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Research Article

Evaluation of Pyrolysis Products of Industrial Wastes as Potential Feedstocks for Bioenergy and Biofuels

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Abstract

This work aimed at evaluating all products from the low-temperature pyrolysis (350°C) of some industrial wastes, cotton stems and seeds (CSS), grape husks and curls (GRH), undigested sewage sludge (USS) and their blends in a fixed bed system and suggesting their possible applications. Solid and liquid products, biochars, and bio-oils were analyzed using various techniques by physicochemical, mineralogical, and chemical analyses. Gases were qualitatively and quantitatively analyzed using a thermogravimetric-mass spectrometry system. All biochar samples could be used for soil amendment. Co-application with composts or other by-products to soils could be more advantageous. USS and its blends with CSS or GRH at percentages 20% and 30% presented an increased potential for carbon sequestration and release of nutrient nitrogen to plants. Biochars of CSS and GRH and their blends with 10% USS, having a significant calorific value (21-24 MJ/kg), could be considered satisfactory for energy valorization purposes. The bio-oils produced from current wastes having density 0.95-1.22 kg/m^3, pH 3.3-6.6, viscosity 118-381 cP, and heating value 20.4-28.1 MJ/kg, could substitute heavy fuel oil in static applications after a de-oxygenation process. The higher heating value of pyrolytic gas corresponding to CSS was low. In contrast, that corresponding to GRH and USS (9-10 MJ/m^3) is considered satisfactory for the energy requirements of the pyrolysis process at low temperatures.

Keywords
Industrial wastes; pyrolysis; biofuels; soil amendments

1. Introduction

The worldwide energy crisis, limited availability, and continuously increasing costs of petroleum and natural gas reserves make bioenergy one of the key options for short and medium-term substitution of fossil fuels and mitigation of greenhouse gas emissions. Biomass materials, such as agricultural wastes, are generated in large quantities in Europe and could fully meet European Union policies for recycling and valorization [1].

Pyrolysis is a promising thermochemical process for sustainable management and reduction of waste materials, converting them into biofuels and added-value products. Conventional pyrolysis at low temperatures (200-400°C) and heating rates (5-10°C/min) is mainly used for charcoal production, but also for liquid bio-oil and syngas composed of H_2, CO, CO_2 and light hydrocarbon gases [2-4]. Atmospheric flash pyrolysis is a more promising process for bio-oil production and has been extensively tested. On the other hand, hydrothermal carbonization, operating at low temperatures (180-250°C) and high pressures (2-10 MPa), may have a future potential. Still, it is in the early stages of development and needs further investigation. This technology has the advantages of converting biomass into biocrude with high heating value and eliminating feedstock pre-drying; however excessive water expenditure and high pressure make the process highly complex, hazardous and expensive [5-7].

The solid product of pyrolysis, biochar, is receiving increased attention, due to its potential to be used as a carbon-rich biofuel, as soil amendment or fertilizer improving soil quality, retention of nutrients and reduction of water contamination, for carbon sequestration to mitigate global climate change, or as a precursor for activated carbon production [3, 8, 9]. Generated bio-oil, consisting of hundreds of organic compounds, is a pool of special chemicals, adhesives and resins and can be utilized for heat or electricity applications in boilers, furnaces, engines and turbines [2, 3, 9-13]. However, its direct use as a fuel creates problems, due to its high viscosity, corrosiveness, instability and low calorific value, requiring upgrading through various processes [3, 9, 14-16]. The gaseous product of pyrolysis, having a low to medium heating value, can be used to dry the biomass, supply the heat of the pyrolysis unit, used for Fischer-Tropsch synthesis, or in combined heat and power industries [2, 3, 10, 12].

The properties of biochar from different biomass materials and suggested applications, particularly for the amelioration of soils, have been extensively studied, including the authors [3, 8, 9, 17-20]. The majority of these studies focused on biochar from agricultural wastes. Also, liquid pyrolysis products from a variety of agricultural or forest species, such as switchgrass and other grasses, palm stones, grape bagasse, rice husk, hornbeam shells, forest wood, and sugarcane bagasse [3, 10, 21-24], have been characterized using chromatographic or spectroscopic techniques.

