



Defatted spent coffee grounds fast pyrolysis polygeneration system: Lipid extraction effect on energy yield and products characteristics

L. Bartolucci, S. Cordiner, P. Mele^{*}, V. Mulone

Department of Industrial Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1, 00133, Rome, Italy

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ABSTRACT

Spent coffee Grounds (SCG), residues after coffee brewing, are a biowaste diffused on a global scale rich of valuable extractives. Pyrolysis is an efficient process to valorize SCG energy content into biofuels. This study aims to experimentally investigate the impact of lipid extraction and conversion to biodiesel on energy yield of pyrolysis products. Microwave-assisted lipid extraction method was employed, and a two-step transesterification process was considered for conversion into biodiesel. Fast pyrolysis of defatted spent coffee grounds (DSCG) was performed with a 300 g/h screw reactor at the temperatures 400 °C and 550 °C. The results show an important impact of pyrolysis temperature on energy distribution of the pyrolysis products. The energy content of the organics from DSCG pyrolysis is very high (up to 32 MJ/kg) and the oxygen content is significantly reduced to 26%. Non-condensable gas composition is enriched of hydrogen and methane with temperature rise. Biodiesel energy contribution significantly improve the energy yield of the pyrolysis system, leading to a more than 10% increase of the energy efficiency at a 550 °C, while a limited increase of 4% in the case of 400 °C. This study outlines how lipids extraction significantly increases the economic potential of SCG pyrolysis-based polygeneration energy system.

1. Introduction

According to the IEA, in 2021 CO₂ emissions reached an all-time record of 36.3 Gt and are mainly related to fossil fuels combustion for power generation, industry and transportation applications [1]. Among renewable energy sources, biomass is the most widely used in Europe and there is a significant unexploited and sustainable biomass potential among agriculture crop residues and bio-waste [2,3]. To increase the attractiveness and share of bioenergy products, biomass can be converted into biofuels through thermochemical processes such as torrefaction, pyrolysis, and gasification [4,5]. Pyrolysis is the only process that can convert the feedstock into three products - bio-oil, char and non-condensable gas - whose yields that can be adjusted adequately setting the operating conditions - i.e. temperature, heating rates, and residence time [4]. Bio-oil is a tarry liquid biofuel that contains a large mixture of oxygenate molecules and hydrocarbons [6]. According to its heterogeneity, bio-oil condensation takes place over a wide range of dew points [7]. Fractional condensation is an advantageous method to recover first condensates with higher organic fraction, leaving high water content in the last condensing stages [8,9]. Various strategies can

be applied to increase the bio-oil value and for compatibility with a wide range of applications, among which the catalytic hydrotreatment is considered the most beneficial for optimum bio-oil quality [10,11].

Polygeneration systems use flexibility in the diversification of output products to maximize both value and conversion rate of residual biomass waste [4,12,13]. In addition, feedstock flexibility enables polygeneration systems to process a wide range of available biomass sources [13,14]. Various studies focused on pyrolysis-based polygeneration systems demonstrated that at optimized operating conditions, high-quality products can be obtained and used as biofuels or materials for diverse industrial applications [14].

Coffee is a widely diffused agricultural global product and its production is estimated at 8 Tg/y [15]. Different waste streams are generated during coffee processing, such as husks and silverskins, but most of the waste material is spent coffee grounds (SCG), the residual fraction of the brewing process. Soluble coffee industry represents almost 50% of the world coffee production, with a proportional amount of spent coffee residues [16,17]. Therefore, the logistics of collection of the feedstock for energy valorization is a reasonable and valid practice [16]. Ecotoxicological issues have been originated from the mismanagement of SCG

^{*} Corresponding author.

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

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disposal [17]; therefore, SCG utilization for energy purposes is a promising alternative [42].

Spent coffee grounds are a lignocellulosic feedstock – i.e., containing mainly hemicellulose, lignin and cellulose – rich in valuable extractives such as lipids 15% (w/w), polysaccharides, polyphenols and proteins [18,19]. Great attention has been paid to the conversion of lipids from SCG into biodiesel and glycerol via transesterification and co-production of biodiesel and pyrolysis deriving bioenergy carriers is a highly efficient valorization strategy of coffee waste [19–23]. Al-Hamamre et al. reported that considering a quantity of lipids extractable from coffee waste of 14% (w/w) %, the use of the oil extracted from SCG could add 1123 M Tg of biodiesel to the annual global fuel consumption [24]. Moreover, biodiesel produced from SCG has been recognized to meet the requirements of the American biodiesel standard [25]. Various extraction techniques and various polar and nonpolar solvents were investigated to maximize extraction yields such as Soxhlet extraction, ultrasonic and microwave extraction [26]. Microwave-assisted extraction has been widely used for its rapid feedstock heating, high extraction efficiency, and reduced organic solvent consumption [26]. Biodiesel synthesis from SCF extracted oil can be performed through a one-step or two-step transesterification process [24]. The difference among the two methods is that one-step transesterification is the direct processing of SCG, without prior lipid extraction (in-situ approach), while a lipid extraction is required from the conventional two-step transesterification method. Several studies demonstrated that a two-step transesterification method reach a rather high conversion yield and a biodiesel product of good quality.

Various studies have explored thermochemical processes to valorize the energy content of spent coffee grounds. Lazzari et al. explored the effect of temperature on the product yield of spent coffee grounds pyrolysis in a fixed-bed reactor and analyzed bio-oils by GC × GC/TOF-MS associated with LTPRI. They found that bio-oil is a mixture rich in highly valuable chemicals and a potential platform to be converted into second generation biofuels [27]. Kelkar et al. carried out spent coffee grounds pyrolysis with a pilot-scale screw-conveyor reactor and found out an increase of liquid yield with decreasing residence time and an increase in temperature up to 505 °C. Finally, they concluded that SCG is an ideal bioenergy feedstock for conversion to high value energy carriers [19]. Vardon et al. studied slow pyrolysis of spent coffee grounds into a batch reactor, considering the impact of lipids extraction on the product characteristics [28]. However, the non-condensable gas energy content was not considered, and an overall energy balance was not carried out properly.

