



## Catalyzed pyrolysis of coffee and tea wastes

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### ABSTRACT

The pyrolysis of food waste has a double environmental advantage as it contributes to the management and treatment of waste and allows the production of renewable fuels. Spent coffee and tea grounds, were characterized by thermogravimetry to determine their composition and evaluating the pyrolysis kinetics of each lignocellulosic pseudocomponent and pyrolyzed in a fixed bed reactor. Tea grounds had about twice the cellulose and higher pyrolysis activation energy than the coffee grounds sample. At 673 K the pyrolysis of the coffee grounds led to a 42% bio-oil yield while the tea grounds produced only 18% of liquid product, which is compatible with its higher cellulose content and the higher activation energy for pyrolysis. The alkaline carbonates used as pyrolysis catalysts led to an increase in the production of a gaseous product, bio-gas, with a reduction in the production of bio-oil but accompanied by a significant increase in the volatile fraction of the produced bio-oils. Pyrolysis data shows that both coffee and tea residues can be used as raw materials to produce pyrolysis bio-oil and that low-value materials such as alkaline carbonates can be used as pyrolysis catalysts improving the characteristics of bio-oils produced such as acidity and volatility.

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## 1. Introduction

The production of biomass residues, food, and products of biological origin in the world has been increasing annually due to the increase in population and human consumption [1]. Municipal wastes (MW) are majorly composed of organic matter with a great potential for energy production [2]. Landfilling waste is the most used method in waste treatment [3], but it promotes greenhouse gas emissions, such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). MW can also be managed through incineration with the concomitant production of thermal energy and a great reduction of the volume of the solid waste, but it produces air toxins such as polycyclic aromatic hydrocarbons (PAHs), dioxins, and particulate matter [4,5]. An effective way to solve the problem of a large amount of waste generated daily and to convert it into value-added products is to use thermal degradation processes, namely pyrolysis. The EU based on these problems developed the Bioeconomy Strategy, which promotes the conversion of this discarded waste into value-added products, such as feed, bio-based products, and

bioenergy [6,7]. Generally, non-edible feedstocks are envisaged as promising feedstocks to produce renewable fuels and valuable carbon-rich materials [8,9] through diverse conversion technologies such as alcoholysis of the extracted oils or thermal conversion of the entire biomass [10].

Pyrolysis, a thermal process, is a complex process in which lignocellulosic matter is converted, in the absence of oxygen, into liquid products (bio-oil), gaseous products (pyrogas), and solid products (biochar) [1,11,12]. The yields of pyrolysis depend on the conditions and technology used and the composition of the biomass (lignocellulosic and inorganic content). Due to the high content of oxygenated compounds in liquid products and to increase their quality and usefulness, it is necessary to add a catalyst to the system to selectively remove oxygen and convert unwanted products into more stable compounds [1,12–15]. Several authors have reported different types of materials used as catalysts for biomass pyrolysis. From acid catalysts (HZSM5, spent FCC) to basic catalysts (Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub>) were used to improve the quality of the bio-oil, reducing acidity [12,16–19].

Any material with organic carbon is a good raw material for pyrolysis [20], thus the organic part of municipal wastes can be used to produce renewable fuel through pyrolysis. Pyrolysis of MW will contribute to reducing the volume of landfill solids, and

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subsequent environmental impacts, with the advantage of energy recovery with simultaneous carbon sequestration [21].

Coffee and tea are the most popular beverages in the world and their consumption is growing year after year [4,5]. Coffee and tea consumption produces large amounts of solid waste such as spent coffee grounds (SCG), coffee silver skin, tea leaves, and used tea bags [4,5,22]. These types of wastes are commonly disposed of via landfills or via thermochemical processes such as incineration and pyrolysis [4,5,23,24].

The coffee and tea wastes can be easily converted into value-added products, by pyrolysis processes due to the high concentration of sugars, fibers, and proteins and compounds such as fatty acids, alcohols, aldehydes, ketones, cellulose, hemicellulose, lignin [4,5].

The pyrolysis of spent coffee grounds was studied by several researchers using different reactors and different reaction conditions, thus making it difficult to compare the published results. For example, the fast pyrolysis of spent coffee grounds in a continuous tilted-slide reactor allowed to 59% of bio-oil yield at 823 K with a viscosity larger than that produced from wood biomass in analogous conditions. The feasibility evaluation of SCG slow pyrolysis in a rotary kiln reactor, in the context of circular economy, led to positive economic indicators [25]. The researchers underlined that spent coffee grounds pyrolysis provides an efficient waste management solution for the coffee shop industry. Kelkar et al. [26] used a screw-conveyor reactor to study the fast pyrolysis of SCG for temperatures in the range 702–823 K and residence time for 23 s–43 s. The highest bio-oil yield (61.8%) was obtained at 773 K. The produced bio-oil contained typical oxygenated compounds and hydrophobic compounds such as fatty acids, fatty acids esters, paraffins, olefines, and caffeine. Due to the large abundance of SCG and their pyrolysis behavior, the authors concluded that coffee waste has great potential as a valuable bioenergy feedstock.

The pyrolysis of spent tea grounds is less cited in the literature than the pyrolysis of spent coffee grounds because tea grounds can be directly used as adsorbents [27]. Among other interesting works stands out that of Fadhil and Saeed [28] which used sulfuric acid-treated spent tea leaves as low-cost solid sorbents for crude biodiesel purification. Uzun et al. [29] reported the pyrolysis of tea waste in a fixed bed reactor for temperatures in the 673–973 K range. They reported a maximum bio-oil yield of 30.4% with aliphatic sub-fraction composed of n-alkanes, alkenes, and branched hydrocarbons, concluding that liquid products can be used as fuels. Recent studies on the tea waste pyrolysis [30] reported interesting values of thermal degradation rates for temperatures in the range 435–866 K, with an activation energy of 225 kJ/mol. The mass spectrometry analysis of condensable products allowed to identify 33 different compounds including alkene, acid, benzene, furan, ketone, phenol, nitride, alcohol, aldehyde, alkyl, and ester. The authors concluded that tea waste meet the requirements to be used in the production of bioenergy.

In this work, the thermal decomposition of spent coffee and tea grounds was studied using microscale pyrolysis experiments (thermobalance) to obtain the kinetics parameters and the proportions of lignocellulosic compounds in the studied biomass samples. These kinetics parameters were estimated using the Kissinger method and related to the distribution of the products obtained in the pyrolysis experiments in a fixed bed reactor. To improve the quality of the bio-oil and, in this way, to value the products obtained from samples of spent coffee and tea grounds, catalytic tests were carried out, in situ, using carbonates catalysts. Cheap and environmentally benign materials were chosen as catalysts to improve the sustainability of the pyrolysis process.

## 2. Experimental section

### 2.1. Materials

The spent coffee and tea grounds were selectively collected and dried in an oven at 333 K (dry atmosphere) overnight. The tea residues were a mixture of black tea, green tea, white tea, and infusions. The dried biomasses were reduced to powder using a blade mill and sieved. The powder fractions above 750  $\mu\text{m}$  were rejected. Commercial xylan, hemicellulose, Whatman filter paper (100% cellulose), vegetable oil, and lignin were used as references for thermogravimetry tests.