However, physical and chemical analyses of all solid, liquid, and gaseous products of pyrolysis are limited through literature, especially for industrial wastes [2, 12]. Selected gases evolved during the pyrolysis of sawdust were qualitatively or semi-quantitatively analyzed by thermogravimetric-mass spectrometry (TG-MS) and gas chromatography-mass spectrometry (GC-MS) techniques [12, 25, 26]. Additionally, a range of chemical products from the pyrolysis of municipal sewage sludge was identified by GC-MS analysis [27]. To the authors' knowledge, there is no data on quantitative measurements of pyrolysis products from cotton stems and seeds (CSS) and grape husks and curls (GRH). Furthermore, sewage sludge with a diverse organic and inorganic composition, which is determinant for its applications and uses, requires a detailed investigation of its properties.

Therefore, the great differences in pyrolysis products, originating from the kind of raw materials used and the conditions applied, point to a separate study to evaluate these materials for various uses. Accordingly, this work aimed to evaluate all products from the pyrolysis of some industrial wastes and their blends in a fixed bed system and suggest their possible applications. Physicochemical, mineralogical, and chemical analyses were performed, employing various techniques. A thermogravimetric/differential thermogravimetric (TG/DTG) analyzer coupled with a mass spectrometer was used for the qualitative and quantitative analysis of gases.

2. Materials and Methods

2.1 Raw Materials Preparation and Characterization

Two agro-industrial wastes were selected for current study: cotton stems and seeds (CSS), provided from a cotton ginning factory in Central Greece, and grape husks and curls (GRH), collected after extraction of juice from a spirit-making enterprise in West Crete. Also, an industrial waste, undigested sewage sludge (USS), which was a mixture of primary and secondary management stages after thickening and dewatering, was provided by the solid waste management company of Chania in West Crete. These wastes were selected because they are produced in large quantities in the country and remain unexploited. About 620 kt of CSS [28], 245 kt of GRH [29], and 146 kt of USS [30] are generated every year in Greece. All raw materials were air-dried, riffled and ground (agro-industrial wastes in a cutting mill, sewage sludge in a ball mill) to a particle size below 1 mm. Mixtures of CSS and GRH with USS were also prepared, with blending ratios of 90:10, 80:20, and 70:30, respectively. For characterization tests, materials were ground to a particle below 250 μm.

For proximate analysis, ultimate analysis and calorific value European standards CEN/TC335 were adopted. Programmable laboratory furnaces, a TG/DTG analyzer of Perkin Elmer, a Flash 2000 CHNS Thermo-Scientific analyzer and an AC-300 Leco calorimeter were used.

Inorganic elements in ashes were identified by an X-ray fluorescence spectrometer (XRF), model S2 Ranger/EPS of Bruker AXS. Mineral phases were detected by an X-ray diffractometer (XRD), model D8 Advance of Bruker AXS and identified by DIFFRAC plus Evaluation software in conjunction with the JCPDS database.

2.2 Pyrolysis Experiments

Production of biochars, bio-oils, and gases was carried out in a stainless steel fixed bed reactor (H = 14 cm, ID = 7 cm), surrounded by a furnace. A detailed description of the equipment can be found in a previous work by the authors [9]. About 15 g of sample was charged onto a grid basket supported by a rod within the reactor, which was sealed and inserted into the furnace. After purging air with the nitrogen flow rate of 150 mL/min for 20 min, the furnace was set to 350°C at a heating rate of 10°C/min and retention time at the final temperature of 30 min. The temperature of 350°C was selected to maximize biochar yield and nutrient retention, to investigate its suitability for soil amendment. It was monitored by a Ni-Cr-Ni thermocouple in contact with the sample bed. Volatile products were passing during the whole experiment through two salt-ice baths. After cooling the reactor with nitrogen, liquid condensates were centrifuged at 6000 rpm for 20 min to collect bio-oil from the top layer. The resulting biochar was weighed and stored, and a mass balance was performed. As discussed below, gas analysis was conducted by the MS, coupled online with the TG/DTG system, by carrying out experiments under the same conditions as in the fixed bed. At least two replicates for each sample confirmed the high reproducibility of the results.

