

Valorisation of by-Products/Waste of Agro-Food Industry by the Pyrolysis Process

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Abstract: Waste valorization practices have attracted a great deal of attention in recent years with the aim of managing waste in the most sustainable way. Agro-food industry waste of the Piedmont Region such as coffee powder, cocoa husks, pellets of parchment coffee, rice husk and hazelnut shell, has been pyrolysed via a lab-scale reactor system. This work studies the yields and properties of pyrolysis products (bio-oil, gas and char) produced from the different feedstocks under two heating rates, 360 and 750 °C/h with the maximum temperature of 750 and 800 °C, respectively. The results show that the bio-oil yield increased when increasing heating rates and temperatures while the char yield decreased.

The main gas products were CO₂ (28-43%), H₂ (19-26%), CO (13-26%) and CH₄ (12-18%). The high heating value (HHV) of the products ranged between 13-17, 27-35 and 18-31 MJ/kg for gas, bio-oil and char, respectively. The HHV of the tar was relatively higher than that of diesel fuel, which is approximately 42 MJ / Kg. The chemical energy yield varied from 72% to 86%, with the highest value for the hazelnut shell. The solid residue was mainly composed of carbon (81-98,6%). The solid rice husk residue presented a particularly high quantity of silica (14,4%).

This study also aimed to investigate the feasibility of applying high-carbon bio-char particles additive to concrete to improve the sustainability of the pyrolysis process to valorize the solid output. As a result, this research developed a cement admixture using nano/micro carbonized bio-char particles from pyrolyzed coffee powder waste to enhance its mechanical strength and toughness without losing its ductility. The flexural test results showed that the strength and ductility increased by adding a percentage equal to 0.08 wt% of Carbon-Coffee particles into the matrix. In fact, the FMAX grows from 130 N to about 180 N and, at the same time, the fracture energy increases by 40%.

Keywords: Waste valorization, Pyrolysis, Green cement, Bio-char-micro-particles.

1. INTRODUCTION

Currently, 80% of the world's energy is provided by hydrocarbon fuel combustion, which has been anticipated to continue to play a significant role in the foreseeable future. Due to the steady increase in energy consumption, the shortage of fuel supply source and greenhouse emissions, it is essential to find the most sustainable and efficient methods to produce the alternative fuel but emit lesser quantity of pollutants [1]. Biomass waste has drawn a great deal of attention as a potential candidate for fossil fuels. Biomass waste-to-energy conversion leads to a decline in greenhouse gas emissions in two different ways. Heat and electrical energy are generated to reduce the dependence on power plants. Greenhouse gases are decreased as the methane emission from landfills is prevented. Moreover, waste-to-energy plants are highly efficient in harnessing the untapped sources of energy from wastes.

On the other hand, the activities of the food chain are characterized by a high production of wastes and of by-products, thus creating serious problems for their management and disposal [1]. In the European Union, there are about 3000 million tons of organic waste per year, and 10% of these are agro-food industry wastes. Despite the recommendation of the European Union, these values are constantly increasing and their disposal is an additional problem for the food industry [2]. In some cases, these wastes are energetically exploited through a direct combustion process to produce thermal energy. Otherwise, they are usually transported to disposal plants, without any kind of use/enhancement and with an extra-cost for the agro-food companies. As a result, this hazardous waste determines the landfills saturation and/or pollution problems [2].

Biomass is comprised of three major components, namely, cellulose, hemicellulose, and lignin, and of some minor constituents such as extractives and minerals [3, 4]. The inorganic material content ends up in the pyrolysis ash. The elemental compositions in the biomass are potassium (K), calcium (Ca), silicon (Si), sodium (Na), manganese (Mn), phosphorus (P), iron

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(Fe), magnesium (Mg), aluminum (Al), chromium (Cr) and zinc (Zn) [5].

Pyrolysis, namely the rapid thermal decomposition of organic materials in the absence of oxygen, is a promising approach to convert biomass wastes into chemical energy, in the form of bio-oil (tar), bio-char, and syn-gas composed mainly of H₂, CO, CH₄, CO₂ and lower molecular weight hydrocarbon gases [6, 7].

The yield and composition of pyrolysis products depend on numerous parameters, such as the chemical and structural composition, particle size and species of the used biomass, as well as the temperature, heating rate, humidity and residence time of the pyrolysis [8-10].

Pyrolysis products (bio-char and gas) have several potential applications that add to the feasible economic viability of the production of bio-oil as a fuel, as well as to the possibility of producing higher-added value chemicals through upgrading [11, 12]. The gases are generally volatile substances with a low heating value and are often burned with other fuels to recycle waste heat and reduce pyrolysis costs [11, 13]. Göring *et al.* [14] have demonstrated the possibility of producing bio-methane by upgrading the gas.

Bio-char has several prospective applications such as the enhancement of soil and carbon sequestration [15], the improvement of soil water and nutrient retention, and the reduction of water contamination [6, 16]. In some cases, the properties of char have been investigated for activated carbon and nanosilica production [6, 17, 18].