To develop a cheap and environmentally friendly catalytic pyrolysis, commercial carbonates catalysts were used:  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$ .

### 2.2. Methods

The dried and grounded biomasses were characterized by thermogravimetry (TG) under  $\text{N}_2$  flow to simulate the pyrolysis process. The thermograms were acquired on a Netzsch STA 490 PC thermobalance using five heating rates: 10 K/min, 20 K/min, 30 K/min, 40 K/min, and 50 K/min. For each test 60–100 mg of powdered sample (<750  $\mu\text{m}$ ) were placed in a 100  $\mu\text{L}$  alumina crucible. During the TG tests the thermobalance oven was flushed with  $\text{N}_2$  (18 L/h) thus creating an inert atmosphere in the sample surrounding. TG data were collected from 303 to 1373 K. The rate of mass loss (DTG) was computed using the equipment software (Proteus).

The DTG curves were deconvoluted using Gaussian curves to estimate the lignocellulosic, among others, the composition of each analyzed sample. Details on the deconvolution procedure are given elsewhere [31]. Xylan, Whatman paper filter, and vegetable oil were used as references for hemicellulose, cellulose, and oils respectively. The thermograms of standard materials were collected and the temperature of maxima decomposition rates was extracted and used as pseudo-component identification in waste materials thermograms. Each pseudo component (cellulose, hemicellulose, lignin, and oil) of the sample was assigned a thermal degradation process simulated by a symmetrical Gaussian curve. The quantification of each component in the sample was made by calculating the area under the Gaussian curve attributed to the respective degradation process, divided by the total area under the DTG curve.

The pyrolysis experiments were carried out in a fixed bed tubular pyrex reactor, at 673 K. The fixed bed is composed of an inert solid material, carborundum (SiC). A small layer of glass wool is placed on top of this material, where the biomass sample is then inserted, as shown in Fig. 1. The biomass sample (10 g with a granulometry <750  $\mu\text{m}$ ) is placed over the top layer. These tests were performed under a nitrogen flow of 300 mL/min for 15 min. Concluded from the biomass pyrolysis experiments, the solid (biochar) was removed from the reactor and weighed. For catalytic pyrolysis tests, 20% of the catalyst was used. The gas composition, composed of biogas and nitrogen, was discarded and quantified by mass balance. The liquid product was obtained in the condensate container and by washing the inert SiC with acetone [16]. The collected liquid was dried in a rotavapor to remove the used solvents and the water from pyrolysis. Samples were dried at 353 K and 120 mmHg for 1 h. The brownish liquid obtained was weighed to calculate the bio-oil yield. The bio-oil samples were characterized by ATR-FTIR spectroscopy. The spectra were recorded on FT-MIR equipment from BOMEN (FTLA2000-100, ABB) with a DTGS detector. More details about this procedure can be found in the previous work [12]. To acquire an appropriate signal-to-noise ratio, sixty-four scans were accumulated for each spectrum, in the range of 600–4000  $\text{cm}^{-1}$ . Also, the Kubelkae Munk (KM) function was

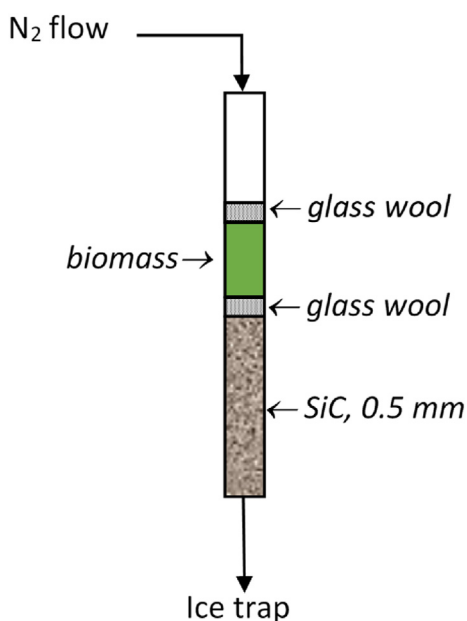


Fig. 1. Composition by layer of the fixed bed pyrolysis reactor.

used to correct the reflectance signal ( $R$ ). After that, the FTIR spectra of different bio-oils characterized were deconvoluted to understand the type of oxygen-containing functional groups that were present in the samples [12].

The volatility of the bio-oils produced was examined by simulated distillation using thermogravimetry [32]. The tests were carried out with 60 mg of bio-oil with a heating speed of 20 K/min and under nitrogen flow. The volatile fraction was considered as the mass fraction lost to temperatures below 623 K by analogy to the distilled fractions of petroleum (light and medium distillate).

### 2.3. Estimation of the biomass composition

To evaluate the biomass composition, the experimental curve DTG uses different individual theoretical curves that correspond to each of the components present in the sample. The characterized biomass samples have the main four components: moisture, hemicellulose, cellulose, and lignin. However, the proportion of each component differs dramatically from the type of biomass sample. The individual theoretical curves are calculated from the decomposition temperature ranges of each component using experimental data obtained from standard chemical components.

In this work, the deconvolution of the experimental DTG curve was made using symmetrical Gaussian type curves. The calculated total DTG curve is the sum of the different theoretical individual curves of the different components. This deconvolution method assumes that the thermal degradation of the different components of the biomass sample occurs individually. The fit of the experimental DTG, using symmetric Gaussian curves, is performed by the optimization of three parameters:  $a_i$ , amplitude;  $b_i$ , position;  $c_i$ , width at half the maximum height,  $T$  indicates the temperature values (in K) and  $i$  refers to the individual component, according to Eq. (1) [33–35].

$$DTG_{cal} = \sum_i a_i \exp \left[ - \left( \frac{T - b_i}{c_i} \right)^2 \right] \quad (1)$$

To minimize the difference between the total calculated curve (with the different individual curves of the Gaussian type) and the

experimental curve of the DTG, the parameters  $a_i$ ,  $b_i$ , and  $c_i$  of Eq. (1) were fitted using the least-squares method.

$$O.F. = \sum_T \left( \frac{DTG - DTG_{cal}}{DTG} \right)^2 \quad (2)$$

This objective function (O. F.), Eq. (2) was performed using Microsoft Excel Solver. This data treatment is described in more detail in previous works [33,34].

### 2.4. Kinetics studies

The kinetics parameters, in particular the activation energy and the pre-exponential factor, will be calculated using the Kissinger, model-free method, from thermogravimetric experimental data obtained at different heating rates according to Eq. (3) [36].

$$\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{AR}{E_a} \right) - \frac{E_a}{RT_m} \quad (3)$$

where  $T_m$  is the temperature corresponding to the maximum rate of thermal degradation,  $\beta$  is the heating rate (K/min)  $E_a$  is the activation energy, expressed in kJ/mol,  $R$  is the ideal gas constant and  $A$  is the pre-exponential factor ( $s^{-1}$ ).