2.3 Analyses of Solid, Liquid and Gaseous Products of Pyrolysis

All biochar samples were characterized in terms of proximate and ultimate analyses, calorific value and chemical and mineralogical analyses, with the same methods as for raw materials mentioned above. pH was measured in 1:5 solid-to-deionized water mixtures with a bench Metter Toledo pH-meter after stirring in an orbital and linear digital shaker for 30 min and settling.

Physicochemical properties of bio-oils, i.e., density, pH, viscosity, ultimate analysis, and heating value, were determined as follows. Density was measured according to ASTM 1298 standard, using a 1 mL micropipette and a high accuracy analytical balance. pH was measured with the bench Mettler Toledo pH-meter. The dynamic viscosity of the bio-oils was determined by a Couette type viscometer, model M3500 of Grace, using an R1-B1-F1 configuration of double gap cylinder sensor (gap size 1.17 mm). Rotational speeds of 3, 6, 100, 200, 300 and 600 rpm (ramp up and ramp down) were tested, to cover the whole range of sheer stress of the equipment. The time between each measurement was set to 60 s and the rheological modification with a shear time of 1 min was tested. The regression technique was employed to fit rheological models to the measured data of shear stress versus shear velocity. The temperature at which viscosity was measured was 50°C.

For ultimate analysis, the Flash 2000 CHNS analyzer was used and the higher heating value (HHV) was calculated by equation [31]:

$$HHV_{biooil} = 0.3383C + 1.422\left(H - \frac{O}{8}\right)$$

The qualitative and quantitative analyses of gases during pyrolysis were performed via the TG/DTG analyzer, which was linked to a quadrupole mass spectrometer (MS QME-200 Balzers). The transfer line of evolved gases comprised of a fused silicon capillary (i.d. 0.32 mm), encased with an insulated stainless steel sheath and heated to 200°C to prevent condensation of species. The tests were carried out under high purity Ar, after 1 h purging, with a flow rate of 35 mL/min, a heating rate of 10°C/min and a final temperature of 350°C. The ions were detected by a Secondary Electron Multiplier (SEM) operated at 82 eV and range of 1-400 atomic mass units, whereas Pyris v3.5 and Quadstar 422 software performed the acquisition of data. The initial sample mass normalized signal intensities, and the contribution of fragments from more than one compound to the intensity of a specific m/z ratio was considered. As explained by the authors elsewhere, calibration factors were determined using standard gases of known concentrations in argon [4].

3. Results

3.1 Raw Materials-characterization and Yield of Pyrolysis Products

The proximate and ultimate analysis of raw materials presented in Table 1 shows that the content of volatiles was high, ranging between 67.2% and 75.4%, whereas that of ash was considerable 8.9-17.2%. CSS had the lowest ash, nitrogen, and sulfur concentrations among samples but the highest oxygen content and a lower calorific value. On the other hand, the increased carbon and hydrogen contents of GRH and USS raised the calorific value of these wastes. Also, the amounts of sulfur and particularly nitrogen of GRH and USS, were significant, implying a higher capacity for plant nutrition if applied to soils after a low temperature treatment.

Table 1 Proximate and ultimate analysis of raw materials (% dry).

Sample	**Volatile matter**	**Fixed carbon**	**Ash**	**C**	**H**	**N**	**O**	**S**	**HHV (MJ/kg)**
Cotton stems and seeds (CSS)	75.4	15.7	8.9	41.5	6.0	1.1	42.3	0.2	15.8
Grape husks and curls (GRH)	72.1	13.2	14.7	49.4	6.5	2.6	26.4	0.4	21.3
Undigested sewage sludge (USS)	67.2	15.6	17.2	42.4	6.7	8.1	23.9	1.7	18.9

The yield of pyrolysis products of the materials under study and their mixtures are compared in Figure 1. As can be observed, the greatest biochar yield and the lowest gas yield were generated by the bio-solid USS. CSS produced a greater amount of liquid condensates. When the agro-industrial wastes were mixed with the USS at proportions 70:30, biochar and condensates increased at the expense of gas.