On the other hand, Won Chang and co-workers studied the possibility of improving the sustainability of the concrete by incorporating the hardwood bio-char [15]. They investigated the effects of the water retention capacity of hardwood bio-char in concrete as well as the chemical and mechanical properties using sample mortar mixes with varying replacement rates of cement containing bio-char. More recently, Ferro *et al.* [19] and R. A. Khushnood [20], have studied the mechanical performance of cement composites by the utilization of micro-sized inert particles from hemp hurds and sugarcane bagasse, respectively. They demonstrated that these particles improve compressive strength and fracture toughness of cement matrix composites. In addition, bio-char derived from switch grass was tested as bio-modifier for asphalt binder. It was found that bio-char increases the rutting resistance

of the asphalt binder. Based on the testing results, bio-char appears to be a more effective binder modifier than commercially activated carbon.

In this frame, this work is a part of the Piedmont region ECOFOOD project [2]. The project is aimed at promoting the environmental sustainability and the energy of some regional food chain/agro-food industries in the Piedmont Region (northern Italy). In other words, the goal of the project is to reduce food industry waste in Piedmont.

The overall objective of this study is the energetic valorization of food industry waste and by-products, via an eco-friendly and sustainable pyrolysis process. Two specific tasks have been set: evaluating the influence of pyrolysis parameters on the distribution of the mass and energy of the obtained products, and identifying any possible alternative uses to the combustion of the solid product of pyrolysis. Therefore, the possible use of char produced from the pyrolysis of agro-food industry residues as an additive to concrete to improve the mechanical performance of the cement composites and to achieve a sustainable green concrete is being studied.

2. MATERIALS

Five different materials have been used for the tests: coffee powder, cocoa husks + cocoa dust (referred to cocoa husk), as well as parchment coffee, rice husk and hazelnut shell pellets. These wastes or by-products were supplied by the agro-food industries in Piedmont that are partners in the aforementioned ECOFOOD project. Their definition are as follows:

- Coffee powder is unroasted coffee that is discarded because it does not meet the quality requirements necessary for commercialization. This biomass is in powder form.
- Cocoa husks are derived from the roasting of cocoa in the chocolate production process, while cocoa dust is instead composed of parts of cocoa beans in the form of tiny particles. According to Italian law (Law 30 of April 1976, no. 351), these particles contain at least 20% of fatty substance, which is calculated on a dry matter weight basis.
- Parchment coffee is composed of the outer shell that covers green coffee before its dry milling, and it is removed from the shelling machine

before the roasting process; the parchment is then pressed to form pellets.

- Rice husk is the hard protecting covering of rice grains. The chaff is separated from the grain using a husking process. The amount of rice husk is approximately 17-23% by weight of paddy rice, depending on the kind of rice, (rice grain and rice husks).
- Hazelnut shell is generated during the processing of hazelnuts. These residues are useless and their large volume creates a disposal problem.

Each sample was separately pyrolyzed to identify the most interesting biomass that produced the desired products. The supplied samples were subjected to pyrolysis without any prior treatment (drying or grinding) to evaluate the possibility of using them to limit costs for the companies. Table 1 summarizes the proximate, ultimate and composition analyses. The ultimate analysis gives the biomass composition in weight percent (wt%) of the main elements: carbon, hydrogen, nitrogen and sulphur (C, H, N and S).

Oxygen was calculated by a difference method. The ultimate analysis of the biomass indicates that the rice husk and hazelnut shells have no sulfur in their composition and have smaller N values than the others. The HHV was measured with a bomb calorimeter.

The samples were characterized in terms of proximate and ultimate analysis, according to ASTM standards (E871, D1102-84) by using a programmable ash oven.

3. EXPERIMENTAL SET-UP

The experimental system was designed for effective thermal control of the sample and for collecting solid, gas and liquid products for off-line analysis.

The pyrolysis experiments were conducted in a lab-scale batch reactor unit. Figure 1 shows a schematic diagram of the pyrolysis unit. It consists of a reactor, a furnace, a water condenser and a gas meter. The reactor was constructed in AISI 316 stainless steel, and has an internal diameter of 27 mm and a height of 130 mm. There are four welded tubes on the top cover.

