3**
Elemental analysis of the heavy-organic phase and calculation of HHV (MJ/Kg).

| | This study | | | Reference | | |
|---|---|---|---|---|---|---|
| | | | | [41] | [13] | [36] |
| Temperature | 400 °C | 450 °C | 550 °C | 450 °C | 500 °C | 400–600 °C |
| **N (% wt.)** | 1.45 (0.01) | 1.89 (0.21) | 2.81 (0.15) | 2.60 | 0.80 | 3.06 |
| **C (% wt.)** | 63.99 (0.2) | 63.39 (0.23) | 59.65 (0.19) | 74.0 | 44.97 | 54.27 |
| **H (% wt.)** | 11.28 (0.36) | 10.20 (0.13) | 9.64 (0.44) | 9.80 | 12.03 | 7.41 |
| **S (% wt.)** | 0.07 (0.03) | 0.10 (0.07) | 0.17 (0.02) | 0.17 | 0.12 | 0 |
| **O (% wt.)** [a] | 23.20 | 20.58 | 27.73 | 13.4 | 42.07 | 35.26 |
| **HHV**[b] (MJ/kg) | 34.81 | 33.36 | 30.34 | 32.3 | – | 12.04–23.19 |

[a] Calculated by difference.
[b] Calculated using the following correlation the Dulong expression (1).

**Table 4**
Elemental analysis of the aqueous phase and calculation of HHV (MJ/Kg).

| Temperature | 400 °C | 450 °C | 550 °C |
|---|---|---|---|
| **N (% wt.)** | 1.04 (0.10) | 1.16 (0.04) | 1.68 (0.06) |
| **C (% wt.)** | 12.43 (0.24) | 12.86 (0.30) | 11.55 (0.54) |
| **H (% wt.)** | 10.75 (0.23) | 10.75 (0.64) | 10.54 (0.22) |
| **S (% wt.)** | 0.10 (0.07) | 0.10 (0.08) | 0.08 (0.01) |
| **O (% wt.)**[a] | 75.66 | 75.11 | 76.15 |
| **HHV**[b] (MJ/kg) | 9.83 | 10.05 | 9.16 |

[a] Calculated by difference.
[b] Calculated using the following correlation the Dulong expression (1).

and a capacity to process 300 g/h of feedstock. A data acquisition LabVIEW system is used to monitor temperatures of the system and sweeping gas flow rates. At the end of each test, the yields of char and bio-oils collected in the various columns are calculated gravimetrically, while the yield of non-condensable gases by difference. The organic and aqueous phases did not naturally separate as reported in many other studies on lignocellulosic biomasses. Therefore, particular care was taken to quantify the two fractions, taking advantage of the different castability of the two fractions as soon as the test was completed. Then, the bio-oil samples were kept in the refrigerator at 5 °C for further analysis. Tests were repeated and the standard deviation was calculated according to the three most significant results.

### 2.3. Solvent extraction procedure

As stated above, a liquid-liquid extraction process was carried out to study the chemical composition of various bio-oil condensates. A method similar to the one suggested by Wei et al. and with the solvents indicated by Ren. et al. for effective extraction of the main organic classes, a two-step solvent extraction procedure was employed, as described in Fig. 2 [38,39]. The method involved the mixing of an aqueous bio-oil phase representative sample (5 g) with 20 g of distilled water, vigorously shaking the mixture with a mini vortexer, storing the mixture in the refrigerator overnight at 5 °C, and centrifuging the mixture for 30 min at 2400 rpm. Adding water to the aqueous bio-oil phase was useful to remove traces of water insoluble fraction within the water soluble one, before the beginning of the solvent extraction process. The water-soluble fractions of the bio-oils, or those not adhered to the inner wall of the centrifugal tube, were employed for subsequent solvent extraction after centrifugation [38]. Phase separation was achieved by adding 20 mL of bio-oil samples to the solvent in an Erlenmeyer flask, magnetically stirring for 30 min, transferring the mixture to a separatory funnel, and leaving the mixture at rest for 24 h. With a volumetric ratio 2:1, chloroform was employed for the first extraction phase. Following separation, the chloroform solvent phase was recovered, and the left aqueous fractions were used for the second step of solvent extraction using the same method. The left unextracted aqueous fractions were stored in the refrigerator for further HPLC analysis while the ethyl acetate extracted fraction was analyzed with the GC-MS.