The applied method was assumed for monomolecular solids [36,37]. Although biomass is not a monomolecular material, the Kissinger method has already been successfully applied to the thermal degradation of biomass. In this work, the Kissinger method was applied to estimate the activation energy of the components of hemicellulose and cellulose, obtained from the deconvolution of the individual theoretical curves of each component. These activation energies were estimated from the maximum temperature of thermal decomposition at different heating rates [33,38].

## 3. Results and discussion

### 3.1. Thermogravimetry analysis (TGA)

Coffee and tea wastes were characterized by TGA to assess the differences during the thermal degradation process in inert conditions (under N<sub>2</sub> flow). To identify the different components present in the samples of biomass residues, standard components such as: xylan, hemicellulose, Whatman paper filter, vegetable oil, and lignin were used. Fig. 2 shows the DTGs of the wastes and standard components. From DTGs of tea and coffee, it can be seen the existence of a first process of loss of mass, which corresponds to the evaporation of water from the sample, in the temperature range 300–500 K. The second loss of mass, more pronounced than the first, occurs in the temperature range of 500–650 K and corresponds to the degradation of hemicelluloses and cellulose. A third process, from 650 K to 800 K, corresponds to the degradation of oils. The degradation of lignin occurs in a wider temperature range, which can be from 425 to 900 K.

Through the DTG of the standard components, in particular xylan (which is a type of hemicellulose) and hemicellulose, it is possible to observe that the samples of spent coffee and tea grounds have two types of hemicelluloses, in the range between 490 and 620 K. Between 620 and 660 K, the predominant component in the waste samples is cellulose.

The DTGs obtained under N<sub>2</sub> flow (Fig. 2) show degradation processes similar to those reported in the literature for spent coffee and tea grounds [39–43].

To develop the kinetics study of the pyrolysis of coffee and tea wastes samples, tests were carried out on the thermobalance at

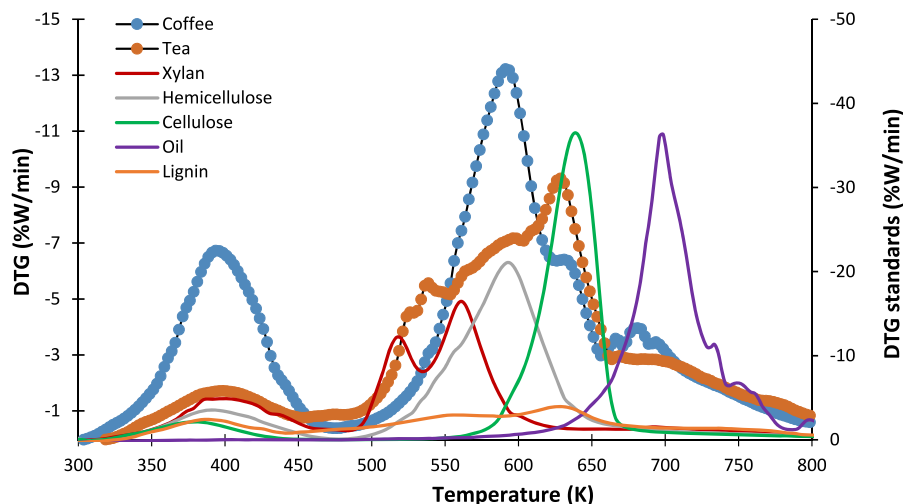


Fig. 2. DTGs for spent coffee and tea grounds and standard components at 20 K/min.

different heating rates from 10 to 50 K/min, Fig. 3. From the DTG of coffee and tea, it is observed that the higher the heating rate, the greater the intensity of degradation rate, and the beginning and end of thermal degradation are shifted to higher temperatures, obtaining a higher maximum temperature of degradation. Several

authors have reported that this increase in the heating rate leads to increased heat transfer limitations [38,44].

To proceed with the kinetics study, in particular the components of hemicellulose and cellulose, it is necessary to do the deconvolution of the experimental DTG curve in symmetric Gaussian curves

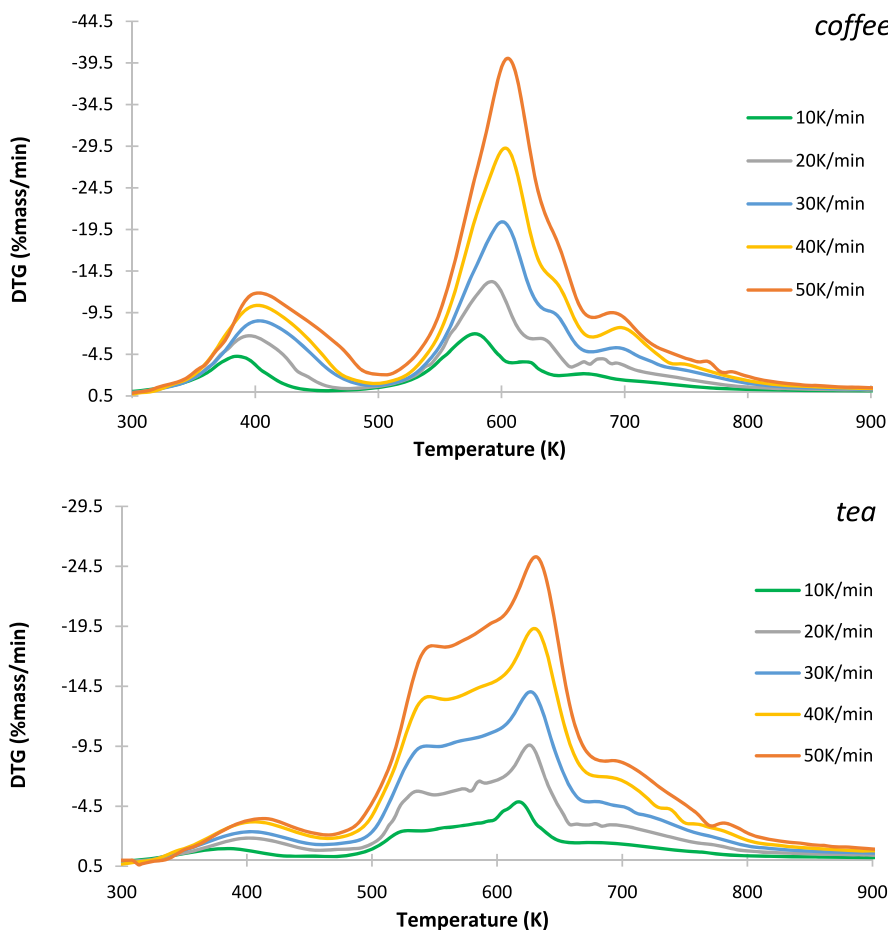


Fig. 3. DTGs for coffee waste and spent tea leaves samples at different heating rates.

for the different compounds. To estimate the lignocellulosic content for coffee and tea samples, the experimental DTG curves of all heating rates were deconvolution with 8 symmetric Gauss curves, considering the different degradation processes that occur in the temperature range of 300–800 K, Fig. 3.