Based on the literature review, this study aims at understanding the impact of lipid extraction and conversion into biodiesel on yield improvement and the economic potential for spent coffee grounds pyrolysis process. Microwave-assisted extraction method was employed for lipids extraction from spent coffee grounds. Based on literature data, a two-step transesterification was modeled for the conversion of lipids extracted to biodiesel. A lab-scale screw reactor was employed for fast pyrolysis of spent coffee grounds/defatted spent coffee grounds in the temperature range of 350–550 °C. Finally, an overall energy balance of the pyrolysis and transesterification integrated processes was performed, evaluating the convenience of the lipid extraction and conversion to biodiesel in terms of product yield and energy efficiency. No studies were carried out on this specific topic, and very limited works are available on defatted spent coffee grounds pyrolysis to the best of our knowledge, as also stated in A.E. Atabani et al. [29].

2. Materials and methods

2.1. Materials

Hexane (HPLC Grade; 99%, mixed isomers) was purchased from Merck (Darmstadt, Germany). Spent coffee grounds (blend of arabica/robusta 40:60 by weight, as specified by the producers) were collected

Table 1
Operating condition for the pyrolysis tests.

Pyrolysis Temperature	350–550 °C
Residence time ^a	15 s
Feeding time	1 h
Feeding Rate	300 g/h
N ₂ flow rate	0.50 L min ⁻¹
SCG particle size	500–850 μm

^a Residence time of the SCG powder.

Table 2
Data reported in the literature on SCG lipids conversion to FAME efficiency.

Conversion yield of lipids into FAME (g/g)	Process Specification	Reference
99.0%	Two step transesterification	[24]
98.6%	Direct transesterification (in-situ method)	[37]
94.0%	Two-step transesterification process	[38]
100%	Two-step transesterification process	[39]
93.4%	Direct transesterification (in-situ method)	[40]
96.0%	Two-step transesterification process	[28]
88.0%	Two step transesterification	[41]
95%	η_b	This study

from the coffee shop of the department of engineering of the University of Rome ‘Tor Vergata’. The feedstock was dried for 12 h in a static oven at 105 ± 1 °C before each test, sieved to obtain a uniform particle size with a mesh between the 500 850 CE μm.

2.2. Microwave-assisted lipid extraction

For lipid extraction a microwave-assisted method was employed. With a procedure similar to the one reported in Ahangari et al., 50 g of dried SCG were mixed with 100 mL of hexane in a sealed 250 mL Erlenmeyer flask. The suspension was subjected to 10 cycles at a power of 800 W for 20 s in a conventional microwave oven [26]. A 20 s cycle duration was selected to minimize possible creation of thermal gradients and cold/hot spot within the SCG/hexane suspension, as suggested by Vadivambal et al. [30]. After each cycle, the flasks were cooled at ambient temperature to avoid overpressures. After 10 cycles, defatted spent coffee grounds were separated from the solvent and the lipid mixture, through vacuum filtering and then dried in oven at 90 °C for 6 h. After that, the lipid extraction efficiency was quantified gravimetrically in the dry residue; the average value of lipid extraction is reported in Table 2. Lipid extraction yields are in line with the values reported in previous studies [22,26,31,32].

2.3. Fast pyrolysis

A laboratory-scale screw reactor was employed to carry out the fast pyrolysis experiment on spent coffee grounds (Fig. 1). A feed hopper allows to control the system with an adjustable mass flow rate in the range of 100–500 g/h. The reactor is a horizontal tube with an external diameter of 20 mm, a thickness of 1 mm and a length of 500 mm made of AISI 304, while the reaction zone is 150 mm long. The screw conveyor, made of AISI 304 as well, is shaftless to reduce the gaseous residence time, improving the bio-oil yield. A variable-speed motor controls the rotation rate of the screw and thus the nominal residence time of the solid biomass over high-temperature zone of the reactor. The heat of reaction is provided to the system through a 1.4 kW NiCr minitubular electrical resistor. The char is moved to a collector bucket, while the volatiles pass through a silica bed filter, maintained at a temperature of

350 °C to avoid tar condensation. Downstream a three-stage quenching system allows the fractional condensation and the collection of the bio-oils produced. The temperature of the condensation stage is kept constant by a cooling system based on a water and ethyl alcohol solution (50:50 v/v) at -5 °C flowing countercurrent with the vapors. The flow rate of the cooling solution is regulated to keep the volatiles condensation temperature in the first stage between 280 °C and 90 °C, in the second stage between 90 °C and 35 °C and in the last stage between 35 °C and 10 °C. Finally, the residual fraction of the non-condensable gas is combusted in a torch. The operating conditions for the pyrolysis tests settled for this study are reported in Table 1. For other technical specifications on the reactor design, more details are available in Ref. [33].

Before testing, the system is heated toward the target process temperature. A N₂ flow rate of 0.5 L min⁻¹ is controlled with an Aalborg GFC mass flow controller and kept constant throughout the duration of the test. A LabVIEW data acquisition system was used to monitor the main temperature values of the system as well as sweeping gas flow rates. At the end of each test, the yields of char and bio-oils collected in the various columns was calculated gravimetrically, whereas the yield of non-condensable gases was evaluated by difference. The organic and water phases did not naturally separate as reported in many other studies on lignocellulosic biomasses [29,34]. 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. All the tests were at least duplicated and the data of the two most significant tests employed and displayed in this study.

2.4. Product characterization

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 weight is attained; 15 °C/min under N₂ atmosphere up to 550 °C for the evaluation of the volatile matter; final 15 °C/min ramp under N₂ and O₂ atmosphere for ash evaluation. Fixed carbon was evaluated by difference.

The CHNS(O) analysis was performed with Elemental Macro's Vario MACRO-cube analyzer. The test and the instrument's 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.