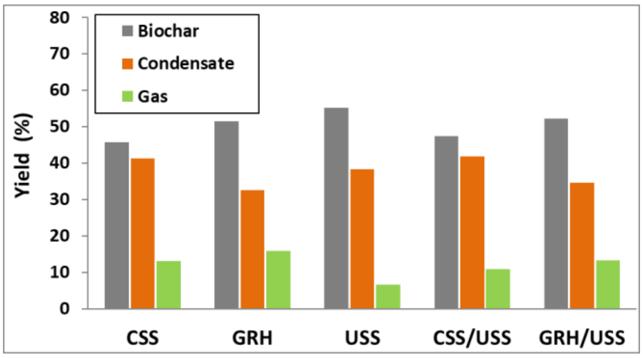

Figure 1 Yield of pyrolysis products.

3.2 Pyrolysis Products-characterization and Evaluation as Biofuels or Soil Amendments

3.2.1 Biochars

Table 2 summarizes the proximate and ultimate analyses of all biochars produced after the devolatilization of raw samples at 350°C, along with their higher heating value. Thermal decomposition at this temperature resulted in the evolution of hydrogen and oxygen-bearing compounds through dehydration, dehydroxylation, and decarboxylation reactions [9], leaving a solid material enriched in carbon and mineral matter. These variations were reflected in the higher heating value, which was raised in comparison to raw fuel (except for the USS sample). Calorific values in the 19-23 MJ/kg range have been reported for other biochar materials [2, 12]. The enrichment of these materials in carbon is known to increase their hydrophobicity, which is important for fuel storage and transportation [32], while their reduction in H/C and O/C molar ratios reveals the development of aromatic structures resistant to chemical and microbial degradation [33], as well as higher carbon stability [8, 9, 21]. It has been reported that if the O/C ratio is 0.2-0.6, biochar could have a mean residence time in soil of 100-1000 years [34]. Concerning the mixtures of the agro-industrial wastes with the bio-solid, it can be noticed from the table that the higher the percentage of USS in the mixture, the lower the organic matter and carbon concentration, whereas the higher the ash content, resulting in a drop in calorific value. Previous investigations by the authors [35, 36] have shown that the specific surface area of biochars, which greatly influences their reactivity during thermochemical processes, or their potential for adsorption of nutrients/heavy metals and organic pollutants, was 3.7 m^2/g for USS and 5 m^2/g for GRH biochars, due to their high ash content and 57.4 m^2/g for CSS biochar.

Table 2 Proximate and ultimate analysis of biochars (% dry).

Sample	**C**	**H**	**N**	**O**	**S**	**H/C**	**O/C**	**N/C**	**HHV (MJ/kg)**
CSS	59.8	4.2	1.4	14.9	0.2	0.84	0.19	0.02	23.5
GRH	51.7	4.7	3.2	11.9	-	1.09	0.17	0.05	21.7
USS	43.3	3.8	8.0	13.3	0.4	1.05	0.23	0.16	16.7
CSS/USS 90:10	58.1	4.1	2.1	14.8	0.2	0.91	0.19	0.03	22.7
80:20	55.1	4.1	2.7	16.1	0.2	0.89	0.21	0.04	19.9
70:30	54.6	3.9	4.2	12.9	0.4	0.86	0.18	0.07	21.2
GRH/USS 90:10	50.8	4.7	3.7	12.0	0.04	1.11	0.17	0.06	21.3
80:20	50.0	4.5	4.1	12.3	0.09	1.08	0.18	0.07	20.7
70:30	49.1	4.3	5.1	11.6	0.3	1.05	0.18	0.09	20.0

According to the above results, biochars of CSS and GRH and their blends with 10% USS, having a significant heating value, can be considered satisfactory for energy valorization through combustion or gasification processes. Furthermore, from the data in Table 2, it can be anticipated that toxic emissions of sulfur and nitrogen will not be of any concern at the low temperature of the process. On the other hand, the bio-solid USS and its blends with CSS and GRH at percentages 20% and 30% present an increased potential for carbon sequestration and release of nutrient nitrogen to plants if applied to soils.