It was assumed that the main pseudo-components considered for the coffee and tea samples were: moisture, extractives, hemicellulose, cellulose, and lignin. In both samples, the presence of two types of hemicellulose and oils were considered. Also, it was considered that coffee waste has a protein content. As previously mentioned, the pseudo-components behave individually, neglecting the chemical interactions between them.

Fig. 4 is shown one example of the deconvolution of the DTG curves in 8 symmetrical Gaussian type curves.

From the deconvolution of the experimental DTG curve into symmetrical Gaussian curves for the different components at different heating rates, it appears that this distribution of components in the thermal degradation of coffee and tea is similar, Fig. 5. What would be expected since the lignocellulosic composition of

the biomass does not change with the heating rate.

Through this method, it is possible to calculate an average of the composition of the coffee and tea samples presented in Table 1. This composition obtained is in the range of those reported in the literature for spent coffee and tea grounds [45–49]. The accuracy of the technique used for biomass composition determination was checked comparing the obtained values with published data. For example, for spent coffee grounds Somnuk et al. [50] reported oil (minor component) contents in the range of 10–15% (weight basis) depending on the coffee variety. It is clear that the composition of the tea, and coffee, wastes varies greatly with the type of tea and coffee used.

From symmetrical Gaussian curves of hemicellulose, cellulose and lignin were determined the maximum temperature of thermal degradation of each heating rate, to calculate the kinetics parameters according to the Kissinger method. The activation energy and preexponential factor obtained by the Kissinger method for spent coffee and tea grounds are shown in Table 2, with the respective correlation coefficients ( $R^2$ ).

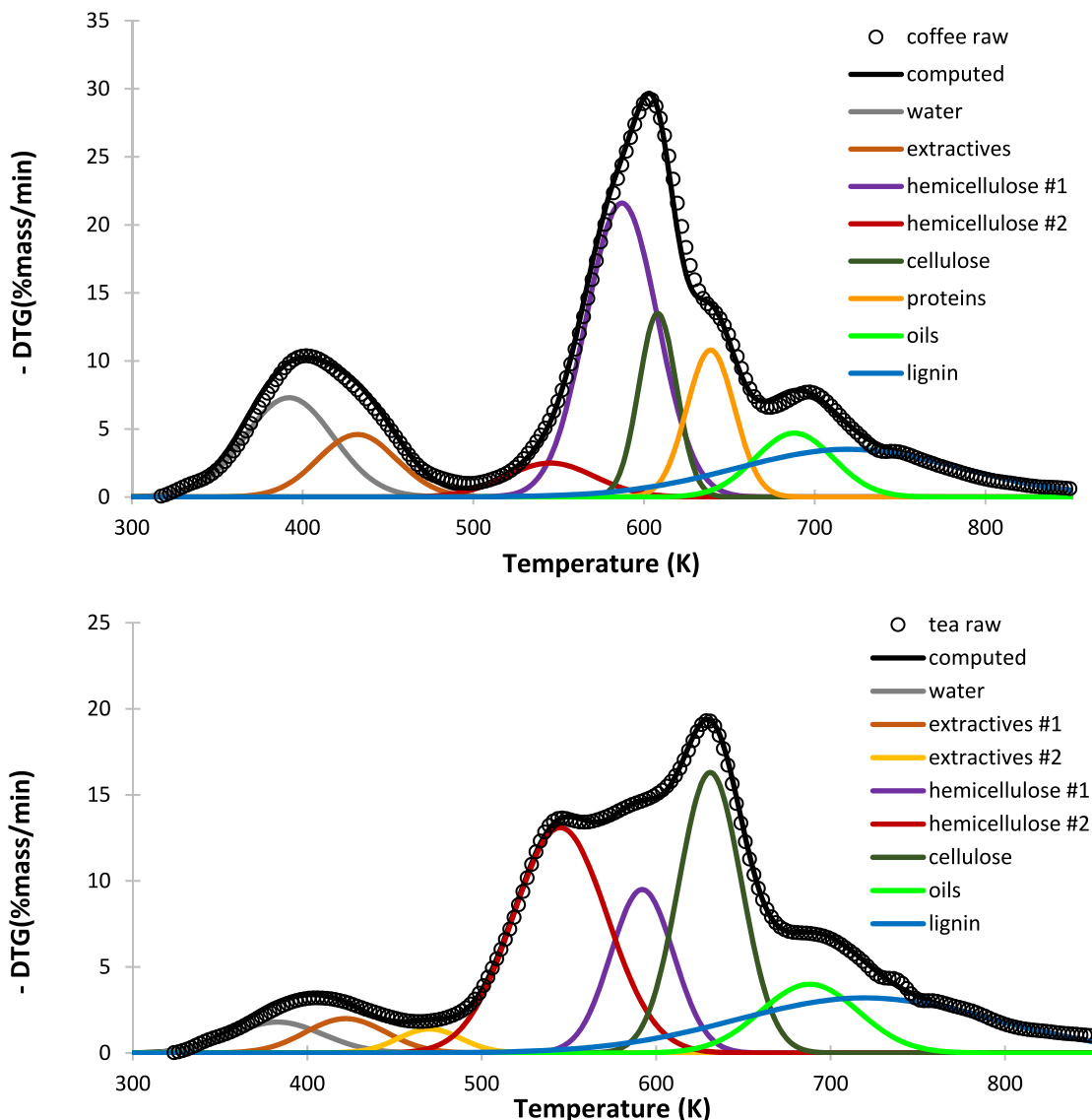


Fig. 4. Experimental and pseudo components deconvoluted DTG profile of coffee and tea samples (at 40 K/min, under N<sub>2</sub> flow).