### 2.4. Analytical methods

The thermo-gravimetric analysis was carried out according to the ASTM E914 using the instrument TGA701 built by LECO Corp and evaluating the results according to the UNI EN ISO 18122:2016, ISO 18122:2015 and the ISO 18123:2015 The thermal program followed was the following: 10 °C/min heating ramp from ambient temperature to 105 °C for moisture determination held until constant mass is obtained, 15 °C/min under nitrogen atmosphere up to 550 °C for the determination of volatile matter and final 15 °C/min ramp under nitrogen and oxygen atmosphere for ash evaluation. Fixed carbon was evaluated by difference.

The CHNS(O) analysis was performed with Elemental Macro's Vario MACRO-cube analyzer, using the "coal50" standard, with flash burning of the samples with a temperature column of 1150 °C (FLASH 2000 – Organic Elemental Analyzer) on about 20–50 mg of milled sample. The test and the instrument calibration with the Sulfanilamide standard was carried out according to the ISO 16948:2015. For the analysis of liquid samples, tungsten oxide was used as sorbent.

For the quantification of high heating values (HHV) of biochar and bio-oil samples, the Dulong equation was employed (1) to take in account the nitrogen and sulfur contribution to the energy value of the feedstock and the products [36]:

$$HHV\ (kJ/kg) = 4.184 \bullet (78.31\ C + 359.32 \bullet (H - O/8) + 22.12\ S + 11.87 \bullet O + 5.78\ N) \quad (1)$$

The chemical composition of the extracted bio-oils was determined by the Shimadzu GC/MS (QP2010SE) equipped with an Equity® 5 capillary column (30 m × 0.25 mm × 0.25 μm). The samples were prepared for the analysis dissolving 0.5 mL of extracted solvent phase into 5 mL solution of ethanol and filtering before the injection using a 0.45 μm PTFE syringe filter to remove the suspended particles. The GC was programmed by maintaining 50 °C for 3 min, followed by heating to 310 °C at a heating rate of 15 °C/min and held at the final temperature for 30 min. The injection took place at 200 °C in a split mode, injecting 1 μL sample. The flow rate of the carrier gas (He) was adjusted at 1.99 mL/min. The ion source temperature was 230 °C and the interface temperature 280 °C for the mass selective detector. Data were acquired in 50–500 m/z scan mode. A solvent cut at 5 min was applied to protect the MS from solvent shock. Identification of compounds was performed by comparing the mass spectra of the peaks with standard spectra of other

**Table 5**
GC-MS analysis of the chloroform extracted water-soluble bio-oil aqueous phase: effect of pyrolysis temperature on the principal compounds identified (peak area %).