The concentrations of the major inorganic elements in biochars are represented in Figure 2. Regarding nutrients, GRH and CSS were rich in Ca and contained a high amount of K, most probably attributed to using fertilizers during the cultivation of parent plants. USS biochar presented a greater content in Ca, Fe, and P than the agro-industrial wastes. These values are comparable to other biochar materials reported by previous studies [17, 37]. The bioavailability of these nutrients in soils is governed by the solubility of the minerals incorporating these elements [17, 37]. As Table 3 shows, Ca in GRH and CSS identified by XRD analysis was mainly present in the forms of calcite and dolomite, whereas K occurred in significant amounts as sylvite and arcanite, minerals that are known to be soluble in water. In contrast, USS bio-solid mineral matter consisted mainly of insoluble whitlockite magnesian and considerable quantities of Ca and Fe bound in calcite, hematite, and Kennedyte. The enrichment of all biochars in alkaline minerals was reflected in their pH value, illustrated in Figure 3, which varied between 8.5 and 10.5. A high pH is beneficial for soil liming or biochars application in agriculture, because it controls the biological activity and solubility of nutrients in soils while preventing the leaching of toxic heavy metals contained in the solid materials [15, 18, 20]. USS biochar, having a pH = 8.5, is recommended for applications at sensitive and low buffer capacity soils [38].

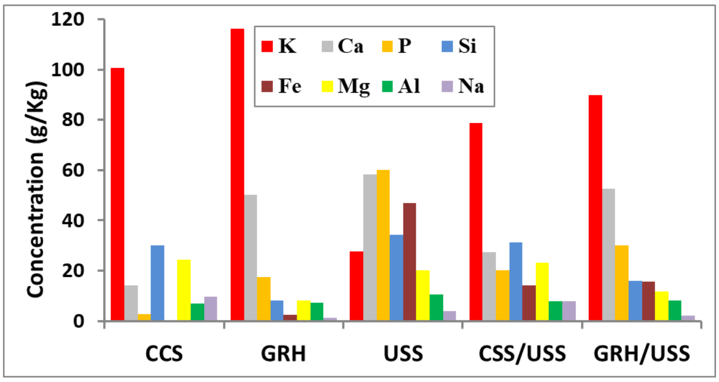

Figure 2 Concentrations of the major inorganic elements in biochars.

Table 3 Mineralogical analysis of ashes by XRD.

Mineral phases	**CSS**	**GRH**	**USS**
Quartz SiO_2	++	+	+
Calcite $CaCO_3$	+	++	++
Periclase MgO	+		
Dolomite $CaMg(CO_3)_2$	++	+	
Sylvite KCl	+++	+	
Arcanite K_2SO_4	++	+++	
Albite $(Na,Ca)Al(Al,Si)_3O_8$	+		
Fluorapatite $Ca_5(PO_4)_3F_{0.94}Cl_{0.1}$	+	+	
Anhydrite $CaSO_4$		+	+
Whitlockite magnesian $Ca_{18}Mg_2H_2(PO_4)_{14}$			+++
Hematite Fe_2O_3		+	++
Halite $NaCl$		+	
Fairchildite $K_2Ca(CO_3)_2$		+	+
Microcline $KAlSi_3O_8$		+	
Magnesite $MgCO_3$		+	
Dawsonite $NaAl(CO_3)(OH)_2$			+
Struvite $MgNH_4PO_4(H_2O)_6$		+	
Kennedyte $Fe_{0.33}Ti_{0.52}Mn_{0.5}Ti_2O$			+
Gmelinite $NaAl(SiO_3)_23H_2O$			+
Hedenberaite $Ca(Fe,Mg)(SiO_3)_2$	+		