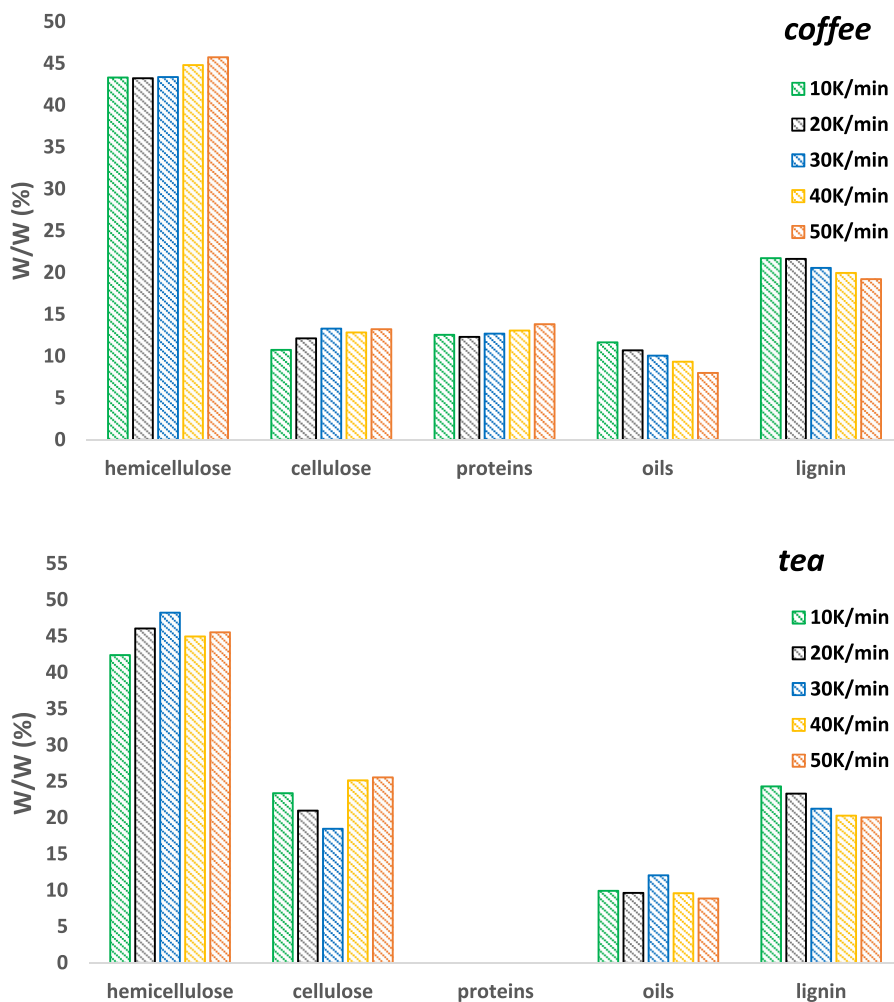


Fig. 5. Spent coffee and tea grounds pseudocomponents composition using thermogravimetry data obtained for heating rates from 10 K/min to 50 K/min.

**Table 1**  
Average composition of spent coffee and tea grounds assessed by thermogravimetry.

W/W (%)	Coffee	Tea
Hemicellulose	44.1	45.4
Cellulose	12.4	22.7
Proteins	12.9	0.0
Oils	10.0	10.0
Lignin	20.6	21.8

**Table 2**  
–Kinetics parameters of spent coffee and tea grounds assessed by thermogravimetry by Kissinger method.

Sample	Coffee			Tea		
	$E_a$ (kJ/mol)	A ( $s^{-1}$ )	$R^2$	$E_a$ (kJ/mol)	A ( $s^{-1}$ )	$R^2$
Hemicellulose #1	186	$5.1 \times 10^{15}$	1	157	$4.8 \times 10^{16}$	0.88
Hemicellulose #2	161	$3.8 \times 10^{14}$	0.99	251	$9.5 \times 10^{21}$	0.87
Cellulose	143	$2.2 \times 10^{11}$	0.98	306	$2.5 \times 10^{21}$	0.81
Lignin	394	$9.1 \times 10^{27}$	0.97	413	$1.7 \times 10^{29}$	0.97
Global biomass	172	$1.8 \times 10^{15}$	0.98	359	$2.6 \times 10^{30}$	0.94

For spent coffee, the activation energy obtained by this method was 186 kJ/mol, 161 kJ/mol, 143 kJ/mol, and 394 kJ/mol, respectively for hemicelluloses #1 and #2, cellulose and lignin while for tea grounds was 157 kJ/mol, 251 kJ/mol, 306 kJ/mol, and 413 kJ/mol

and. From Table 2, the pre-exponential factor for tea samples is greater than for spent coffee. It is possible to observe that the spent tea has a low correlation coefficient ( $R^2 < 0.90$ ) for both hemicelluloses and cellulose. One possible reason for that could be due to a change in the kinetics mechanism during the heating rate of 20 K/min and 30 K/min.

Some authors have reported that cellulose pyrolysis is described by a single first-order reaction with high activation energy

(191–320 kJ/mol) [38,51–53]. Anca-Couce reported that the activation energy values for hemicellulose values ranged from 70 to 215 kJ/mol [53,54]. These ranges of values are following the values obtained, presented in Table 2.

From Table 2, it appears that the activation energy values of lignin for both coffee and tea residue samples are high, 394 and 413 kJ/mol, respectively. High values of activation energy for lignin have already been reported in the literature [53,55]. Ferdous et al. reported from Alcell lignin thermogravimetry data, the activation energy intervals obtained were 129–361 kJ/mol and for the pre-exponential factor were  $6.2 \times 10^{11}$  to  $9.3 \times 10^{22}$  ( $s^{-1}$ ). Ferdous et al. [55] also suggested that the kinetics parameters depend heavily on the type of lignin used and its origin, and the type of equipment used for pyrolysis reactions [55]. In the case of pyrolysis of tea samples, as mentioned in previous works, the simultaneous degradation of lignin and cellulose causes an increase in the activation energy of the lignin obtained from the Kissinger method, since the presence of lignin fibers reinforces the cohesion of the cellulose and hemicellulose fibers thus increasing the activation energy of pyrolysis [38].

The values obtained in this work for individual components are in line with what was reported since one of the assumptions was that there is an individual decomposition of each pseudo-component and the interactions between the various components in the biomass were not considered.

The values of activation energies obtained by the Kissinger method for spent coffee and tea grounds are 172 and 359 kJ/mol, respectively. These values are consistent with the activation energy values for hemicellulose and cellulose pyrolysis, respectively. It should be noted that from Fig. 4, the maximum temperature of degradation in the coffee samples corresponds to the temperature range of the hemicellulose while in the case of the tea samples this temperature corresponds to the cellulose.

### 3.2. Fixed bed reactor experiments

The thermal and catalytic degradation experiments of spent coffee and tea grounds were carried out at 673 K in a fixed bed reactor. The temperature of 673 K was chosen from the thermal degradation profiles as the temperature corresponding to the maximum rate of thermal degradation. It is also suggested in the literature that temperatures above 673 K, the quality of the bio-oil increases but this increase in temperature leads to a decrease in the bio-oil yield due to the prevalence of secondary reactions of the pyrolysis vapors, which causes an increase in the amount of gaseous products [46]. The pyrolysis product yields (w%) of wastes samples with and without a catalyst at 673 K and 300 mL/min continuous flow rate of  $N_2$  during 15 min is shown in Fig. 6 (Fig. 7).

From Fig. 6 it can be seen that the uncatalyzed pyrolysis of tea samples shows the highest values of biochar yield (43%) and the lowest bio-oil yield (18%) while the coffee has 25% of biochar yield

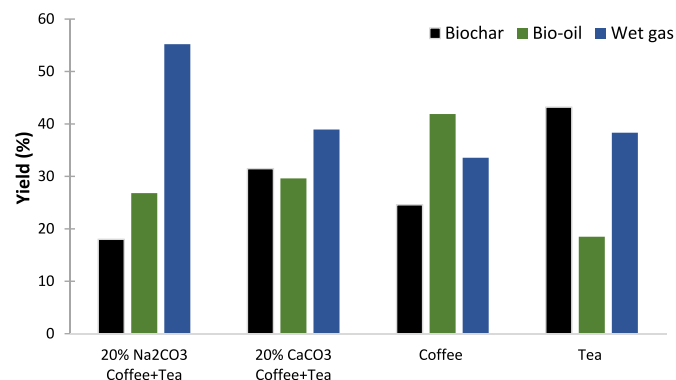


Fig. 6. Pyrolysis yields obtained using 20% (w/w) of alkali carbonate catalysts (Na and Ca) at 673 K.

and 42% of bio-oil yield. The bio-oil from non-catalyzed pyrolysis of coffee grounds produced a pungent and viscous liquid that separated into two phases, one less viscous, light brown (aqueous), and the other high viscous, and dark brown (organic).