Table 1: Results of Proximate, Ultimate, and Composition Analysis of the Biomass

Analysis	Coffee Powder	Cocoa Husks	Coffee Pellets	Rice Husk	Hazelnut Shells
Ultimate analysis (dry, wt.%)					
C (%)	51.7	44.7	45.9	38.5	55.1
H (%)	6.7	6.1	5.9	5.1	6.3
N (%)	2.7	2.4	2.8	0.5	1.6
S (%)	0.1	0.2	0.2	-	-
O (%)	33.3	38.6	36.2	51.3	35.2
Ash (by difference) (%)	5.5	8.0	8.6	4.6	1.8
Proximate analysis (wt.%)					
Moisture (% p/p)	2.3	7.4	5.5	9.4	5.3
Volatile matter	90.1	85.1	86.2	83.4	77.1
Fixed carbon	4.4	6.9	5.2	12	21.1
Ash (%)	5.5	8.0	8.6	4.6	1.8
Composition of lignocellulosic material (wt.%)					
Cellulose	26.1	34.4	37.1	37.5	30.5
Hemicellulose	30.2	37.4	27.2	15.4	25.9
Lignin	30.8	18.7	31.5	34.5	35.1
HHV (MJ/Kg)	18.5	18.2	18.4	15.4	18.8
PH	5.1	4.8	5.8	7.2	5.3
Average size	<1 mm	0.5 cm	Pellets (1cm)	0.5 cm	0.5 cm

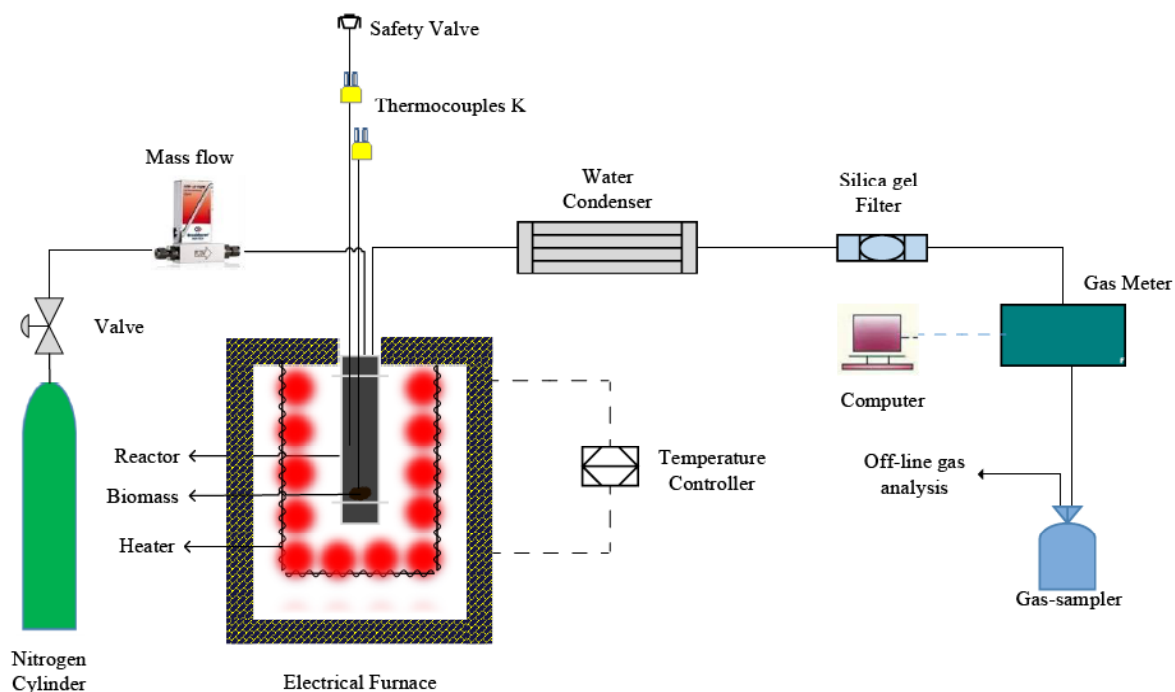


Figure 1: Schematic diagram of the experimental apparatus for biomass pyrolysis.

One of these tubes allows the gases and vapors to exit and being transferred to the condenser (Figure 1). A second tube instead allows the inert gas to enter the reactor and an internal thermocouple measuring the temperature was put in contact with the biomass inside this tube. There is a second shorter thermocouple, in the third tube, which reaches half of the capsule. The thermocouple communicates directly with the oven temperature controller. In the fourth tube was inserted a safety valve to limit the reactor pressure to 2 bar in case the tube connected to the condenser is obstructed. The heating takes place by means of a 400 W electric heater. The maximum temperature of the oven is 1000 °C. The temperature ramps can be implemented and managed by a temperature PID controller.

The condenser operates in countercurrent to optimize the heat exchange and to promote the condensation of gas.

4. PYROLYSIS EXPERIMENTS

A cleaning procedure was adopted before each experiment: the condenser and the reactor were flushed with 100 ml/min nitrogen for 30 minutes to remove the air from the system. In order to ensure the reproducibility and the accuracy of the analysis, each experiment for one biomass was performed three times using the two different heating rates (HR). The results

show a slight difference in the solid, gaseous and liquid product yields for the tests performed with the same biomass. These results demonstrate that the experimental apparatus is reliable and offers a satisfactory reproducibility. Two different heating rates, 360 (HR1) and 750 (HR2) °C/h, with final temperature points of 750 and 800 °C, respectively, were used in the experiments. After a pre-defined reaction time, the reactor was set to cool to room temperature. The total amount of biomass used in each experiment was 3 g. The effluent gas produced in the reactor passed through a condenser, where the condensable liquid fraction was collected. The non-condensable pyrolysis gases passed through a silica gel filter and subsequently through the gas meter, where the volume and the flow rate of the exit gas was recorded. Then, the gases (after coming out from the flowmeter) were gathered in a gas-sampler. As soon as the test completed, the gas products were submitted to micro gas chromatography to determine the compositions.