+++: high intensity ++: medium intensity +: low intensity

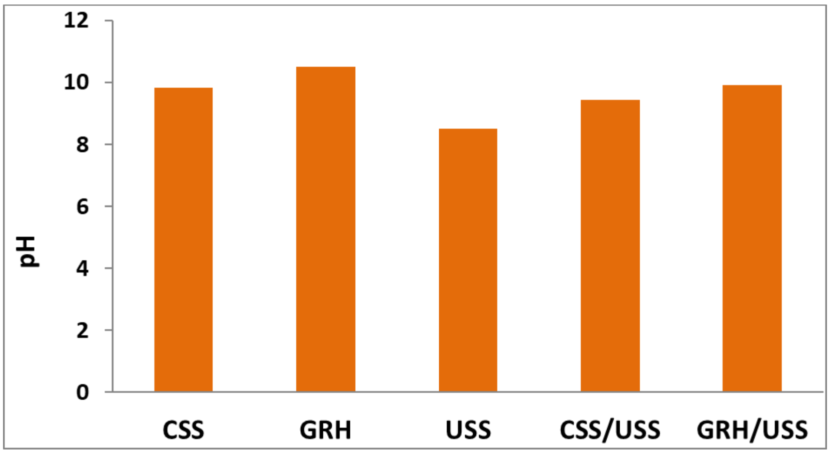

Figure 3 pH value in biochars.

The physical, chemical and mineralogical analyses of the biochars in a study presented above indicate that all samples could be used for soil amendment. However, the high extractability of K and Ca predicted for GRH and CSS wastes on the one hand, and the low extractability of Fe and P predicted for USS bio-solid on the other, suggest that co-application with composts or other by-products to soils could be advantageous, allowing the slower release of nutrients and retention of hazardous heavy metals.

3.2.2 Bio-oils

The physicochemical and fuel properties of bio-oils are summarized in Table 4 and compared to those of heavy fuel oil and typical flash pyrolysis oil [15]. The density of CSS and its mixtures with USS was similar to that of heavy fuel oil, whereas the density of the rest of the samples, ranging between 1-1.22 kg/m^3, was closer to that of flash pyrolysis oil. An increase in fuel density leads to an advantage in its injection timing in engines, as well as to lower fuel spray penetration [39]. The pH values of the liquid products varied between 3.3 and 6.6. The lower values, corresponding to CSS oil and its mixtures with USS, agree with data in the literature [12, 14, 21]. However, the higher values of the other samples imply their lower content in carboxylic acids, such as acetic and forming, making these bio-oils less corrosive [14, 21]. Furthermore, one of the key fuel properties of bio-oils is known to be viscosity, which is important for the design and operation of the fuel injection system, the atomization quality and subsequent combustion properties [40]. Table 4 shows that current values were within the range of heavy fuel oil and flash pyrolysis oil, except for the viscosity value of GRH and its blends. However, they were comparatively higher than bio-oil viscosities reported at the same temperature by several authors [10, 21]. The viscosity of GRH material is considered very high and exceeded measured data for grape bagasse bio-oil [10]. Nevertheless, it should be noticed that bio-oils under study did not include water, which reduces the viscosity and enhances the oil’s fluidity.

Table 4 Physicochemical and fuel properties of bio-oils.

	CSS	**GRH**	**USS**	**CSS/USS**	**GRH/USS**	**Heavy fuel oil**	**Flash pyrolysis oil**
Density (g/cm^3)	0.95	1.01	1.22	0.98	1.16	0.94	1.23
Dynamic viscosity (cP)	131.4	381.1	118.4	125.3	143.0	180.0	55-180
pH	3.3	6.1	6.6	3.9	6.3	-	2.4
C (%)	52.7	57.1	51.0	52.2	52.2	85.2	44-46
H (%)	6.7	9.8	9.7	7.6	9.8	11.1	6.6-7.1
N (%)	1.7	4.0	6.2	3.0	4.7	0.3	0
S (%)	0.05	0.2	0.3	0.1	0.2	2.3	-
O (%)	38.9	28.9	32.7	37.0	30.1	1.0	47-49
HHV (MJ/kg)	20.4	28.1	25.3	21.9	27.3	40.0	15.0-17.5

