Survey on the valorization of wood and agribusiness wastes for their application as fossil carbon substitutes in metallurgical processes

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1. Introduction

Fossil carbon sources are widely used in a number of extractive metallurgical processes (e.g., in copper and steel production), its replacement with a biogenic origin carbon source can help decarbonize these high-carbon-footprint industrial sectors, while opening up new and profitable connections between several strategic industrial sectors widely developed in Italy (e.g., furniture, agribusiness and transportation). In fact, reducing the environmental impact of key industrial processes for the country (e.g., steel production) and achieving a sustainable way of valorizing their waste have become major drivers of innovation. However, these alternative carbon sources may be characterized by a different chemical composition, carbon content and physical properties than commonly used fossil carbons. This heterogeneity is due to the different possible origins of biogenic carbons and the different valorization treatments applicable for their conversion into so-called "biochar" (e.g., pyrolysis, torrefaction, hydrothermal carbonization). These aspects could have an impact on the scalability of the industrial process and therefore should be considered when evaluating the opportunity of their use. The MICS (Made in Italy Circolare e Sostenibile) project, aims at finding the most viable solution for the application of biochar in the Italian industrial sector and at solving the main barriers to the use of wooden derived biochar in metallurgy, namely the availability of the raw material, its cost and the most appropriate conversion process of the starting matrix. For this reason, the recovery of wood waste from the furniture, transportation, and food industries should be considered strategic for national development and would speed up the creation of a biochar supply chain to replace the metallurgical fossil carbons currently used. For example, RILEGNO, the national consortium that deals with the collection, recovery and recycling of wood packaging, manages more than 1.5 Mt of wood packaging out of a total availability of 3 Mt in the Italian market [1]. In addition, agriculture can provide other suitable matrices as feedstock, namely 2.5-3 Mt/y of olive pomace [2].

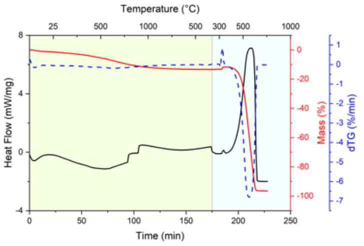
2. Materials and Methods

Several wood matrices have been explored for their conversion into biochar suitable for metallurgical applications. They include commercial wood chips, commercial pellets for pellet kilns, olive pomace and exhaust wood pallets. To figure out which matrix is best suited for the production of biochar for metallurgical applications, three sets of microscale experiments were carried out using thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) to simulate the pyrolysis process. The first set of experiments aimed to estimate the activation energy of pyrolysis according to the Kissinger–Akahira–Sunose (KAS) method [3]. Pyrolysis temperature and activation energy was evaluated by means of TGA-DSC in argon atmosphere (2 Nl/h) at three heating rates (20, 25 and 30 °C/min) by heating up the samples from RT up to 700 °C. The second set of experiments aimed to identify the possible transformation occurring during the pyrolysis by heating the samples from RT up to 900 °C at 10 °C/min in nitrogen atmosphere (2 Nl/h). The third set of experiments aimed to verify the effect of isothermal heat treatment on pyrolysis work-in-progress by heating the samples in argon atmosphere (2 Nl/h) from RT up to 350 °C at 30 °C/min and a dwell time at the target temperature of 30 min.

Based on the micro-scale results, the most promising carbon matrices were chosen to perform the macro-scale pyrolysis. The pyrolysis was performed under a continuous under argon flow (10 Nl/h) on batches of 100 grams of wooden matrix per time, with a heating rate of 16.5 °C/min from RT up to the desired temperature and a dwell time of 25 min before cooling. The biochar samples produced were wooden pellets pyrolyzed at 750 °C (P-BC), wood chips pyrolyzed at 350 °C (BC), olive pomace pyrolyzed at 350 °C (S350) and 750 °C (S750). The amount of total carbon (C_{tot}) and sulphur content (S) of the obtained biochar were obtained by means of LECO analysis, whereas the amount of moisture (M), volatile matter (VM), ash (A) and fixed carbon (FC) were evaluated through proximate analysis [4]. Furthermore, the samples were mineralogically and chemically characterized by means of Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDS), X-Ray Diffraction analysis (XRD). Finally, their properties were compared with those of commonly used carbons, particularly graphite (GR) and coke (CO).