The non-condensable gas composition was determined with a DANI GC-1000 unit equipped with a ShinCarbon column (ST, 100/120 mesh, 2 m, 1/16in. OD, 1.0 mm ID 19808) and a TCD sensor. This allowed measuring composition and yield as functions of the elapsed time. The GC method was attended as follows: oven GC temperature kept fixed at 40 °C for 3 min, and then increased at 8 °C/min up to 250 °C, then holding time of 10 min, Ar grade 5.5 was used as carrier gas with a constant flow rate of 10 mL/min. The TCD temperature was kept fixed at 260 °C. At the holding time selected for this study, the only peaks identified and measured were associated to H₂, N₂, O₂, CH₄, CO and CO₂. Data on non-condensable gas composition were presented excluding N₂ content and normalizing to unity. A linear calibration of the instrument with at least two points per species was performed for volume quantification of the non-condensable gas composition.

The Dulong equation was employed for the quantification of high heating values (HHV) of char and bio-oil samples, (1) to take into account the N₂ and S contribution to the energy value of the feedstock and the products [35]:

Table 8

Results of SCG lipid extraction yield with the various techniques employed in the literature.

Lipid Extraction Yield (w/w)	Extraction Technique	Reference
16.7%	Soxhlet	[26]
13.79%	Microwave-assisted	[26]
17.32%	Soxhlet	[37]
15.2%	Liquid Extraction	[38]
10.58%	Ultrasonic/Microwave-assisted extraction	[32]
9.47%	Microwave-assisted	[49]
15.3%	Soxhlet	[24]
11.54%	Microwave-assisted	[50]
12.35% ± 0.32%	Microwave-assisted	This Study

$$HHV \left(\frac{kJ}{kg} \right) = 4.184 \cdot \left(78.31 \cdot C + 359.32 \cdot \left(H - \frac{O}{8} \right) + 22.12 \cdot S + 11.87 \cdot O + 5.78 \cdot N \right) \quad (1)$$

2.5. Statistical analysis

A two-way analysis of the variance (ANOVA), with balanced design, was carried out using Matlab Version: 9.13.0 (R2022b) Update 2. The statistical analysis allowed the evaluation of the mutual impact of temperature and pre-treatment (lipid extraction) on the pyrolysis product yield.

2.6. Polygeneration system modeling

For the evaluation of the performances of the SCG and DSCG poly-generation system proposed in this work, energy yield E_y and pyrolysis system efficiency ϵ_{pyr} (8) were used as parameters, as proposed by Parvez et al. [4]. The energy yield is reported in (2):

$$E_y \left(\frac{MJ}{kg} \right) = E_{char} + E_{o.p.} + E_{n.c. gas} + E_{biodiesel} \quad (2)$$

Where E_{char} , $E_{o.p.}$, $E_{n.c. gas}$ and $E_{biodiesel}$ are the energy contained in the char, organic bio-oil fraction non-condensable gas output and biodiesel obtained by lipids transesterification in fatty acids methyl esters (FAME) streams. The biodiesel energy stream is present only for the case of DSCG pyrolysis. The water fraction energy content was excluded from the balance, as discussed in the next section. Equations (3)(4) (7) (6) report the expressions for energy yield calculation, where Y_{char} , $Y_{o.p.}$, $Y_{n.c. gas}$ and $Y_{biodiesel}$ are mass yields of char, organic phase and non-condensable gas yields respectively. HHV_{char} and $HHV_{o.p.}$ are calculated with the Dulong equation (1), once known the elemental composition of the samples at each operating condition. $E_{biodiesel}$ was quantified according to (6) and the parameters used for the calculation are reported in Table 2. Table 8 reports the results of different studies investigation on the conversion yield of lipids to FAME. A value of 95% for lipids conversion efficiency to biodiesel was selected for this study (Equation (6)) and a HHV of biodiesel of 39.6 MJ/kg, as reported in the study of Al-Hamamre et al. [24]. For non-condensable gases the high heating value is calculated from the mass composition of the principal gaseous species (hydrogen, carbon dioxide, carbon oxide and methane), multiplying the mass yield of the i-species $Y_{n.c. gas, i}$ for the heat of combustion of i-species $h_{n.c. gas, i}$, according to equation (7).

$$E_{char} \left(\frac{MJ}{kg} \right) = Y_{char} HHV_{char} \quad (3)$$

Table 3
Elemental and proximate analysis of the feedstock used in this study.

Elemental composition (dry basis, in mass percentage (w/w %))		
	SCG	DSCG
<i>Ultimate Analysis</i>		
N	2.13 ± 0.25	2.50 ± 0.16
C	51.34 ± 1.13	49.54 ± 1.34
H	6.91 ± 0.65	5.85 ± 0.76
S	0.08 ± 0.02	0.15 ± 0.03
O ^a	37.35 ± 2.05	39.62 ± 2.29
<i>Proximate Analysis</i>		
Moisture	4.67 ± 0.05	3.01 ± 0.03
Volatile Matter _{d,b}	76.7 ± 0.07	75.46 ± 0.47
Fixed Carbon _{d,b}	21.09 ± 0.08	22.20 ± 0.49
Ash _{d,b}	2.19 ± 0.02	2.34 ± 0.03
HHV (MJ/kg) ^b	22.1 ± 1.84	19.32 ± 2.13

^a Calculated by difference.

^b Calculated using the following correlation the Dulong expression (1).

$$E_{o.p.} \left(\frac{MJ}{kg} \right) = Y_{o.p.} \cdot HHV_{o.p.} \quad (4)$$

$$E_{n.c. \text{ gas}} \left(\frac{MJ}{kg} \right) = Y_{n.c. \text{ gas}} \cdot HHV_{n.c. \text{ gas}} \quad (5)$$

$$E_{biodiesel} \left(\frac{MJ}{kg} \right) = Y_{lip} \cdot \eta_b \cdot HHV_{biodiesel} \quad (6)$$

$$HHV_{n.c. \text{ gas}} \left(\frac{MJ}{kg} \right) = \sum_i Y_{n.c. \text{ gas},i} \cdot h_{n.c. \text{ gas},i} \quad (7)$$

The pyrolysis system efficiency ϵ_{pyr} was considered as the ratio between the energy output and the energy contained in the SCG feedstock E_{bio} , for unit of mass (8). The high heating value of SCG feedstock was obtained again with the Dulong equation (1). The pyrolysis system efficiency is slightly different to the energy efficiency formula since the thermal energy input of the system was not included in the energy balance. However, due to the relatively low value of the enthalpy of lignocellulosic biomass compared to the biomass energy input, the two parameters are expected to be very close in value [36].