A chemical analysis of the gas phase was performed using an SRA Micro GC equipped with a thermal conductivity detector (TCD) attached directly to the sampling point. Column Molsieve 5A was used to separate H₂, O₂, N₂, CH₄ and CO with argon as the carrier gas. Moreover, a PPU column was used to detect the CO₂, C₂H₂, C₂H₄, C₂H₆, C₃H₈/C₃H₆ and C₄ compounds, with helium as the carrier gas.

Table 2: Composition of the Portland Cement “CEM I 52,5R”

Chemical Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₃ O ₄	SO ₃	MgO	K ₂ O
Content (wt.%)	44.00	9.50	26.50	2.50	12.00	1.30	0.60

After each test, the liquid and solid phases were recovered for off-line analysis. The produced amount of tar was determined by weighing the condenser. The char was recovered from the bottom of the reactor and was weighed by an analytical balance. The weight of the gases was calculated by measuring the total volume and the percentages of their constituents.

5. BIO-CHAR-CEMENT SAMPLES PREPARATION

5.1. Materials

The inert micro bio-char particles from pyrolysis of coffee powder was used in this first step of the attempt to develop a cement mixture.

Portland cement (CEM Type I, grade 52,5R) provided by Buzzi Unicem, Italy, was employed for the cement composite sample preparation and the chemical composition is described in the Table 2.

Distilled water was used for the mixing formulations step, instead of normal tap water for the curing step of the samples. A superplasticizer (MAPEI Dynamon SP1, Italy; modified acrylic based polymer) for effectively dispersing the inert particles embedded in the cement paste was utilized. In this way, it greatly improves the workability of the dough, without affecting the mechanical properties of the sample, once solidified. Table 3 shows the technical data.

Table 3: Technical data of Superplasticizer “Dynamon Sp1”

Product Identity	Value
Colour	Amber
Density [g/m ³]	1.09
pH	6.5 - 9.0
Dry content	30.50%

5.2. Method

As mentioned before, the cement composite samples were prepared with an ordinary Portland cement that was added with a water reducer to provide fluidity and workability to the cement composites. All the carbonaceous additives were incorporated into one

commonly used cement at different concentrations to obtain the optimal content.

First, the particle size distribution was analyzed with the aim to move the particle size curve towards the micro-nano-scale to have a small particle size but a large specific surface area. The char was grinded by mortar and then pestle. 70 ml of water was added to the powders, and then, the size of grinded material was further reduced with the help of the attrition milling. Attrition milling was carried out for 3 hour by using 250g of alumina balls and 220 ml of distilled water as grinding media. During this process, every hour the particle size was measured by a laser-granulometer using a Mastersizer 2600/3600 Particle Sizer by Malvern Instruments. When the average particle size was in the range between 3,0 to 3,8 μm, the solution was sonicated for 15 minutes.

To optimize the specimen's preparation, knowing the initial weight of the charred coffee (2,55g), the amount of cement was fixed (214g) and the amount of super-plasticizer (3,21g). Using a water to cement ratio equal to 0,35, we have studied the amount of “coffee-solution” and water to be added to obtain specimens with different percentages by weight of carbonized inert.

Composition details of cement mixes are reported in Table 4. The indicated percentages of inert refer to the amount of cement used for the preparation of the samples.

Table 4: Composition of Cement Composites

Notation	Inert Carbonized Particles	
	Weight (%)	Weight (mg)
CEM	0	0
CEM +0.025% CCF	0.08	53.5
CEM +0.050% CCF	0.20	107
CEM +0.080% CCF	1.00	171.2
CEM +0.200% CCF	3.00	428
CEM +0.300% CCF	3.00	642

*For each mix 214 g of cement, 75g of water and 3.21g of superplasticizer were used.

The cement composite samples were prepared as following [19]:

- The pyrolyzed inert particles are then combined with the solution of water and superplasticizer and the mixture is put in an ultrasonic bath for 15 minutes, to ensure a uniform dispersion of micro particles.
- Then, the solution was stirred with the cement in a mixing bowl at 440 rpm for 60 seconds and then at 660 rpm for 2 minutes.

The mixture obtained is then poured into plexiglass molds and kept for 24 hours in an airtight container filled with water. Subsequently, the specimens were demolded and soaked in tap water for 28 days at room temperature.