For spent coffee grounds Ktori et al. [56] observed a maximum bio-oil yield (36%) at 813 K followed by a drop for higher pyrolysis temperatures. The differences in bio-oil yield between the current work (46% at 673 K) and the work by Ktori et al. [56] may be related to the different geometries of the reactors used and the different coffee grounds used.

The formation of two phases in the bio-oil is commonly referred to for the slow and intermediate pyrolysis of biomass [57] but was never reported for coffee ground bio-oil. The results from this research showed that the formation of the two liquid phases, instead of one, depends on the pyrolysis conditions as reported in the literature and, clearly, on the composition of the biomass and the presence of catalysts. The pyrolysis of tea grounds, and mixtures of tea and coffee grounds with catalysts delivered bio-oil with only one phase (organic). Some authors reported a bio-oil yield around of 20–37% at 673–813 K of spent coffee grounds pyrolysis [25,56,58]. In the pyrolysis of waste tea, some authors obtained at 673–723 K, around 12–28% of bio-oil yields [4,29,39]. The yield values obtained in this work are in accordance with what was reported in the literature.

In the case of catalytic experiments of coffee and tea mixtures, as expected, the alkali carbonates catalysts promoted the gasification reactions which showed the increase of wet gas yields [59]. The  $Na_2CO_3$  catalyst, led to higher wet gas yields and to lower biochar yields which are agreed with the catalyst behavior described in the literature. According to Fonseca et al. [60] the sodium carbonate is an efficient pyrolysis catalyst allowing pre-cracking and partial deoxygenation of the feedstock. The  $CaCO_3$  catalyst had an almost null effect on the pyrolysis products distribution. This result seems to contradict the recent findings of Luo et al. [61], which described a beneficial effect of Ca catalysts on the pyrolysis liquid product obtained from sludge with 50% of moisture. The authors claimed a secondary cracking process of biomass volatiles in the presence of calcium catalysts, which was probably favored by the high moisture content of the biomass used (steam cracking). The low moisture content of the spent coffee and tea grounds used in this study is responsible for lessening the effect of the calcium catalyst in promoting the yield of pyrolysis bio-oil.

### 3.3. Bio-oil characterization

The dried bio-oils were characterized by ATR-FTIR spectroscopy to identify the functional groups of the major compounds, following the band attribution from literature (Table 3). The IR band nonunivocal attribution due to the overlap of distinct vibration modes makes the analysis of the IR spectra of the pyrolysis bio-oils a complex process. The acquired IR spectra of bio-oils were like those published for bio-oils obtained by biomass pyrolysis [62], showing IR features belonging to maltenes (pentane, hexane or heptane soluble components of asphalt) as reported by Al-Layla et al. [8] and Fadhil [10]. All spectra showed a broad band in the 3600–3050  $cm^{-1}$  range ascribable to OH groups of carboxylic acids, alcohols, and phenols [8,63]. For the less viscous phase (aqueous phase) of the coffee grounds bio-oil the band in the 3600–3050  $cm^{-1}$  range is a complex band with a shoulder around 3250  $cm^{-1}$  which can arise from amines, but the expected amine band at 1640  $cm^{-1}$  is absent, which led to discarding the contamination of this bio-oil with amines. The Millard reaction [64] between proteins and sugars, of coffee grounds, seems to keep the N-containing compounds in the solid pyrolysis product (biochar). The viscous oils bio-oils showed similar IR spectra except for tea

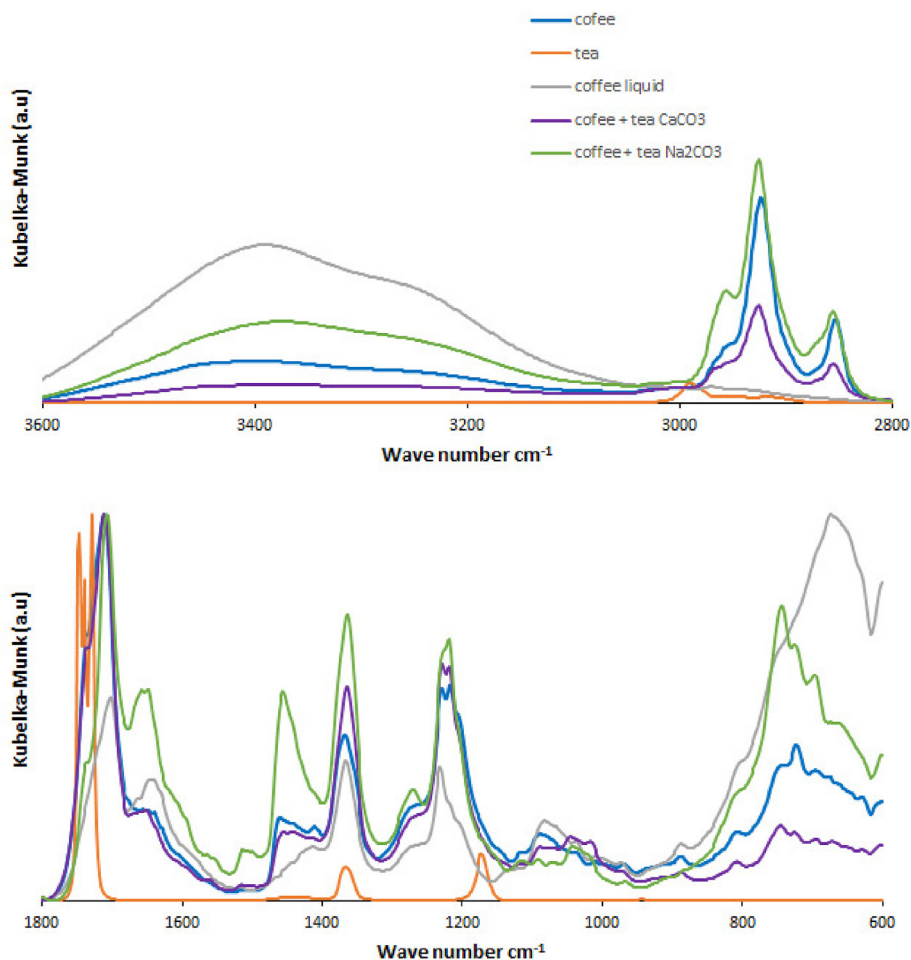


Fig. 7. ATR-FTIR spectra of dried bio-oils obtained by catalyzed and non-catalyzed pyrolysis.