$$\epsilon_{pyr} = \frac{E_y}{E_{bio}} \quad (8)$$

$$E_{bio} \left(\frac{MJ}{kg} \right) = 1 \cdot HHV_{bio} \quad (9)$$

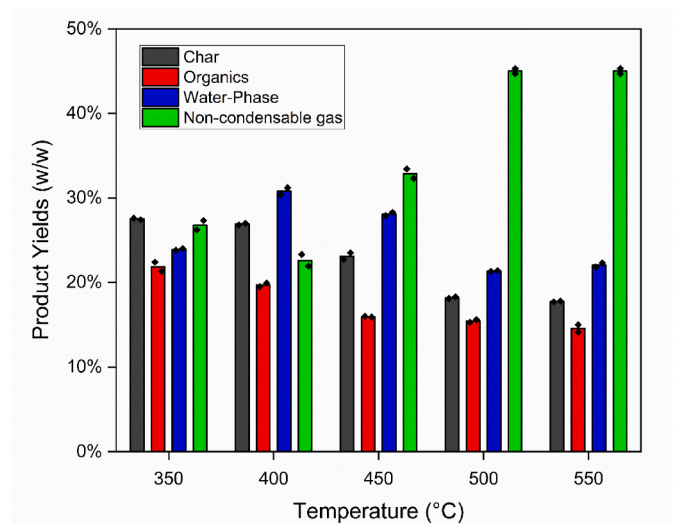


Fig. 2. Products yield of SCG fast pyrolysis in the temperature range 350–550 °C.

A two-step process for the modeling of transesterification of SCG extracted lipids into biodiesel, consisting in a first acid-catalyzed pre-treatment and an alkali-catalyzed transesterification, was selected [24]. The main parameters involved are reported Table 2. All the calculations were carried out considering the dry basis parameters of the products, including the HHVs.

3. Results and discussion

3.1. Feedstock characterization

Table 3 presents the results of proximate and ultimate analysis of SCG and DSCG after drying. As expected, the lipids extraction procedure resulted in a slight reduced C and H content of DSCG feedstock and a consequent increase of N and S. The data reported are in line with the literature and a previous work on DSCG pyrolysis [28]. HHV of the SCG is 21.83 MJ/kg, demonstrating the high energy value of such feedstock [29]. Lipid extraction has an impact on HHV, as DSCG is characterized by 19.32 MJ/kg and a higher oxygen content. An increase of fixed carbon after the extraction is thus expected and confirmed by the proximate analysis.

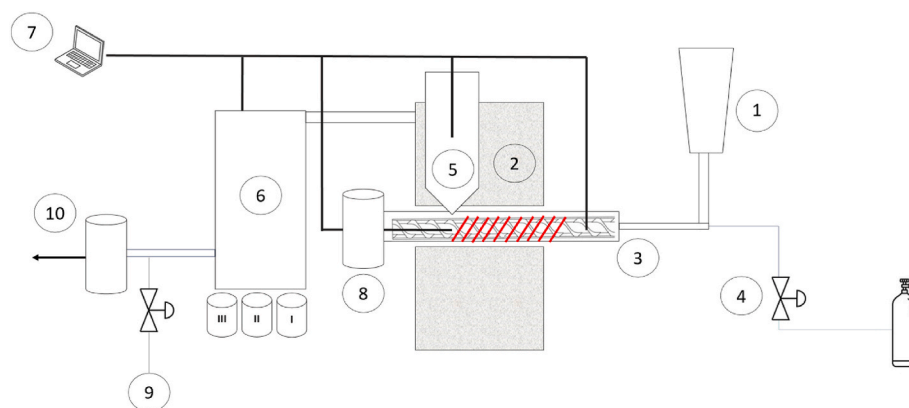


Fig. 1. Scheme of the shaftless screw reactor for fast pyrolysis tests. The main components are: 1 Feed Hopper; 2 Electrical-heated oven; 3 Shaftless screw driver; 4 Mass flow controller; 5 Sand filter; 6 Multistage water-glycol cooled condenser; 7 DAQ system; 8 Char collector; 9 Valve for non-condensable gas sampling; 10 Flare.

Table 4
Char and organics yields of SCG fast pyrolysis in the temperature range 350–550 °C.

Product yields in mass percentage (w/w)					
Pyrolysis Temperature	Char Yield			Organics Yield	
	This Study	Kelkar et al., 2015 [19]	Lazzari et al., 2018 [27]	This Study	Lazzari et al., 2018 [27]
350 °C	27.5 ± 0.14	–	–	21.85 ± 0.78	–
400 °C	26.9 ± 0.13	–	35.31	19.70 ± 0.38	17.4
450 °C	23.1 ± 0.34	19.50	24.17	15.95 ± 0.07	27.5
500 °C	18.2 ± 0.14	18.28	26.79	15.45 ± 0.21	30.8
550 °C	17.8 ± 0.07	15.85	22.15	14.55 ± 0.64	27.4

Table 5
Results of the char characterization.

Elemental composition (dry basis, in mass percentage (w/w %))					
Proximate analysis (dry basis, in mass percentage (w/w %))					
	Pyrolysis Temperature				
	350 °C	400 °C	450 °C	500 °C	550 °C
Proximate analysis					
Moisture	6.76 ± 0.65	2.13 ± 0.01	3.35 ± 0.16	4.14 ± 0.13	7.58 ± 0.12
Volatile Matter ^{d,b}	44.35 ± 1.7	36.42 ± 0.57	31.47 ± 2.02	29.32 ± 1.95	23.22 ± 0.20
Fixed Carbon ^{d,b}	49.29 ± 2.02	56.42 ± 0.56	60.38 ± 2.35	62.15 ± 1.32	66.62 ± 0.25
Ash ^{d,b}	6.37 ± 0.32	7.17 ± 0.01	8.15 ± 0.34	8.54 ± 0.08	10.16 ± 0.04
Ultimate Analysis					
N	1.98 ± 0.12	2.39 ± 0.08	2.39 ± 0.03	2.01 ± 0.16	2.03 ± 0.17
C	68.29 ± 1.22	74.60 ± 0.77	76.76 ± 1.32	74.91 ± 2.93	77.89 ± 4.06
H	2.71 ± 0.24	2.52 ± 0.09	1.96 ± 0.52	1.25 ± 0.27	0.63 ± 0.25
S	0.09 ± 0.05	0.08 ± 0.12	0.10 ± 0.02	0.07 ± 0.01	0.17 ± 0.04
O ^a	20.96 ± 2.60	13.39 ± 0.95	10.90 ± 2.23	13.56 ± 3.88	9.84 ± 6.20
HHV (MJ/kg) ^b	24.55	26.19	26.04	24.48	24.49