Each cement composite sample was analyzed in Three Points Bending (TPB) to establish the bending strength according to ASTM C348 [21], by using a Zwick-Line Z010 single column capacity of 1 kN, as being illustrated in the Figure 2. The test was carried out controlling the Crack Mouth Opening Displacement (CMOD) of the samples and starting a displacement rate of 0,005 mm/min. The portions of broken prisms were tested in compression, according to ASTM C349 [22].



Figure 2: Experimental setup for the TPB test.

6. RESULTS AND DISCUSSION

The influence of two different heating rates (HR1 and HR2) on the pyrolysis of coffee powder, cocoa

husks, and parchment coffee pellets, rice husk and hazelnut shell has been investigated.

6.1. Pyrolysis Tests

The raw materials show different thermal decomposition behavior, due to their different compositions. The wastes and lignocellulosic biomass by-products undergo three decomposition steps as can be seen in Figure 3 for each used biomass [23].

First, a drying phase occurs up to 100 °C in which the free moisture in the biomass and the water weakly bound to the biomass is released and then the biomass underwent an exothermic dehydration between 100-300 °C, which allowed the water and low molecular weight gases, such as CO and CO₂, to evaporate. The moisture was released completely at 300 °C.

Then, the main gas products (primary pyrolysis) from the decomposition of hemicellulose and cellulose were obtained between 250 °C and 500 °C, as reported in the literature [3, 23]. Finally, above 500 °C, the remaining gas products corresponded to the slow degradation of lignin.

Lignin shows a broad decomposition interval. It starts to decompose even earlier than hemicellulose at 200 °C and continues to decompose up to 800-900 °C [23]. Lignin is the main source of char in a pyrolysis process with complementary condensables. Both hemicellulose and cellulose mainly produce condensables. This can be explained considering the covalent bonds between lignin and hemicellulose, and this connection cannot be easily cracked through pyrolysis. Cellulose and hemicellulose, however are linked by much weaker hydrogen bonds [24, 25]. The gas production for coffee powder, cocoa husks, and parchment coffee are higher than that produced from rice husk and hazelnut shell due to the hemicellulose composition.

Focusing attention on gas production, as the main desirable product from the pyrolysis, it is possible to evaluate the operating temperatures from these graphs.

The peaks, in the drying and in the primary pyrolysis phases, under HR2 conditions, appear to be shifted to slightly higher temperatures than in the HR1 conditions. The maximum gas production peaks of all the biomasses in HR2 are much more pronounced than in the HR1 conditions. This difference can also be explained considering the increased heating rate and