**Table 3**  
Pyrolysis bio-oil FTIR bands attribution from literature.

Band position (cm <sup>-1</sup> )	Functional group	Band assignment	Reference
1767	C=O	Lactones	[65]
1740	C=O	unconjugated alkyl aldehydes and alkyl esters	
1713	C=O	carboxylic acids (and fatty acids)	
1696	C=O	unsaturated aldehydes, ketones	
1640	C=O	hydroxyunsaturated ketones, aldehydes	
1600	C=C	aromatics with various types of substitution	
1575	C=C		
1517	C=C		
1501	C=C		
3008	C=C	symmetric stretching vibration of aromatics	[63]
3000–2800	C–H	Aliphatics	
3650–3100	OH	carboxylic acids, alcohols and phenols	
1645	NH	Amines	[66]
3363 (broad)	OH	water, alcohols, organic acids	[67]
	NH		
1659	C=C	stretching vibration of carbon-carbon double bonds	
	C=O	stretching vibration of carbonyl groups	
1455	CH <sub>2</sub> , CH <sub>3</sub>	bending vibrations of aliphatic groups	
1406	C–H	rocking vibrations of olefins	
1028	C–O	stretching vibration of ester groups	
880	C–H	out-of-plane deformation vibration of terminal olefins	
666 (broad)	CH <sub>2</sub>	overlapping of the rocking vibration and the out-of-plane vibration of <i>cis</i> -disubstituted olefins	

grounds derived bio-oil. For those spectra, the band in the range 3000–2800 cm<sup>-1</sup> shows that NaCO<sub>3</sub> catalyst increases the amount of bio-oil olefins, which is compatible with his catalytic role

described in the literature [12]. The calcium carbonate catalyst slightly decreases the olefins contents of bio-oil. The complex spectral features in the range 800–600 cm<sup>-1</sup> reinforce the fact that



sodium carbonate catalyst increases the olefins content while calcium carbonate depletes it. According to the literature [61] calcium salts promote aromatization reaction which is compatible with our finding.

For all the spectra the most intense IR bands are located in the 1750 - 1650  $\text{cm}^{-1}$  range belonging to C=O stretching from aldehyde, ketone, carboxylic acids, ester and quinone groups, being these compounds the main components of pyrolytic bio-oil derived from wood biomass [12].

Such compounds are also referred to be the main drawback of pyrolysis bio-oil because they are responsible for high acidity, high oxygen content, and high instability during storage [68]. Due to the relevance of carbonyl compounds the IR bands in the range 1750–1650  $\text{cm}^{-1}$  were deconvoluted (Fig. 8) following the methodology of Lievens and co-workers [65] to infer the relative amounts of different compounds with carbonyl groups, and aromatics (Fig. 9).

From Fig. 9 the organic phase of coffee differs significantly from the aqueous phase in terms of product distribution. The organic phase is mainly composed of fatty acids, alkyl esters/aldehydes, and hydroxy unsaturated aldehydes/ketones (40, 20, and 19%, respectively). Minor compounds such as aromatics, unsaturated aldehydes/ketones, and cyclic esters (10, 8, and 2%, respectively) were also detected. Previously published data for the composition of the coffee grounds bio-oil showed 30% acids, 4% esters, 7% hydrocarbons, 10% nitrogen compounds, and 13% aromatic compounds [46,69–71]. It was also mentioned that the fatty acid and ester content of the bio-oil indicates that the triglycerides of the coffee are not thermally decomposed (there is only a break in the ester link with the glycerol) and that during the roasting and coffee extraction process there is a partial decomposition of coffee grounds glycerides into fatty acids [46,69]. The coffee grounds bio-oil aqueous phase is mainly composed of fatty acids, unsaturated aldehydes/ketones, hydroxy unsaturated aldehydes/ketones, and aromatics (18, 25, 34, and 16%, respectively). Traces of cyclic esters and alkyl esters/aldehydes were also detected. Literature data for the bio-oil aqueous phase reported the presence of phenols (42%), ketones (21%), nitrogen compounds (17%), aldehydes (15%), alcohols (6%). Researchers underline that nitrogen compounds in bio-oil are due to the high caffeine content in spent coffee grounds [46,72]. The slow pyrolysis conditions in this study, with high residence time, are responsible for the absence of N-containing compounds in the liquid products [64].

The compound groups identified in the tea bio-oil differ from

coffee bio-oil. Bio-oil from tea grounds does not contain aromatics, unsaturated aldehydes/ketones and, hydroxy unsaturated ketones/aldehydes. Tea grounds bio-oil present a higher content of cyclic ester and alkyl ester/aldehydes and a similar content of aliphatic/fatty acids than coffee.

The bio-oils produced by catalyzed and non-catalyzed pyrolysis showed different compositions. The sodium carbonate catalyst reduces the presence of carbonyl groups, namely the carboxylic acid groups, thus contributing to the improvement of the quality of the bio-oil. An analogous beneficial effect of sodium carbonate catalyst, during wood biomass pyrolysis, was reported by Soares et al. [12]. Calcium carbonate does not affect the distribution of carbonyl groups of the produced bio-oil. Contrary to the reported by Luo and co-workers [61] the calcium carbonate catalysts do not improve the aromatics content of bio-oil.

Several methods are reported in the literature for pyrolysis bio-oil upgrade, via decreasing acidity and oxygen content. Recently, authors upgraded coffee grounds pyrolysis bio-oil using ethanol supercritical esterification over supported metal catalysts [73]. The authors reported an important decrease of bio-oil acidity with a simultaneous drop of oxygen content. This process seems to be more complex than the in situ catalyzed pyrolysis, with cheap and environmentally benign catalysts, used in the current work.

The thermogravimetric simulated distillation of the produced bio-oils was used to evaluate the fraction of medium and light distillates. Data in Fig. 10 shows the rate of simulated distillation of all the bio-oils, underlining the interesting effect of alkaline carbonate catalysts on the volatility of bio-oil. This result is compatible with the volatilization effect usually attributed to sodium carbonate pyrolysis catalyst [12].

The volatile fraction, Fig. 11, computed as the weight loss for temperature lower than 623 K clearly shows the beneficial effect of carbonate catalysts on the bio-oil quality. Moreover, comparing the volatile fractions of bio-oils obtained by uncatalyzed pyrolysis of both biomasses, stand out the role of the lignocellulosic composition on the quality of the produced bio-oil. The spent tea grounds with twice the cellulose than the spent coffee grounds produce a much more volatile bio-oil. The spent coffee grounds proteins seem to be also responsible for such a result. The calcium catalyst promoted the secondary cracking effect reported by Luo et al. [61] leading to the production of a more volatile bio-oil despite its null effect on the yield of this pyrolysis product.