| Organics Identified | Peak Area (%) | | |
|---|---|---|---|
| | 400 °C | 450 °C | 550 °C |
| **N-containing compounds** | | | |
| Caffeine | 74.22 % (0.9) | 68.81 % (1.5) | 68.49 % (0.9) |
| **Ketones** | | | |
| 1,2-Cyclopentanedione, 3-methyl | 3.19 % (0.1) | 4.68 % (0.3) | 6.63 % (0.2) |
| 2-Cyclopenten-1-one, 2,3-dimethyl | 0.61 % (0.1) | 1.15 % (0.1) | 1.33 % (0.2) |
| 2-Cyclopenten-1-one, 2-methyl | 1.37 % (0.1) | 1.96 % (0.4) | 1.82 % (0.2) |
| 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy | 0.98 % (0.2) | 0.68 % (0.3) | 0.95 % (0.1) |
| 2-Cyclopenten-1-one, 3-methyl | 1.87 % (0.1) | 2.66 % (0.8) | 3.84 % (0.1) |
| **Aldehydes** | | | |
| *cis*-9-Hexadecenal | – | – | 0.08 % (0.1) |
| 9-Octadecenal, (Z)- | 0.48 % (0.2) | 0.98 % (0.2) | – |
| **Furans** | | | |
| 2-Furanmethanol (Furfuryl alcohol) | 5.10 % (0.2) | 7.57 % (0.9) | 3.35 % (0.1) |
| 2(5H) -Furanone | 3.28 % (0.4) | 4.45 % (0.3) | – |
| **Esters** | | | |
| 2-Propenoic acid, pentadecyl ester | | | 0.87 % (0.2) |
| Stearic acid, allyl ester | – | 0.29 % (0.4) | 1.66 % (0.2) |
| **Fatty Acids** | | | |
| n-Hexadecanoic acid | 3.71 % (0.2) | 0.42 % (0.2) | 0.19 % (0.1) |
| 9-Octadecene, (E) | – | – | 0.18 % (0.1) |
| 9,12-Octadecadienoic acid (Z,Z) (Linoleic acid) | 1.21 % (0.4) | 0.98 % (0.2) | – |
| Octadecanoic acid (Stearic acid) | 0.59 % (0.1) | 0.79 % (0.9) | – |
| **Alkanes** | | | |
| Tridecane | 0.70 % (0.2) | 0.66 % (0.1) | 0.06 % (0.1) |
| **Phenols** | | | |
| Phenol | 2.69 % (0.3) | 3.93 % (0.1) | 5.38 % (0.5) |
| Phenol, 2-methyl (o-Cresol) | – | – | 1.06 % (0.2) |
| Phenol, 3-methyl (m-Cresol) | – | – | 2.98 % (0.4) |
| **Carbohydrates** | | | |
| 1,4:3,6-Dianhydro- alpha -d-glucopyranose | – | – | 0.45 % (0.1) |

compounds using the NIST library to obtain the most probable matches (quality match superior to 85 %). The study reported a qualitative analysis of the main organic compounds, considering for each chemical species the concentration as the ratio between the peak area associated with the ith-species compared with the total area of the identified peaks. For each sample, the solvent extraction process and the GC-MS analysis were at least duplicated for accuracy and reproducibility of the data presented.

HPLC analyses were carried out with a Waters–Alliance E2695 separation module. Before injection, samples were filtered using a 0.45 μm PTFE syringe filter. Organic acids were separated with a Waters Atlantis dC18 (3 μm −100 A° −150 × 4,6 mm, 30 °C) column; mobile phase 20 mM $Na_2HPO_4$ 20 in phosphoric acids (pH = 2.7, 0.5 ml/min). Chemicals were detected with the UV–Vis detector (Waters 2489, 210 nm). Calibration with standard pure chemicals solutions allowed to compute the concentrations detected in the samples assayed by HPLC. Samples were injected with a 1:20 dilution ratio with the mobile phase.

## 3. Results and discussion

### 3.1. Product yields

The results of the SCG feedstock characterization after drying, as specified in the method section, are reported in Table 1. In Fig. 3 the average value of product yields of the pyrolysis tests performed with the screw reactor are reported. As expected, the increase of dehydration, decarboxylation and depolymerization reaction rates with the temperature led to a monotonous reduction of the char yield (ranging from 27.0 % to 17.8 %): a similar trend was reported in a previous study of Bok et al. [36]. The total bio-oil yield is maximum at 400 °C, with a yield of 51.2 %, that is a value in line with other studies on spent coffee grounds fast pyrolysis [13–21]. Non-condensable gas yield increases steadily within the temperature range investigated, due to the enhancement of secondary tar cracking reactions [19]. The gas yield values were higher than those reported in the literature for the fast pyrolysis of SCG; this could be due to slight over-temperatures in given areas of the reactor.

Table 2 reports on the effect of pyrolysis temperature on the bio-oil fractions yields. Pyrolysis oil can be considered composed of a water-soluble phase (aqueous fraction in this study) and a water-insoluble (heavy organic) composed by oligomers with higher molecular weight, i.e. pyrolytic lignin-not completely depolymerized. For SCG, the fractionation of pyrolysis oil into such phases does not occur spontaneously, but requires extra processes [3,36]. As shown in the table, while the yields of the fraction in mass decrease as the process temperature is increased, the aqueous to organic ratio holds constant, as it is also reported in the paper by Primaz et al. [40]. The yields of the aqueous phase are consistent with the ranges reported in the literature for lignocellulosic biomass fast pyrolysis i.e. 15-75 wt% of the total pyrolysis oil [24].