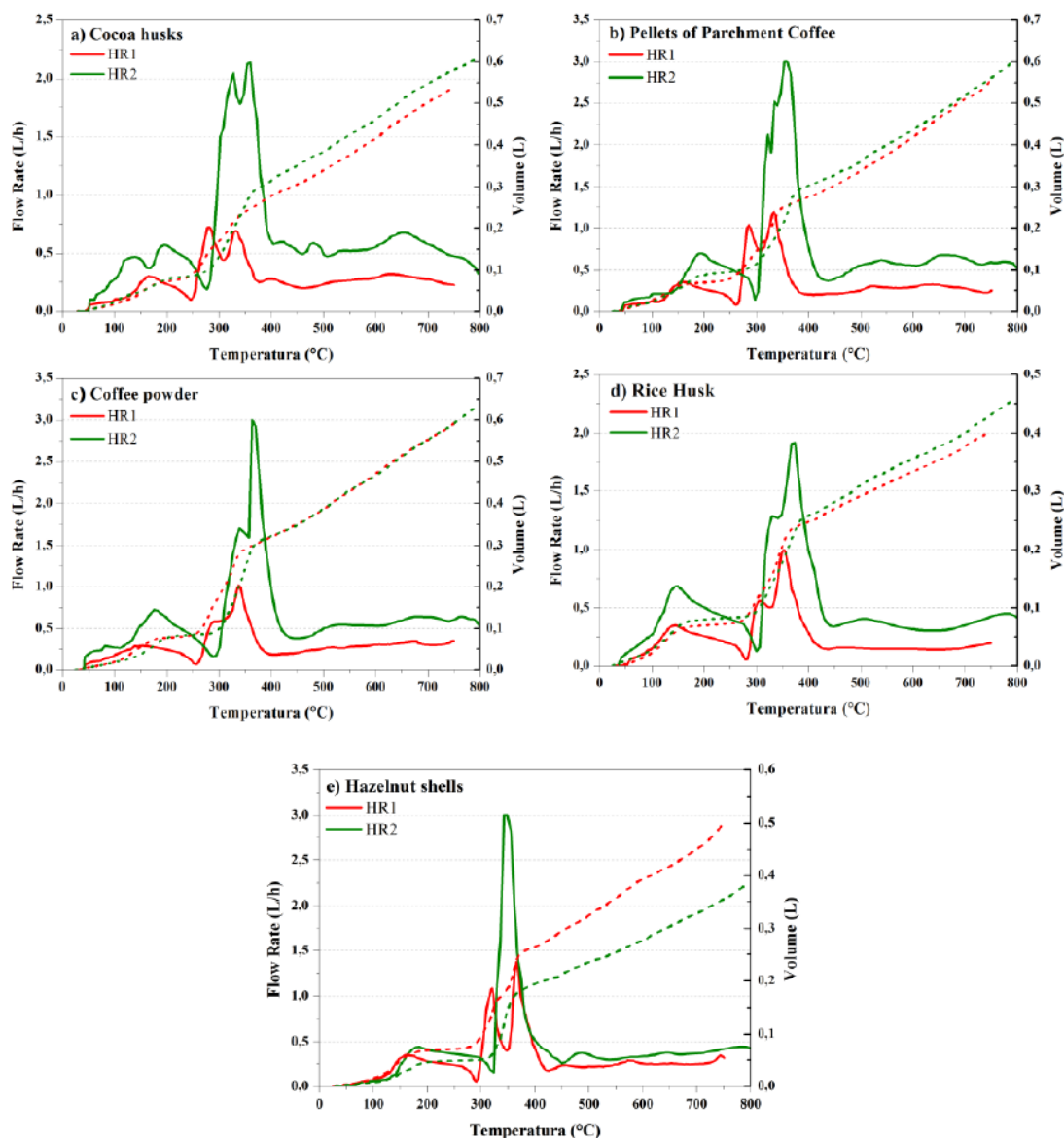


Figure 3: Gas production from the pyrolysis of biomass at HR1 and HR2 conditions.

the shorter reaction time. In fact, the gas is produced faster, over a shorter time, and thus a greater flow is obtained.

After 450 °C, the entire biomass still has a discrete gas flow, which is maintained between 0, 1 – 0, 4 l/h until the end of the process.

The major flow rate peaks (HR2) are those of the coffee powder (Figure 3 (c)), parchment coffee pellets (Figure 3 (b)) and hazelnut shell (Figure 3 (e)). The flow rate of rice husk is the lowest in all of the samples. The percentages of the products vary in terms of the nature of the biomass and of the operating conditions. Their weight percentages change within the following ranges: gas (15-25%), liquid (46-54%) and solid (25-37%).

Product Yields

Figure 4 shows the weight percentages of the pyrolysis products for each biomass, for the two considered operating conditions.

It can be clearly seen that there is an increase in the percentage of liquid from HR1 (slower heating) to HR2 except for the rice husks which remain constant, and a decrease in the char. This finding is in agreement with the work of Choi and co-workers [18]. Moreover, the rice husk and the hazelnut shell produced less gas and more char than the other biomasses. This could be explained in term of the lignin quantity, the main source of char.

Gas Fraction

The resulting gas was rich in light hydrocarbons, which are of more importance because of their high heating values. The main gas constituents are CO₂, CO, H₂ and CH₄. Figure 4 shows the gas composition, in volume percentage. The percentages of the obtained compounds depend on the nature of the original biomass and on the operating conditions. The gas composition ranges were the following: CO₂ (28-45%), H₂ (19-26%), CO (13-26%) and CH₄ (12-18%). Additionally, ethylene, ethane, propane and C₄ compounds were obtained in very small quantities. The hazelnut shells showed higher percentage of CH₄. The rice husk also presented higher quantities of CH₄ and CO, but a smaller quantity of CO₂ than the other biomasses. This aspect can be considered an advantage, because CH₄ and CO can be used as fuel components, unlike CO₂.

Heating Value

After recovering the products, the liquids and the solids were subjected to determine the high heating value.

The calorific value of the gas was calculated on the basis of the compounds analyzed by means of gas chromatography. Table 5 describes the HHV gas, tar and char fraction values. It emerges that the highest HHV value of the char (30,9 MJ/Kg) was achieved for the hazelnut shells, due to their high carbon content in the char itself (98%). No significant changes in caloric values were observed for the two different HR conditions. The calorific values of the products were within the following ranges: gas 13-17 MJ/kg, tar 27-35 MJ/Kg and char 18-24 MJ/kg.

The calorific value of the tar was relatively high, especially for the case of cocoa husks, and the pellets of parchment coffee and hazelnut shell (34,5 MJ/kg),