Comparing the elemental composition of the bio-oils from the agro-industrial and industrial wastes investigated with that of flash pyrolysis and heavy fuel oils, it can be observed that those bio-oils were superior to the former while inferior to the latter, as they had higher concentrations of carbon and hydrogen and lower of oxygen than the flash pyrolysis oil, leading to an increased heating value. The heating value, ranging between 20 MJ/kg and 28 MJ/kg, was higher than that of bio-oils produced from other biomass feedstocks, such as rice straw, oak, eucalyptus and pitch pine [21]. Still, the oxygen content is considered high for transport fuels and results in high viscosities and boiling points, lower energy density, poor chemical stability and immiscibility with hydrocarbon fuels [2, 10]. However, it is beneficial for catalytic steam reforming the oils to hydrogen and carbon dioxide [15].

Summarizing, the bio-oils produced from the waste materials studied could substitute fuel oil in static applications such as boilers, furnaces, engines and turbines for heat or electricity generation, only after de-oxygenation through a mild catalytic process. Chemical upgrading is recommended for liquids from GRH sample and its mixtures with USS to reduce viscosity and optimize fuel handling and combustion characteristics. For the production of transportation fuels from these oils, high-severity chemical catalytic processes are required [14, 15].

3.2.3 Gases

A representative evolution profile of pyrolytic gases during the pyrolysis of the CSS sample, as monitored by the TG-MS system, is illustrated in Figure 4. As can be seen, CO_2 was the principal contributor to pyrolysis gas up to 350°C, associated with the cracking of C-C and C=O bonds from the thermal decomposition of hemicellulose and cellulose components [41]. The peak rate occurred at about 330°C. A lower amount of CO and minor quantities of CH_4, H_2 and C_xH_y were produced below 350°C, with peak intensities obtained above 480°C, attributed to the cracking of stronger aliphatic or aromatic functional groups [17]. The higher heating value of the pyrolytic gas corresponding to CSS waste was low, as Figure 5 shows. In contrast, that corresponding to GRH and USS (9-10 MJ/m^3), the combustible gases of which were greater, is considered medium and satisfactory for the energy requirements of the pyrolysis process at low temperatures [9].

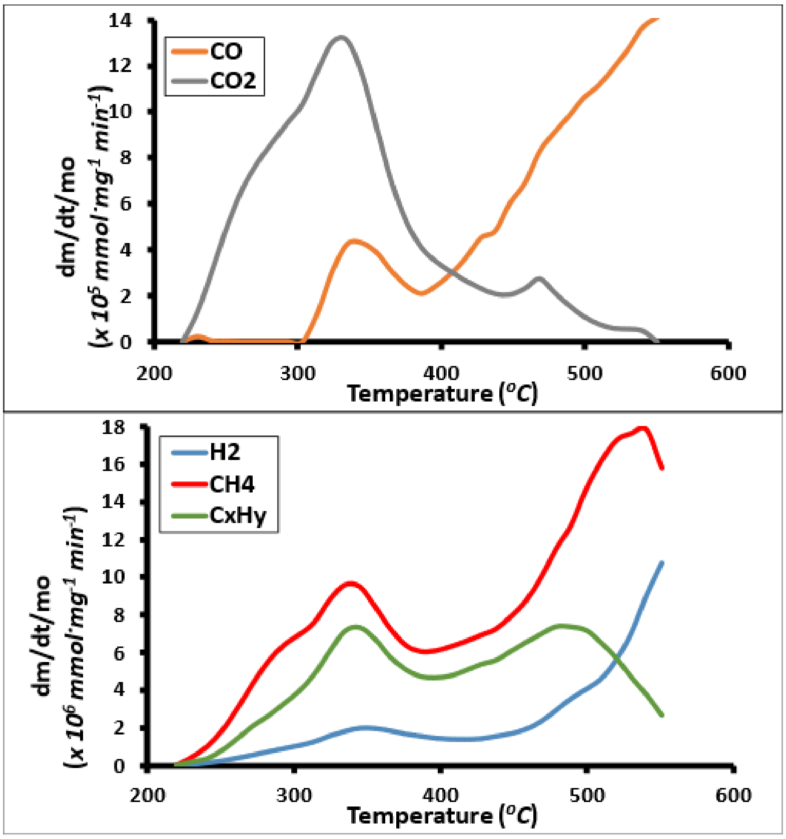

Figure 4 Evolution profile of gases during the pyrolysis of CSS sample.