### 3.2. Bio-oil composition

Table 3 and Table 4 report on the elemental composition of the heavy organic and aqueous phases of SCG pyrolysis oil at the temperature of 400, 450 and 500 °C. By comparison between the two tables, it is evident that the whole bio-oil is rather heterogeneous and the subdivision of the two fractions is crucial to carry out both the carbon and energy balances of the whole energy system.

An interesting outcome of this study is in fact that the heavy organic phase is characterized by high carbon and hydrogen content, leading to a rather high estimation of the HHVs, calculated in this study with the modified Dulong expression, that is reported in the method section. The carbon content of the organic bio-oil phase exceeds the 59 % wt. in all the conditions tested, with a maximum value of 63.99 % at 400 °C. On the other hand, the hydrogen content undergoes a reduction with temperature. The values for the elemental composition shown in Table 3 are

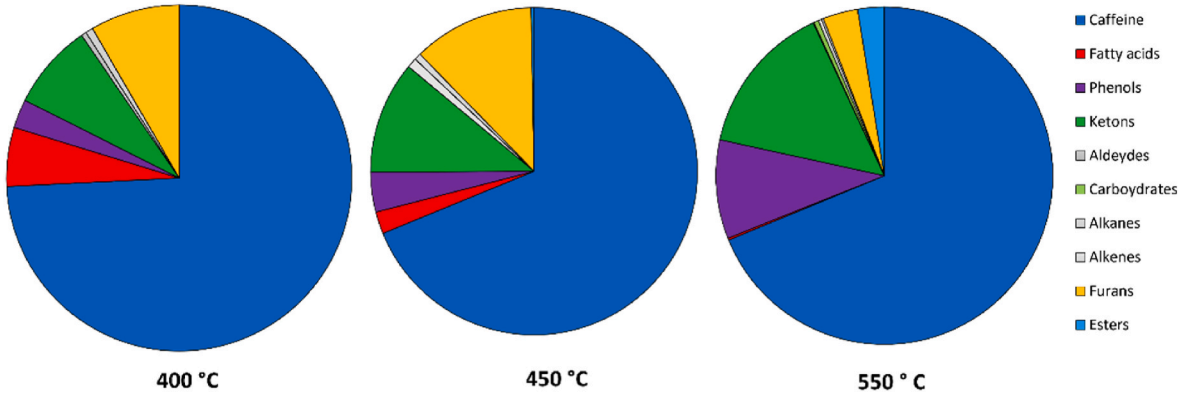


**Fig. 4.** Effect of pyrolysis temperature on the organic classes identified form GC-MS analysis of the chloroform extracted aqueous bio-oil.