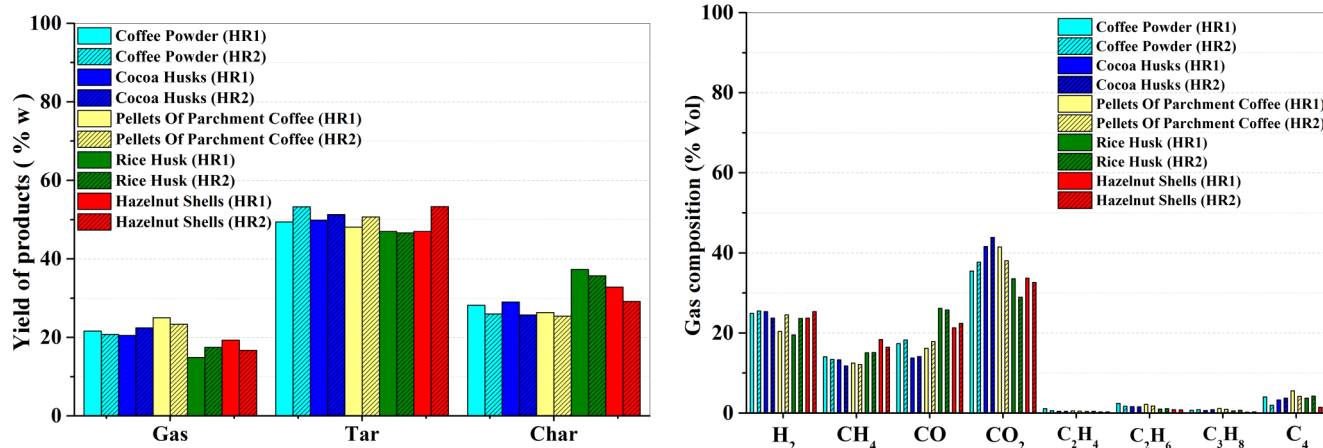


Figure 4: left) Effect of the HR1 (solid line) and HR2 (dashed line) conditions on the product distribution. Right) Composition of the gas products from pyrolysis of the biomasses under HR1 and HR2 conditions.

Table 5: Results of HHV Analysis of Gas, Tar (Oil Phase) and Char

Biomass	Char [MJ/Kg]		Tar (oil phase) [MJ/Kg]		Gas [MJ/Kg]	
	HR1	HR2	HR1 (% oil phase)*	HR2 (% oil phase)*	HR1	HR2
Coffee Powder	23.5	22.4	32.7 (23.6%)	33.2 (28.2%)	16.0	13.9
Cocoa Husks	21.9	21.4	33.0 (24.2%)	34.5 (25.2%)	13.7	12.8
Pellets of Parchment Coffee	22.4	21.6	34.5 (23.2%)	33.9 (28.8%)	15.2	14.5
Rice Husk	20.0	18.6	27.3 (23.5%)	27.0 (26.7%)	15.0	16.8
Hazelnut Shells	30.9	30.2	31.0 (22.1%)	34.4 (27.4%)	13.9	14.1

* P/P_{total liquid products}

compared to the diesel fuel value which was around 42 MJ/Kg [23].

Chemical Energy Yield

The chemical energy yield, that is the energy stored as chemical compounds in the pyrolysis products, was evaluated with reference to one of the original biomasses. The chemical energy yield is the ratio between the HHV of the products and the HHV value of the original biomass.

This parameter is therefore an indication of the efficiency in converting chemical energy from one form (biomass) to another one (pyrolysis products), while neglecting the thermal energy the latter has at the outlet (whose possible integration in the process has not been taken into account). As can be clearly seen from Figure 5, the higher chemical energy yields of 86% and 84% pertain to the hazelnut shells and rice husk, respectively, for the HR2 conditions.

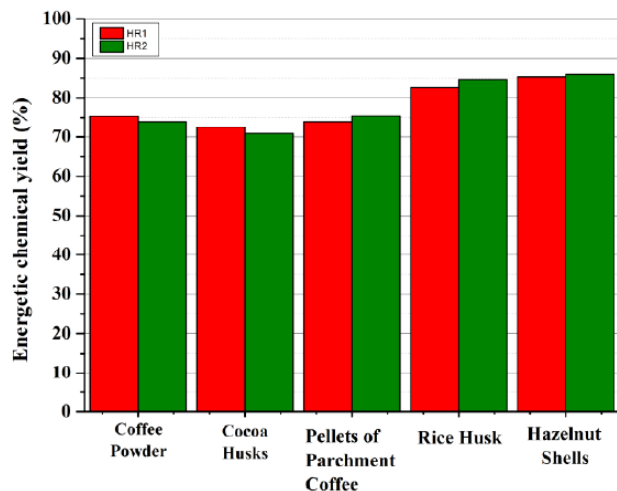


Figure 5: Percentage of energetic chemical yield of the biomasses pyrolyzed under HR1 and HR2 conditions.

This could be due to the small amount of CO₂ in the gas product, compared to the compounds, with a high calorific value such as CO and CH₄. For the same reason, the cocoa husk shows lower yields because its CO₂ percentage is higher than that of the other biomasses, especially for the HR2 condition.

Solid Fraction (Char)

The elemental composition of the char was determined by Wavelength Dispersion XRF (WD-XRF). The results from Table 6 indicate that the hazelnut shell char has a high carbon composition (98%) compared to the others.