^a Calculated by difference

^b Calculated using the following correlation the Dulong expression (1)

3.2. Effect of temperatures on SCG fast pyrolysis

The effect of temperature on the SCG fast pyrolysis products yield are reported in Fig. 2. The char yield is slightly decreased in the temperature range explored, bio-oil yield reaches a maximum of 46.5% at the temperature of 400 °C and non-condensable gas yield is increased considerably at the higher temperatures. This may be attributed to the secondary volatile cracking reaction which is dominant at the higher temperatures [4,6,27]. With respect to previous studies on SCG fast pyrolysis, the bio-oil yield peak occurs at lower temperatures; both Kelkar et al. and Bok. et al. reported a peak for 500 °C, while Lazzari et al. found out a maximum bio-oil production for 600 °C [20,28,34].

Table 6
Elemental composition of organic and water phase of SCG pyrolysis oil in the temperature range 350–550 °C.

Elemental composition (dry basis, in mass percentage (w/w %))					
Organic Phase	Temperature				
	350 °C	400 °C	450 °C	500 °C	550 °C
Organic Phase					
N	1.52 ± 0.06	1.45 ± 0.01	1.89 ± 0.21	2.88 ± 0.02	2.81 ± 0.15
C	58.00 ± 1.2	63.99 ± 0.2	63.39 ± 0.23	67.79 ± 2.28	59.65 ± 0.19
H	9.39 ± 0.42	11.28 ± 0.36	10.20 ± 0.13	10.83 ± 1.09	9.64 ± 0.44
S	0.08 ± 0.01	0.07 ± 0.03	0.10 ± 0.07	0.12 ± 0.14	0.17 ± 0.02
O ^a	31.02 ± 1.69	23.20 ± 0.60	20.58 ± 0.64	18.38 ± 3.53	27.73 ± 0.80
Water phase					
HHV ^b	28.91 ± 1.43	34.81 ± 0.75	33.36 ± 0.43	36.09 ± 3.24	30.34 ± 0.92
N	0.77 ± 0.01	1.04 ± 0.10	1.16 ± 0.04	1.52 ± 0.06	1.68 ± 0.06
C	12.75 ± 0.24	12.426 ± 0.24	12.86 ± 0.30	10.69 ± 0.12	11.55 ± 0.54
H	11.47 ± 0.23	10.75 ± 0.23	10.75 ± 0.64	11.91 ± 0.31	10.54 ± 0.22
S	0.10 ± 0.38	0.10 ± 0.07	0.10 ± 0.08	0.02 ± 0.01	0.08 ± 0.01
O ^a	74.91 ± 0.75	75.66 ± 0.64	75.11 ± 1.06	75.87 ± 0.50	76.15 ± 0.83
HHV ^b	11.09 ± 0.64	9.81 ± 0.59	10.03 ± 1.32	10.95 ± 0.63	9.15 ± 0.71

^a Calculated by difference.

^b Calculated using the following correlation the Dulong expression (1).

Table 4 shows the comparison of the char and organic bio-oil fraction yield with previous studies. The char yield is very close to values reported by Kelkar et al. whose reactor design and operating mode are similar to this work [20]. Again, the comparison of organic bio-oil fraction yield with the data reported by Lazzari et al. in Table 4 shows little agreement; this could be due both to a different feedstock biochemical composition and the different operating mode.

Fig. 2 shows the composition of the bio-oil between water and organic fraction. It is worth noting that water fraction is in general greater than the heavy organic fraction. In the literature there is a disagreement regarding the composition of the bio-oil between water and organic and fractions. According to Lazzari et al. the ratio of the two mass fractions is close to one, varying with the temperature [27]. Vardon et al. reported that for the SCG slow pyrolysis at 450 °C, the organic fraction is slightly higher compared with the water one. Elmously et al. investigated the fast pyrolysis process with an additional post-reformer step, where the produced char acted as catalyst in the temperature range 500–700 °C. They found a limited organic fraction yield compared with the water fraction (7.33% and 46.75% mass yield respectively at the pyrolysis temperature of 400 °C and 500 °C of post-reforming stage).

The enhanced process severity and increased rate of solid-gas reactions with the temperature – i.e. dehydration, decarbonylation and decarboxylation—are confirmed analyzing the char characterization results provided in Table 5 [6]. Char proximate analysis shows a significant reduction in the volatile matter fraction while the fixed carbon and ash contents are progressively intensified. The progressive increase in inorganics can explain the low bio-oil yield above mentioned. As reported in several studies, the presence of Alkali and Alkaline Earth Metallic (AAEM) increases tar cracking and limits the bio-oil potential that can be recovered [43,44]. The char carbon content increase and oxygen and hydrogen loss with the process temperature increase are in line with those reported in the literature [19,28,34,45].

Table 7

Non-condensable gas composition for SCG fast pyrolysis in the temperature range of 350–550 °C.