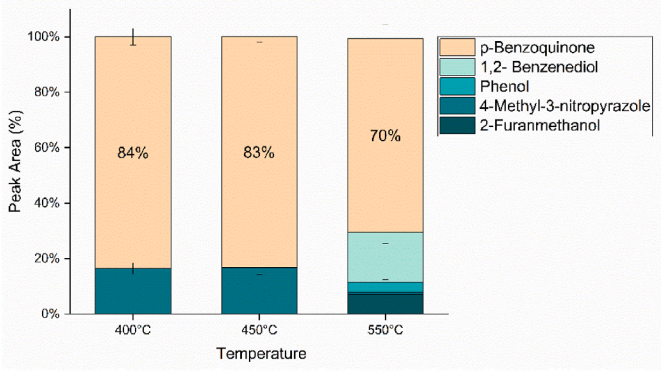


**Fig. 5.** Effect of pyrolysis temperature on the selectivity of ethyl acetate for p-benzoquinone extraction.

similar to those reported by Vardon e al [41]. However, in the studies of J.P. Bok et al. [36] and S. Kelkar et al. [13] the carbon, hydrogen and energy content of the bio-oil appears slightly lower. Both heavy organic and aqueous phases are characterized by high nitrogen content, due to the high content already present in the biomass feedstock, with nitrogen content increasing with the pyrolysis temperature in the heavy organic phase. The aqueous phase composition is stable with temperature and presents on average 12 % w.t. carbon and over the 74 % w.t. oxygen, suggesting a high water content. The elemental composition of the aqueous phase, reported in Table 4, is in line with the values for palm shell aqueous fraction (C 15.3 wt %, H 11.58 wt % and O 72.9 wt %) reported by Abnisa et al. [24] Thus, the aqueous bio-oil fraction HHVs results limited: the aqueous stream utilization for chemicals recovery is investigated in the next sections.

### 3.3. Sequential extraction by chloroform and ethyl acetate

As mentioned in the methods section, a sequential solvent extraction procedure was carried out to fractionate the molecules solubilized in the aqueous phase of the bio-oil into various groups, based on their affinity. The results of the first step of the solvent extraction procedure, in chloroform, for the aqueous phase outlined in Fig. 2 are shown in Table 5, where a list of the principal compounds identified in the chloroform extracts is reported. Caffeine is the dominant compound of the aqueous fraction, presenting at the various pyrolysis temperatures a relative peak area percentage greater than 68 %. Moreover, caffeine abundance presents a negative trend with temperature. E. Lazzari et al. [22] and C.Primaz et al. [40]reported the distribution of classes of compounds in the SCG and coffee silverskin pyrolysis oil. Caffeine did not result so abundant; however their analysis was focused only on the

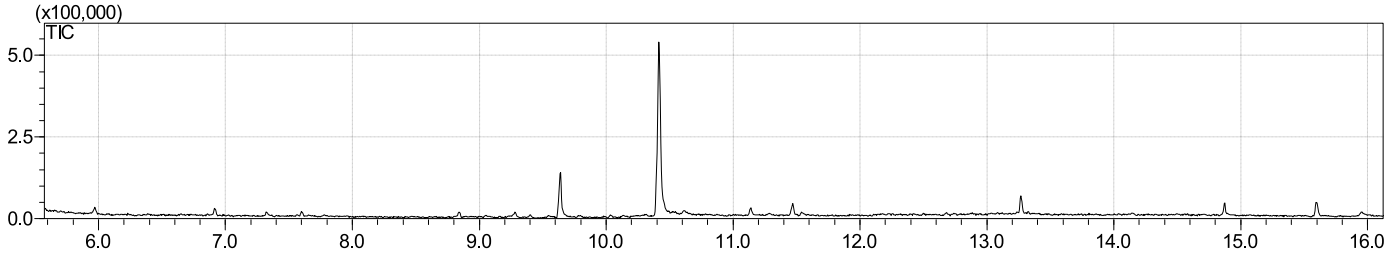


**Fig. 6.** Spectrum of GC-MS analysis of ethyl acetate extracted aqueous phase pyrolysis oil at 550 °C.

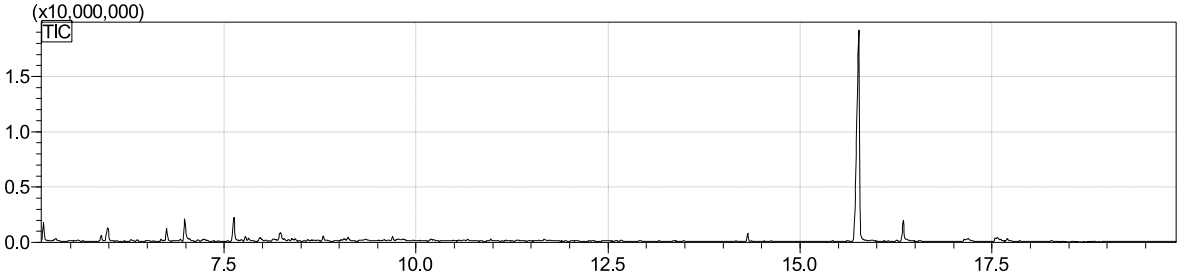


**Fig. 7.** Spectrum of GC-MS analysis of chloroform extracted aqueous phase pyrolysis oil at 550 °C.

**Table 6**
HPLC analysis and quantification of organic acids yield in the water residue from SCG aqueous-phase solvent extraction.