As far as the inorganic content is concerned, the char composition has a significant amount of K and Ca, while P, Mg and Al are present in minor quantities. The relatively lower, K content in the rice husk (1,37%) and hazelnut shells (1,04%) compared to the 6,22 % in the coffee powder, 7,35% in the cocoa husks and 9,15% in the parchment coffee pellets is an added advantage, because a higher K amount can contribute to slag formation in furnaces, and to a decrease in the ash melting point [26].

The added presence of P could increase the char yield during the pyrolytic decomposition of a biomass [5]. The solid residue of the rice husk presents a particularly high quantity of silica (14,4%) compared to the other materials, and it could be used as an adsorbent to clean contaminated waters [16].

6.2. Results of Bio-Char Incorporation in Cement

The notched specimens were tested for bending at three points and their average modulus of rupture

Table 6: Elemental Composition of Char

Component (%)	Coffee Powder	Cocoa Husks	Pellets of Parchment Coffee	Rice Husk	Hazelnut Shells
C	87,00	80,90	82,90	83,30	98,5
N	-	7.46	-	-	-
Mg	1.10	1.49	1.35	0.18	-
Si	0.85	0.48	0.30	14.4	-
K	6.22	7.35	9.15	1.37	1.04
Ca	2.28	0.62	4.74	0.23	0.384
P	0.27	0.84	0.20	0.09	-
Al	0.67	0.14	0.17	0.07	-
S	0.25	0.15	0.30	0.03	-
Fe	-	-	-	-	0.0814

(MOR) was evaluated according to the following equation:

$$\sigma_{\max} = \frac{3 F_{\max} l}{2 wh^2} \quad (1)$$

where F is the maximum force in the load deflection curve, l is the span length, w is the distance between the knife edges on which the sample was supported and h is the specimen height.

The optimum content of addition is revealed to be 0.8 wt%. Typical Force-CMOD curves for cement composite specimen with and without inert carbonized particles is shown in Figure 6.

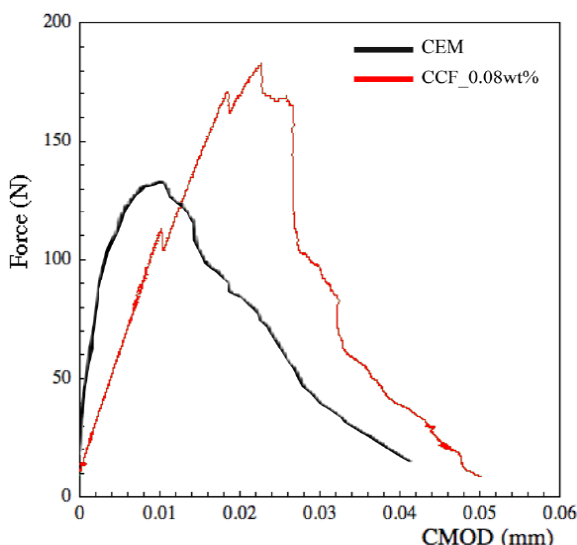


Figure 6: Typical Force vs CMOD curves for Cement (CEM) and Cement with 0.08wt% Carbonized Coffee (CCF_0.08wt%).

The area under the stress-separation curve represents the total energy dissipated by fracture per unit area of the crack plane. The flexural test results show that by adding a percentage equal to 0.08wt% of Carbon-Coffee particles into the matrix, there is an increase of strength and ductility also. In fact, the FMAX grows from 130 N to about 185 N and, at the same time, the fracture energy increases by 45% with respect to blank cement sample, without carbon particles (CEM). The results shown that it is possible to use the char-coffee waste particles in cement matrix to enhance the fracture properties.

7. CONCLUSION

The pyrolysis of coffee powder, cocoa husk and parchment coffee, rice husk and hazelnut shell pellets has been carried out in this study. The influence of two

different conditions on the distribution of the mass and energy of the obtained products has been investigated. The results show that the bio-oil yield increases for increasing heating and temperature rates while the char yield decreases. The main gas products are CO₂ (28-43%), H₂ (19-26%), CO (13-26%) and CH₄ (12-18%). The calorific value of the products ranges between 13-17, 27-35 and 18-31 MJ/kg for the gas, bio-oil and char, respectively. The hazelnut shell biomass substrate has generated the highest energetic chemical energy yield (86%). The rice husk char could be used as an adsorbent to clean contaminated waters due to the high silica content [16]. A feasibility study on the use of high-carbon bio-char admixture/additive in concrete in order to improve the sustainability of the pyrolysis process to valorize the solid output is currently being carried out. In this frame, this work can be considered a first attempt to develop a sustainable green cement admixture employing bio-char from the pyrolysis of agro-food industry residues. The research has demonstrated that coffee powder can be used to produce micro-sized inert carbonized particles. These inert carbonized particles are capable of generating high performance cement composites, by increasing the compressive strength, the peak load under bending, and their fracture energy and can improve the post peak response. These inert carbonized particles also modify the fracture path, thus resulting in a larger fracture zone. Moreover, these particles are easily dispersed in the cement matrix and are able to produce composites with higher and more uniform characteristics.

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