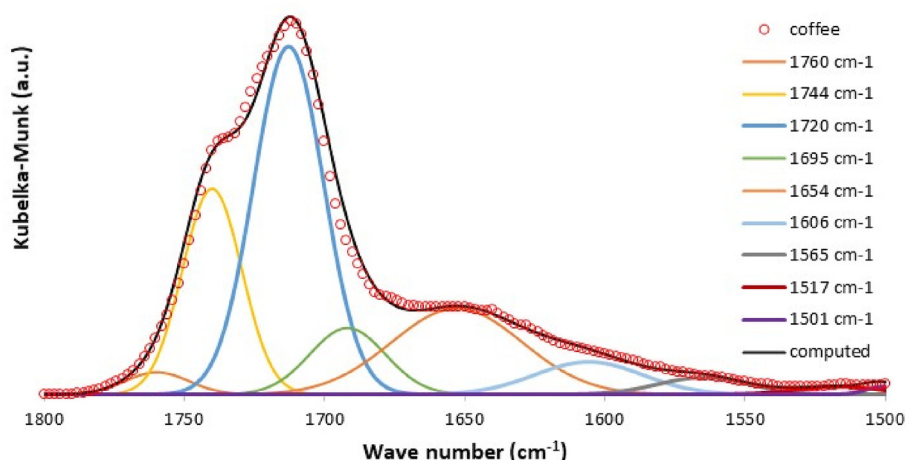


Fig. 8. Deconvolution of FTIR spectrum in the region of 1800–1400  $\text{cm}^{-1}$  for the bio-oil (organic phase) obtained by uncatalyzed pyrolysis of coffee.

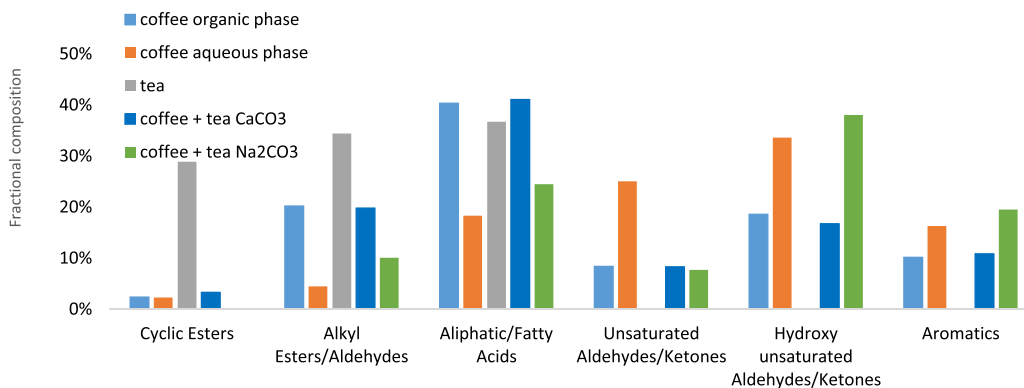


Fig. 9. Functional groups of the produced bio-oils assessed by deconvolution of ATR-FTIR spectra.

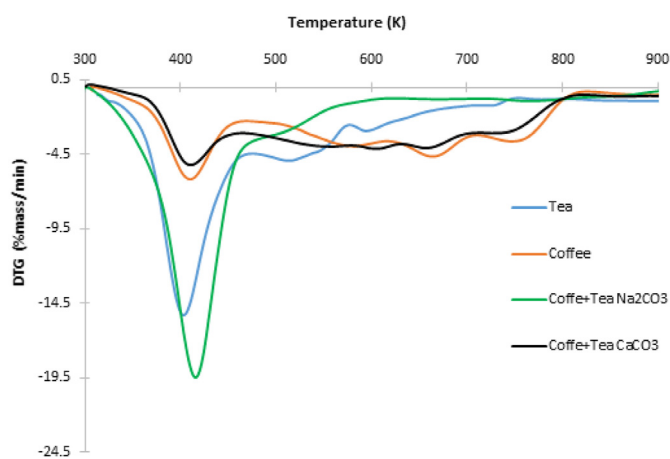


Fig. 10. Rate of simulated distillation of the bio-oils obtained in the catalytic, and non-catalytic pyrolysis at 673 K. Thermograms were acquired under N<sub>2</sub> flow and a heating rate of 20 K/min.

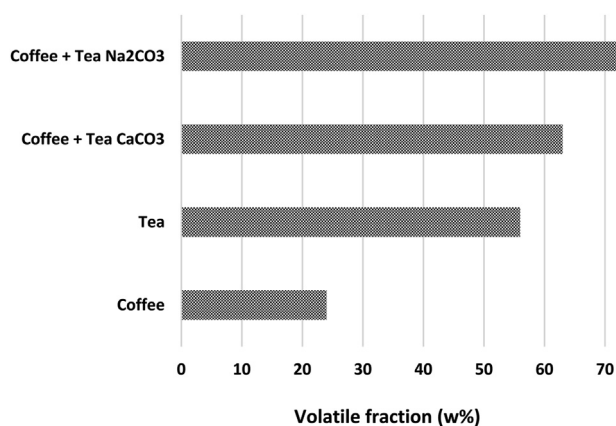


Fig. 11. Bio-oils volatile fraction (weight loss for T < 623 K) assessed by thermogravimetry (Fig. 10).

#### 4. Conclusions

Spent coffee and tea grounds were characterized by thermogravimetry and pyrolyzed in a fixed bed reactor using sodium and calcium carbonates commercial materials as catalysts. The thermal

degradation profiles of both materials were deconvoluted using a pseudo-component model to assess biomasses composition, revealing the presence of proteins for coffee grounds in addition to lignocellulosic and oils which were common to both samples. The spent tea grounds had higher cellulose content than spent coffee grounds (almost double) while hemicellulose, and lignin, levels were roughly the same. The Kissinger method used to evaluate pyrolysis kinetics parameters, for both samples, revealed higher activation energy for spent tea grounds, which had lower bio-oil yield when pyrolyzed in the absence of a catalyst. Calcium carbonate and sodium carbonate revealed excellent catalytic performances during pyrolysis. Both catalysts promoted gasification reactions, being sodium carbonate more effective than calcium carbonate. The proteins of spent coffee grounds do not contaminate the bio-oil with nitrogen containing compounds because the slow pyrolysis allowed Maillard reactions, prompted by alkali elements used as catalysts, thus removing N-containing molecules from liquid products. Data from pyrolysis catalyzed by low-value materials such as alkaline carbonates show that coffee and tea residues can be used biorefinery feedstock, allowing the management of these residues within the framework of the circular economy, fulfilling the objectives of reducing and valuing residues. The selective collection of spent coffee and tea grounds is an operational problem for the scale-up of the pyrolysis process reported above. The selective collection of coffee grounds is already done by some brands of coffee capsules and the same can be done for tea grounds by placing specific containers at the points of separate collection of other waste such as paper, cardboard, plastics, and glass.

#### Author contribution

Bruna Rijo: Writing – review & editing, Formal analysis. Ana Paula S Dias: Conceptualization, Resources, Supervision. Marta Ramos: Writing – original draft. Nicole de Jesus: Investigation, Formal analysis. Jaime Puna: Supervision.

#### 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.

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