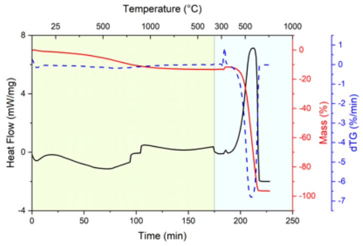
3. Results

The summary of the biochar characterization after the pyrolysis process, as well as the comparison with the metallurgical carbons, is given in Figure 1. The higher yield of BC sample can be related to the lower processing temperature and the absence of binder in the starting matrix, that increase the amount of mass loss and slightly reduces the process yield. Contrary, the higher yield of the S350 rely on lower compound decomposition due to the lower thermal range. It is noteworthy that the thermal profile of P-BC is perfectly superimposed on that of GR. Specifically, the P-BC is formed by more than 80 %wt. of fixed carbon with very low amount of ashes, moisture and volatile matters. These results are of a great interest for its application as metallurgical reductant, since by increasing the amount of fixed carbon it is possible to better reduce the metallic oxide, obtaining a higher metallization and iron carburation. BC, S350 and S750 show instead a higher volatile fraction that lead to significant mass loss during the first heating step under inert atmosphere.



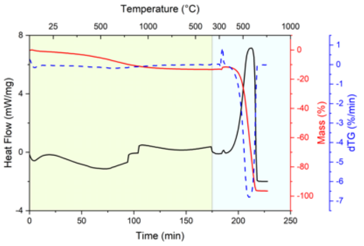
P-BC	%wt.
Yield	20.00
M	0.80
VM	12.48
A	3.58
FC	83.14
C_{tot}	93.51
S	-

(a)



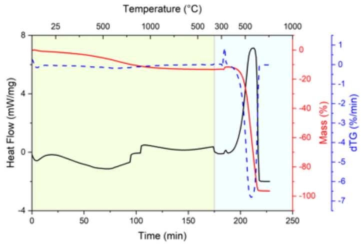
BC	%wt.
Yield	25.70
M	5.60
VM	41.10
A	6.73
FC	52.22
Ctot	55.23
S	0.003

(b)



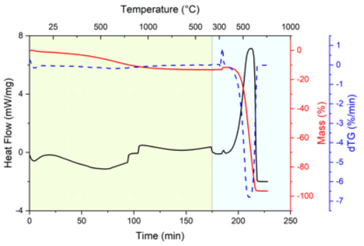
S350	%wt.
Yield	40.00
M	2.12
VM	62.59
A	16.19
FC	21.12
C_{tot}	65.23
S	0.059

(c)



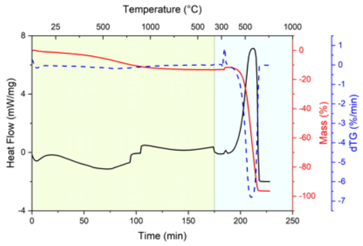
S750	%wt.
Yield	30.00
M	2.72
VM	51.90
A	16.96
FC	31.14
C_{tot}	69.87
S	0.110

(d)



GR	%wt.
Yield	-
M	0.05
VM	6.25
A	4.40
FC	89.40
C_{tot}	100
S	-

(e)



CO	%wt.
Yield	-
M	1.00
VM	5.20
A	8.60
FC	85.20
C_{tot}	80-95
S	0.2-6.0

(f)

Figure 1. Yield of the pyrolysis process and proximate analysis of wooden pellets pyrolyzed at 750 °C (a); wood chips pyrolyzed at 350 °C (b); olive pomace pyrolyzed at 350 °C (c) and 750 °C (d); graphite (e) and metallurgical coke (f)

The chemical and mineralogical characterization highlighted several differences based on the starting wooden matrix. P-BC samples showed basically pure carbon, with a very small fraction, hardly identifiable, of residual ashes. On the other hand, although amorphous carbon and graphite was observed in the BC sample, a significant fraction of periclase (MgO) was also identified. The S350 XRD pattern revealed the presence of sylvite (KCl), calcite ($CaCO_3$), hemicellulose and graphite. Finally, the mineralogical phases of sample S750 were consistent with the previous sample, containing mainly graphite, calcite and sylvite plus quartz (SiO_2) and kalicinite ($KHCO_3$).

4. Conclusions

The valorization of wood waste from furniture, agribusiness and transportation through pyrolysis appears to be an attractive solution for the creation of a value-added biogenic carbon source that can replace fossil carbon sources currently used in metallurgical processes. Among the matrices analyzed, wood pellets pyrolyzed at 750 °C provided the biochar with the closest properties to graphite. On the other hand, although more volatile matter has been observed in the other matrices (wood chips and olive pomace), the amount of total carbon can be considered acceptable for their use as reducing agents for the recovery of valuable metals (e.g., iron) by pyrometallurgical processes.

Hence, one of the next steps in the MICS project will be the recovery of iron from metallurgical waste by such processes. Indeed, in the event of positive results, the industrial feasibility of creating a national biochar supply chain capable of replacing currently used metallurgical fossil coals would be more than strengthened. Finally, since the amount of S in each biochar is far less than that of commonly used metallurgical coke and their mineralogy seems suitable for the creation of a desulfurizing slag during iron recovery, it is already conceivable that the recovered iron will be free of metallurgical pollutants, thus providing an additional advantage for biochar over fossil carbon sources.

References

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