| Organic Acids Quantified | 400 °C | 450 °C | 550 °C |
|---|---|---|---|
| Formic acid (g/L) | 21.6 ± 0.6 | 18.8 ± 0.2 | 17.2 ± 1.4 |
| Lactic acid (g/L) | 5.7 ± 1.4 | 4.0 ± 0.4 | 3.8 ± 0.2 |
| Acetic acid (g/L) | 54.1 ± 3.9 | 34.8 ± 4.1 | 21.9 ± 1.8 |
| Propionic acid (g/L) | 6.5 ± 0.9 | 5.6 ± 1.6 | 4.1 ± 0.6 |
| **Total organic acids (g/L)** | **87.9 ± 6.8** | **63.2 ± 6.3** | **47.0 ± 4.0** |
| Aqueous Phase Yield (wt. %) | 31.3 % ± 3.69 % | 28.3 % ± 6.02 % | 22.7 % ± 6.21 % |
| Total yield of organic acids (g acid/g SCG) | 2.75 % ± 0.02 % | 1.79 % ± 0.03 % | 1.07 % ± 0.03 % |

organic phase.

Ketones are mainly derived from the depolymerization of hemicellulose (cyclopentenone and other methylates/ethylates of cyclopentenone are the main identified compounds for ketons), the main biopolymer reported for dried SCG [42]. According to the studies of Thangalazhy-gopakumar et al. [43] there was a sudden increase in the concentration of 3-methyl 2-cyclopenten-1-one by increased temperature.

Long-chain fatty acids/aldehydes such as palmitic, oleic and stearic acids, were reported to be the most abundant compounds from Lazzari et al. and Primaz et al. for SCG bio-oil, and are present only in limited amounts [22,40]. This is probably due to highly abundant fatty acids in the heavy-organic fraction, whose GC-MS analysis was not the strict object of this study. As found by Bok et al. [36] in fact, there is a strong link between the fatty acids content and energy content of the bio-oil, and therefore the heavy organic phase is expected to be rich in those compounds. However, a slight increase of fatty acids abundance appears remarkable for the chloroform extract at 400 °C.

Furanic compounds, whose peak area range lies between the 3.35 % and 12.10 %, are products generated by the dehydration of carbohydrates. A similar percentage area was reported by P.Kim et al. [44] in the GC-MS analysis carried out on pine wood pyrolysis oil.

Phenol peak area rises with temperature, similar to the trend highlighted in the study of A. Demirbas et al. for a wide broad of feedstocks. Thangalazhy-gopakumar et al. [43]outlined an increase of cresol concentration with the pyrolysis temperature.

A more compact view of the main classes of compounds constituting the extract in chloroform of the aqueous fraction of bio-oil is reported in Fig. 4 and the spectrum of the GC-MS analysis of a typical sample is shown in Fig. 7. Fig. 4 shows clearly that chloroform is highly selective towards the extraction of ketones, phenols and furans, the most abundant classes in the extracted fraction. S.Ren et al. [39] obtained similar results on the solvent extraction of the aqueous fraction of switchgrass pyrolysis oil, using chloroform as solvent and a solvent to oil equal to 1. Similarly, Y. Wei et al. [38] carried out a screening procedure among various organic solvents, both polar and non-polar, on the extraction efficiency towards molecule classes of Douglas fir pellet water-phase of pyrolysis oil. They found out that chloroform was very effective in extracting guaiacols, furans and esters.