Gas composition, in volume percentage (mol/mol %)					
Species	Pyrolysis Temperature				
	350 °C	400 °C	450 °C	500 °C	550 °C
H_2	0.98 ± 0.60	1.39 ± 0.13	1.20 ± 0.03	7.54 ± 0.01	15.72 ± 0.15
CO	27.07 ± 0.02	25.05 ± 1.37	24.82 ± 0.16	27.91 ± 0.02	30.55 ± 1.01
CH_4	2.36 ± 0.01	4.66 ± 0.57	4.29 ± 0.22	9.21 ± 0.01	12.03 ± 0.21
CO_2	69.59 ± 0.14	68.91 ± 2.76	69.68 ± 0.60	55.34 ± 0.79	41.71 ± 1.35
HHV (MJ/kg)	2.61	3.06	2.93	5.40	8.18

Elemental composition of both water and organic fraction of spent coffee grounds pyrolysis oil is reported in Table 6. Carbon and oxygen, as well as the energy content of the water and organic phase, differ greatly; therefore, for an accurate energy analysis of a SCG pyrolysis-based polygeneration system, it is crucial to pay attention on this aspect. Table 6 shows that pyrolysis temperature increase is beneficial to obtain a high-energy dense organic phase with a reduced oxygen content. 500 °C is in fact the temperature value where organic phase presents the best characteristics as biofuel. Nitrogen content increases with the temperature as well, requiring further assessment towards the potential NO_x emissions during combustion. Water phase composition is stable with temperature and presents an average 12% carbon content in mass and more than 74% of oxygen, suggesting a high-water content. Thus the water bio-oil fraction energy contribution was excluded in the overall energy balance of the polygeneration energy system that is reported in the following section.

Non-condensable gas volumetric composition at various temperatures is presented in Table 7. As reported in Bok et al. carbon dioxide,

carbon oxide, methane and hydrogen are the main gaseous species in terms of mass concentration [34,45]. Table 7 shows that in the temperature range of 350–450 °C non-condensable gas composition is stable with the temperature, while at higher temperature there is progressive hydrogen and methane enrichment. As stated in many studies, cellulose and hemicellulose are the biomass fractions that undergo thermal degradation for lower temperatures, leading to carbon oxide and dioxide enriched non-condensable gas [6,44]. Hydrogen and methane are gaseous species deriving mainly from lignin fraction de-polymerization that occurs for higher temperatures [46]. Kinetic studies specific for SCG confirmed that lignin is the last pseudo-component released during pyrolysis process at higher temperatures [47].

Non-condensable gas energy content is deeply affected from composition and the HHV trend with temperature is reported in Table 7. Hydrogen and methane enriched non-condensable gas are highly valuable products for industrial applications. Therefore, the pyrolysis temperature of 550 °C is considered relevant for the pyrolysis-based polygeneration system proposed in this work, although at this temperature the bio-oil yield is not optimal.

Fig. 3 summarizes in a ternary plot the elemental composition of the solid and liquid product of SCG pyrolysis, comparing the results of this study with the outcomes of previous works. There is a general agreement regarding feedstock and char elemental composition since the elliptical area is limited. However, for bio-oil the literature reports a highly different value in the elemental composition: for the studies that distinguished among organics and water phases the results are close, whereas the works that considered bio-oil as a homogenous phase presents values outspread on the diagram. A differentiation among the two phases was then crucial to carry out an energy analysis of a poly-generation system, to have reliable track of the energy flows involved.

3.3. Lipid extraction yield

The results of lipid extraction yield are reported in Table 8, where the yield is compared with other studies found in the literature. As shown, liquid-liquid extraction gives generally higher results in term of lipid extraction yield, since the higher extraction times leads to higher

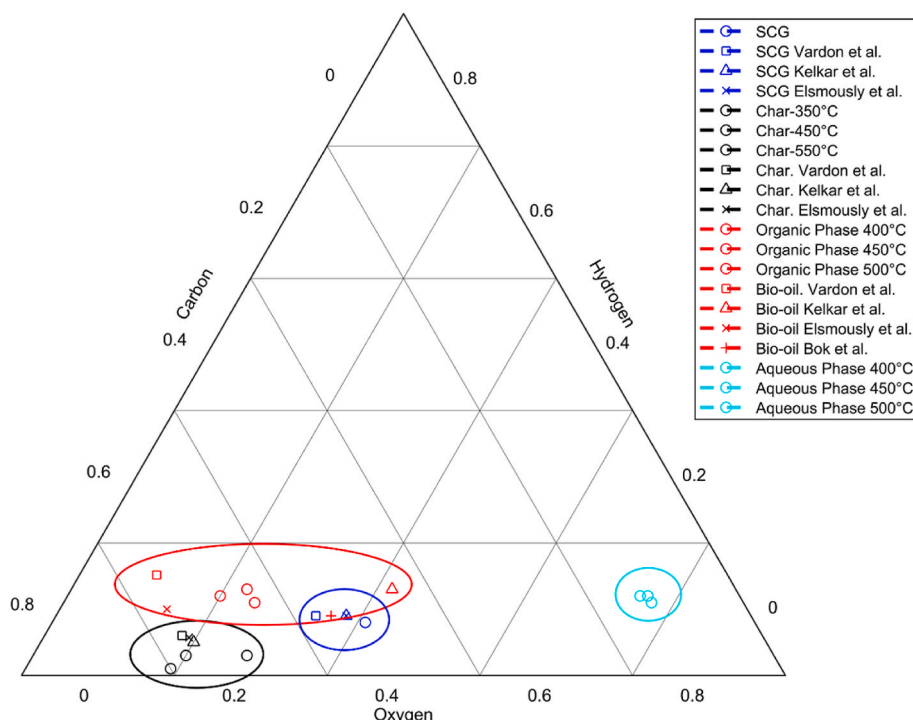


Fig. 3. Ternary plot of SCG, char and bio-oil (organics and water phase) elemental composition of SCG pyrolysis.

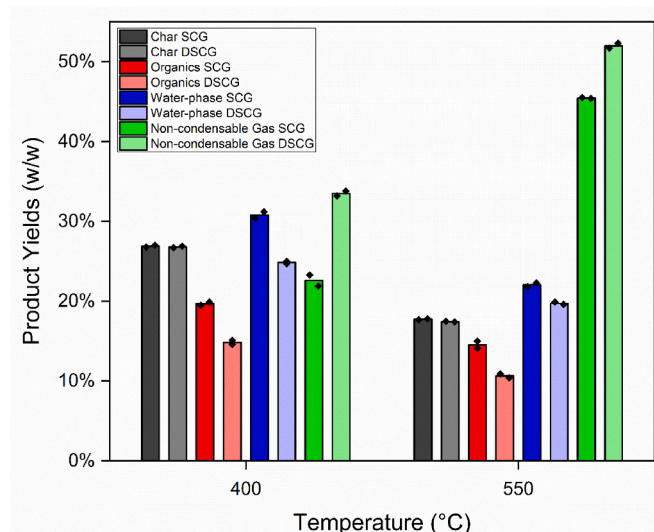


Fig. 4. Product yields of SCG and DSCG fast pyrolysis at the temperature of 400 °C and 550 °C.

relative speeds between solvent and SCG. However, microwave extraction methods are fast, cost-effective and represent of the main alternatives currently under investigation to meet optimal industrial production requirements [48]. In this study, the lipid extraction obtained is 12.35% (w/w) in line with the values reported in the literature.