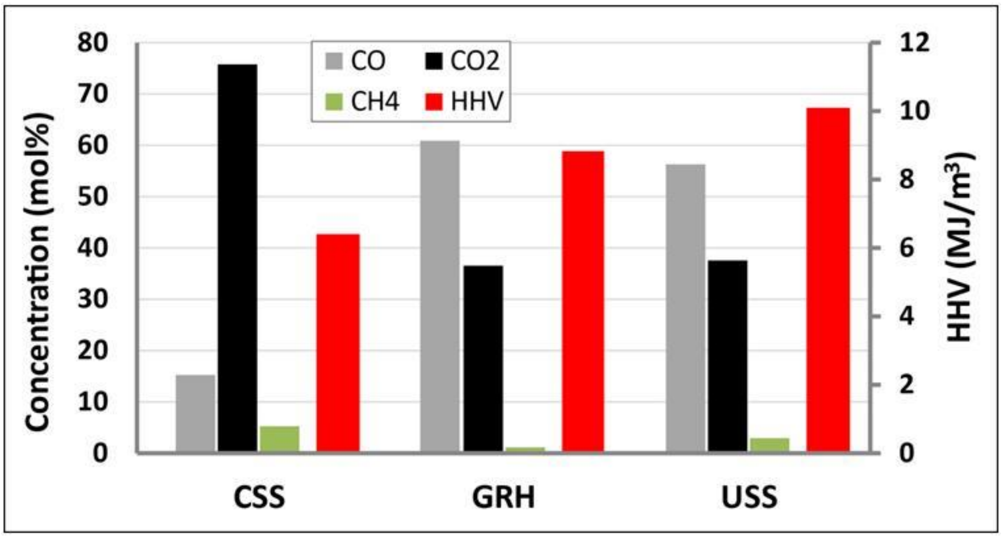

Figure 5 Comparison of the flue gas composition (left axis) and gross heating value (right axis) between the three fuel samples.

4. Conclusions

Upon thermal treatment of the waste materials studied at 350°C the greatest biochar yield was generated by the bio-solid USS (55%), the higher amount of bio-oil was produced by cotton stems and seeds (CSS, 41%), whereas that of gas by grape husks and curls (GRH, 16%).

All biochar samples, enriched in aromatic carbon and alkaline minerals, could be used for soil amendment. Co-application with composts or other by-products to soils could be more advantageous. Undigested sewage sludge (USS) and its blends with CSS and GRH at percentages 20% and 30% presented an increased potential for carbon sequestration and release of nutrient nitrogen to plants. Biochars of CSS and GRH and their blends with 10% USS, having a significant calorific value (21-24 MJ/kg), could be considered satisfactory for energy valorization purposes.

The bio-oils produced from current wastes having density 0.95-1.22 kg/m^3, pH 3.3-6.6 and viscosity 118-381 cP and heating value 20.4-28.1 MJ/kg, were superior to flash pyrolysis oils and could substitute heavy fuel oil in static applications after a de-oxygenation process.

The higher heating value of pyrolytic gas corresponding to CSS was low. In contrast, that corresponding to GRH and USS (9-10 MJ/m^3) is considered satisfactory for the energy requirements of the pyrolysis process at low temperatures.

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Author Contributions

Conceptualization, D.V.; methodology, D.V.; software, K.E., D.M.; investigation, D.V., K.E., D.M. G.K.; writing—review and editing, D.V.

Competing Interests

The authors have declared that no competing interests exist.

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