Another outcome of this study is the high selectivity of ethyl acetate towards specific chemicals in the second step of solvent extraction. Fig. 5 in fact summarizes the main chemicals identified in the ethyl acetate extracted from SCG aqueous oil at the various process temperatures and Fig. 6 is the chromatogram of the GC-MS analysis. As Fig. 6 clearly shows, ethyl acetate was very selective to extract specific molecules, for all the cases. There is a noteworthy relative abundance of p-benzoquinone i.e. in the range of 69 % and 83 % of peak area, a key-player chemical for pharmaceutical/pesticide intermediates, as previously stated [33–45]. In the case of 400 °C and 450 °C, where the selectivity for p-benzoquinone is very high, the presence of residual phenol is also evident. However, a 550 °C, p-benzoquinone selectivity is lower (69 % peak area), but 1–2 benzenediol (pyrocatechol), a platform chemical with plenty of industrial applications. S.Ren et al. [39] highlighted how the second extraction step in ethyl acetate, after the first one in chloroform, was selective for 1–2 benzenediol recovery, whose residual concentration in the water unextracted was very low. Therefore, a potential precipitation and recovery appears feasible for the small number of molecules identified in the GC-MS analysis.

Table 6 reports on the results of the HPLC analysis of water residues after extraction of the SCG aqueous-phase pyrolysis oil. The analysis was targeted to identifying and quantifying the organic acids, considered the main species for abundance in the aqueous fractions of pyrolysis oil [24]. The results show high abundance of acetic acid (21.9 g/L −54.1 g/L), formic acid (17.2 g/L – 21.6 g/L), propionic acid (4.1 g/L - 6.5 g/L) and lactic acid (3.8 g/L – 5.7 g/L). Table 6 outlines how, for all the organics, there is a drop in concentration by increased temperature. A similar trend in the composition of the aqueous-phase pyrolysis oil is reported for a wide variety of feedstocks [31].This evidence can be explained by considering that acetic acid is a heat-labile product, thus it is susceptible to cracking reaction at higher temperatures. Table 6 reports on the yield of organic acids in the unextracted water fraction, with respect to the original feedstock. The values lie in the range between 1.1 wt % and 2.7 wt %. These results are in line with the data presented by A. S. Pollard et al. [46], where acetic and formic acids represented the 5 wt % and 3 wt% of bio-oil respectively. Similarly, Q. Lu et al. [47] found a yield of acetic acid in the range of 3–4 wt % for four lignocellulosic biomass. However, in that case, the yield was calculated on the whole bio-oil, and not for the aqueous fraction only. Propionic acid concentration in the unextracted water fraction is in line with the values reported by S.Ren et al. [39]. Given the high amount of organic acids in the unextracted water phase of bio-oil, a further step of solvent extraction step appears very promising.

## 4. Conclusions

This study was focused on the characterization of spent coffee grounds pyrolysis oil and the fractionation of the water phase through a two-step liquid-liquid extraction. The elemental analysis outlined that organic bio-oil phase is an energy-dense and carbon-rich biofuel, while the aqueous phase is abundant in oxygenated compounds. The GC-MS analysis revealed that the chloroform employed in the first extraction step of SCG aqueous-phase of bio-oil is selective towards xanthines (caffeine), ketones, furans and phenols. The fraction subsequently extracted in ethyl acetate is rich in p-benzoquinone, a platform chemical used in diverse applications for the petrochemical industry. High quantities of organic acids - acetic, propionic, and formic- are present in the unextracted aqueous residue. This study then demonstrates that liquid-liquid extraction is a promising strategy to increase the value of SCG pyrolysis products, thus improving the economic potential of SCG pyrolysis-based biorefinery.

## CRediT authorship contribution statement

**L. Bartolucci:** Conceptualization, Investigation, Data curation, Supervision, Resources, Writing – review & editing. **S. Cordiner:** Supervision, Resources. **A. Di Carlo:** Methodology, Investigation. **A. Gallifuoco:** Methodology. **P. Mele:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **V. Mulone:** Conceptualization, Data curation, Supervision, Resources, Writing – review & editing.

## Declaration of competing interest

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

## Acknowledgements

The authors would like to acknowledge Salvatore Ricotta (University of Rome 'Tor Vergata') for the key technical support to develop the setup of the pyrolysis reactor. We would like also to thank BL Sistemi s.r.l (Italy) for the technical assistance for the experimental set-up, the employees of the Coffee Bar of the school of Engineering for supplying the feedstock. Special thanks to the technicians of the Dept of Industrial Engineering at the University of L'Aquila for the HPLC analysis.

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