3.4. Defatted spent coffee grounds pyrolysis

Pyrolysis of defatted spent coffee grounds was performed at 400 °C and 550 °C, considered to be the most interesting temperatures. Considering Fig. 2, at 400 °C bio-oil yield is maximized while at 550 °C non-condensable gas yield is optimal. As stated in the introduction section, the objective of this work is to assess the impact of lipid extraction in the various operating regimes, both when the bio-oil and non-condensable gas yields are maximized. The results of DSCG pyrolysis are reported in Fig. 4 where the product yields are compared to the case of SCG pyrolysis. As shown, the char yield is very similar, while both organic and water bio-oil phase yields undergo a significant reduction in the case of DSCG. In fact, thermal degradation occurs during the pyrolysis process of lipids to fatty acids/aldehydes, significant components of the organic phase. The pre-treatment process removes lipids, explaining the reduction of the organic phase. For both the temperature values, non-condensable gas yield is increased, as expected, due to the decrease in bio-oil yield. However, such a significant rise was not expected since lipids crack more easily if compared to cellulose/hemicellulose volatiles. Vardon et al. [28] reported for the

Table 9

Pyrolysis oil and char elemental composition of SCG and DSCG fast pyrolysis at 400 °C and 550 °C.

Elemental composition (dry basis, in mass percentage (w/w %))													
Temperature (°C)	Water Phase				Organics				Char				
	400 °C		550 °C		400 °C		550 °C		400 °C		550 °C		DSCG
	SCG	DSCG	SCG	DSCG	SCG	DSCG	SCG	DSCG	SCG	DSCG	SCG	DSCG	
N	1.04 ± 0.10	2.24 ± 0.10	1.68 ± 0.06	1.6 ± 0.06	1.45 ± 0.01	1.79 ± 0.03	2.81 ± 0.15	3.42 ± 0.15	2.39 ± 0.08	2.54 ± 0.14	2.03 ± 0.17	2.59 ± 0.03	
C	12.426 ± 0.24	12.45 ± 0.24	11.55 ± 0.54	10.67 ± 0.54	63.99 ± 0.2	61.87 ± 0.32	59.65 ± 0.19	57.98 ± 0.19	74.60 ± 0.77	73.12 ± 0.89	77.89 ± 4.06	74.12 ± 0.65	
H	10.75 ± 0.23	9.83 ± 0.23	10.54 ± 0.22	10.5 ± 0.22	11.28 ± 0.36	10.21 ± 0.42	9.64 ± 0.44	8.98 ± 0.44	2.52 ± 0.09	2.45 ± 0.14	0.63 ± 0.25	0.48 ± 0.09	
S	0.10 ± 0.07	0.10 ± 0.07	0.08 ± 0.01	0.08 ± 0.01	0.07 ± 0.03	0.09 ± 0.05	0.17 ± 0.02	0.66 ± 0.02	0.08 ± 0.12	0.12 ± 0.09	0.17 ± 0.04	0.39 ± 0.06	
O ^a	75.66 ± 0.64	75.38 ± 0.64	76.15 ± 0.83	77.03 ± 0.83	23.20 ± 0.60	26.04 ± 0.82	27.73 ± 0.80	28.96 ± 0.8	13.39 ± 0.95	15.87 ± 1.75	9.84 ± 6.20	12.11 ± 0.98	

slow pyrolysis of DSCG a slight increase of the char yield, reduced bio-oil yield and a significant rise of non-condensable gas yield, according also to the results presented in this study. Table 9 shows the elemental composition of char and bio-oil of DSCG pyrolysis at 550 °C. The lipid extraction has a slight impact on the product composition: carbon and hydrogen are more abundant in SCG respect to DSCG organics and this is reflected in the higher HHV of the former. The effectiveness of lipids extraction is confirmed by a higher availability of nitrogen and sulfur containing compounds in both the organic and water phases.

Fig. 5 highlights that non-condensable gas compositions of SCG and DSCG pyrolysis are very similar. A slight reduction of hydrogen yield and a limited increase of methane concentration are the main outcomes of this analysis. Except for a reduced lipids content, SCG and DSCG have very similar bio-polymeric nature, hence a similar products composition was expected, also proving the stability of the process.

Table 10 shows results of the statistical analysis of DSCG pyrolysis test. The analysis of variance was intended to understand the impact of temperature (400 °C and 550 °C) and lipid extraction on the product yield. As reported, the p-value is very limited and always lower than 0.05 for the analysis of the impact of the single factor (temperature or pre-treatment). The analysis of variance showed that the interaction of the two factors i.e. temperature and pre-treatment, has a significant impact on the water phase and non-condensable gas yield, while for char

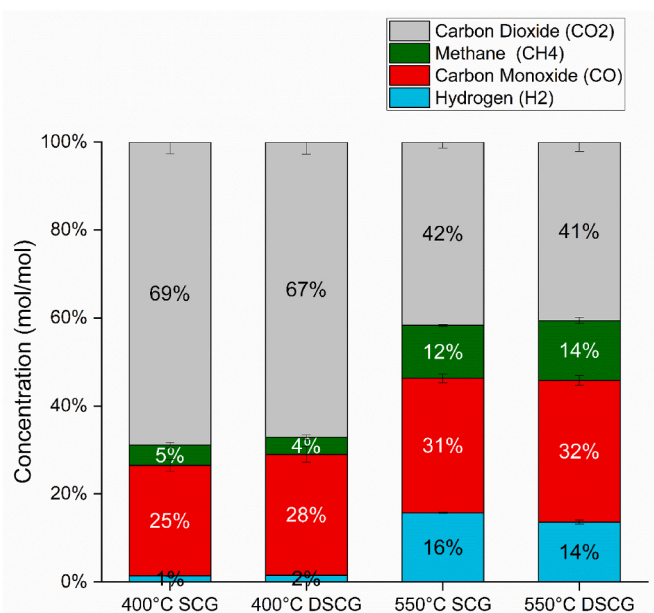


Fig. 5. Comparison of non-condensable gas composition for SCG and DSCG fast pyrolysis at 400 °C and 550 °C.

Table 10

2-way analysis of the variance (ANOVA) of the impact of temperature and lipid extraction on product yield.

Char					
Source of Variation	Sum of Squares (SS)	Degrees of Freedom (DF)	Mean squares (MS)	F0	p-Value
Temperature (°C)	0.151	1	0.15	17.29	0.014
Pre-treatment	168.361	1	168.36	19241.29	0
Interaction	0.001	1	0.001	0.14	0.724
Error	0.035	4	0.009		
Total	168.549	7			
Organics					
Temperature (°C)	43.7112	1	43.7112	237.88	0.0001
Pre-treatment	38.2812	1	38.2812	208.33	0.0001
Interaction	0.4512	1	0.4512	2.46	0.1922
Error	0.735	4	0.1837		
Total	83.1787	7			
Water phase					
Temperature (°C)	102.961	1	102.961	1752.53	0
Pre-treatment	38.281	1	38.281	651.6	0
Interaction	8.611	1	8.611	146.57	0.0003
Error	0.235	4	0.059		
Total	150.089	7			
Non-condensable gas					
Temperature (°C)	854.91	1	854.911	2542.49	0
Pre-treatment	152.25	1	152.251	452.79	0
Interaction	9.46	1	9.461	28.14	0.0061
Error	1.34	4	0.336		
Total	1017.97	7			

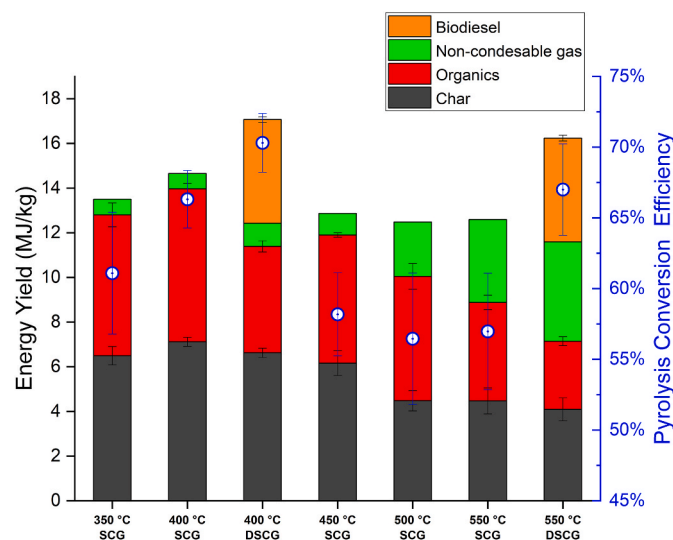


Fig. 6. Energy yield and system efficiency for SCG and DSCG polygeneration energy system.

and organics there is not a significant influence.

3.5. Energy analysis of the polygeneration system

The energy performance of SCG/DSCG fast pyrolysis-based polygeneration system are presented in Fig. 6. The plot shows the energy distribution among the pyrolysis products - char, organic bio-oil phase

and non-condensable gases. Biodiesel is an additional energy output of the polygeneration energy system, present only in the case of DSCG. As previously mentioned, water fraction energy yield is not considered in this analysis, due to the low specific energy content and high oxygen content. The lipid extraction yield and the data for the modeling of the transesterification process for the conversion of extracted lipids into fatty acids methyl ester (FAME) are reported in Table 2, evaluated according to equation (6) reported in the method section. Fig. 6 shows that the energy yield of a SCG polygeneration system lies between 12.48 and 14.66 MJ/kg and that the maximum energy yield is obtained for 400 °C. In terms of energy distribution among the different products, it is worth noting that, in the temperatures range of 350–450 °C, more than 90% of the energy output is contained in the char and in the bio-oil. At 550 °C the output yield is more uniformly distributed among the products, and the non-condensable gas energy yield counts 30% of the overall energy output. These data are in line with a study of D. Chen et al. where a poplar wood pyrolysis based polygeneration system was considered; more in detail, D. Chen reported higher energy yield than the one presented in this study, accounting also for the water phase contribution. Parvez et al. reported for a similar study on corn stalk, pine wood and algae based microwave assisted pyrolysis polygeneration process a value of system efficiency of 63.6, 55.3 and 62.6% respectively, for optimized conditions [4]. In Fig. 6, the energy performance of SCG and DSCG polygeneration energy systems are compared, in the case of 400 °C and 550 °C. This result confirms the thesis of this work, i.e. that the integration of the pyrolysis process with the conversion of lipids (previously extracted) into biodiesel is convenient from an energy point of view. Results show in fact that at 400 °C the pyrolysis energy output is maximized with a pyrolysis energy efficiency of 71.2%. However, the increase of the energy yield due to lipid valorization in biodiesel is moderate (+4.1%). At 550 °C the lipids conversion into biodiesel lead to increased energy yield and pyrolysis system efficiency (10% points). This can be explained considering that at 550 °C the SCG polygeneration energy system is less efficient if compared with 400 °C, and the HHV of biodiesel is considerably higher than the average of other pyrolysis products.

4. Conclusions

The objective of this study was to demonstrate that impact of pretreatment on a spent coffee grounds pyrolysis-based polygeneration system in terms of products yield and energy efficiency. The results showed that biodiesel contributes positively to the energy yield in both the two configurations proposed (400 °C and 550 °C). A significant improvement of 10% points of energy yield was found for the case of 550 °C, while a slighter increase of energy yield was evidenced for the case of 400 °C. The results of this paper highlight how the pretreatment is a key to improve the energy performance and the flexibility of a biomass polygeneration energy system according to multi-operation modes.

Data availability

Data will be made available on request.

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