

Modeling of the biogenic carbon composite agglomerates degree of reduction for effective biochar valorization and utilization

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1. Introduction

Fossil carbon sources are widely used in various extractive metallurgical processes, among which the steel sector is currently one of the largest consumers of coal with about 950 million tons used in 2022, resulting in the emission of 2.6 giga tons of CO₂ in the same year (International Energy Agency, 2023). In the ongoing quest for more sustainable steel production, most companies have begun to include the fossil-to-biogenic carbon transition in their short- and medium-term plans for impact mitigation.

Interestingly, despite the several possibilities for introducing biochar within the steelmaking cycle (e.g., blending material, direct injection, as a carburizing agent or slag foaming agent), the most stringent threshold is the amount of volatile matter in the biochar itself, which limits the use of exclusively high fixed-carbon biogenic carbon sources for achieving acceptable performance (Echterhof, 2021). One of the practices to overcome this problem and also take advantage of high-volatile biogenic carbon sources is their use as reductant in biogenic carbon composite agglomerates (bio-CCAs) made of iron ore and biochar for the efficient recovery of iron once charged inside metallurgical furnaces. However, since most studies still rely on the use of ores as carriers of iron oxide, from an industrial point of view this would result in the depletion of mineral resources, thus preventing the environmental benefits of bio-CCAs (Das et al., 2024; Liu et al., 2018). In contrast, the utilization of metallurgical residues (e.g., mill scale) with an amount of iron still recoverable within them has been less studied (Vitikka et al., 2024).

In this regard, in a previous work of the authors (Dall'Osto et al., 2024a) on the thresholds of fixed carbon-to-volatile matter of biochar for the effective iron recovery from mill scale, a sigmoidal trend of the degree of reduction in function of the heat treatment temperature was highlighted. Consequently, from these results, the present study aims at a more in-depth modeling of the reduction mechanism as a function of biochar properties in order to understand, based only on the amounts of fixed carbon and volatile matter, which biochar would benefit the most from its valorization as a reductant in bio-CCAs.

2. Materials and Methods

Starting from the biogenic carbon matrices presented by the authors at the 11th International Conference on Sustainable Solid Waste Management (Dall'Osto et al., 2024b) and valorized as part of the MICS (Made in Italy Circular and Sustainable) project, three matrices were selected as reductant for the mill scale following their agglomeration in bio-CCA. Specifically, wood pellets pyrolyzed at 750 °C (PE750) and olive pomace pyrolyzed at 350 °C (OP350) and 750 °C (OP750). A fourth carbonaceous matrix was also identified in sewage sludge hydrothermally carbonized at 210 °C/20 bar (HC). The specifics of each bio-CCAs recipe used is given in **Table 1**.

Table 1 Recipe composition (MS: mill scale, PE: pellets pyrolyzed at 750 °C, OP750: olive pomace pyrolyzed at 750 °C, OP350 olive pomace pyrolyzed at 350 °C, HC: sewage sludge hydrothermally carbonized at 210 °C, db: dry basis).

	Biochar-to-mill scale	Total carbon-to-mill scale	Fixed carbon-to-volatile matter
	(g g ⁻¹)		(wt.% _{db} wt.% _{db} ⁻¹ in the mixture)
PE750/MS	0.21	0.20	6.65
OP750/MS	0.29	0.20	0.66
OP350/MS	0.31	0.20	0.34
HC/MS	0.47	0.20	0.01

The degree of reduction (DoR) was evaluated between 750-1200 °C (with an increase of 150 °C in each measurement) and in accordance with a modified version of BS ISO 11258:2015 in which the carbon gasification process was also considered to avoid any measurement bias (Dall'Osto et al., 2024a). The sigmoidal trend of DoR as a function of temperature was verified using the modified Avrami solution approach (**Equation 1**).

$$\ln(-\ln[1 - DoR(T)]) = \ln K + n \ln T \quad (1)$$

Subsequently, the parameters K and n obtained from each regression curve were plotted vs. the specific fixed carbon-to-volatile matter ratio of the recipes and modeled to maximize the correlation coefficient of the regression curve model used.

3. Results and discussion

The regression curve of the DoR respect to the temperature, as well as those of the Avrami equation parameters versus the fixed carbon-to volatile matter ratio are shown in **Figure 1**.

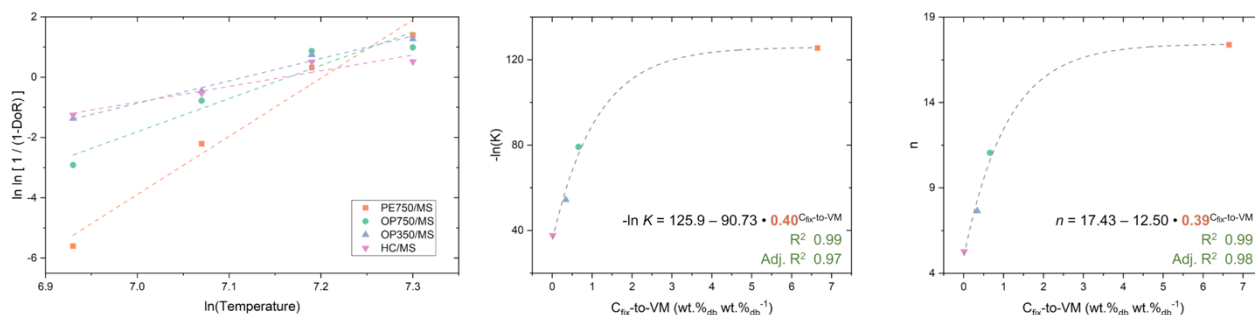


Figure 1 Linearized plot of the degree of reduction respect to temperature of the specific bio-CCA recipe and regression curve of the resulting Avrami equation parameters respect to the fixed carbon-to-volatile matter ratio.

The results of the linearized plot showed a strong correlation regardless of the biochar matrix used in each recipe, thus confirming the sigmoidal trend of DoR versus heat treatment temperature. Specifically, the R^2 and adj- R^2 of the PE750/MS, OP750/MS, OP350/MS, and HC/MS curves were 0.92 and 0.88, 0.93 and 0.90, 0.97 and 0.96, and 0.92 and 0.88, respectively. Moreover, in the case of using $-\ln(K)$ with respect to the absolute value K , both the curve of the Avrami equation parameters versus the fixed carbon-to-volatile matter ratio followed an identical trend, almost perfectly describable by an asymptotic exponential function (R^2 and adj- R^2 greater than 0.97). Even more interesting than the actual modeling, the analysis of the regression equation showed an almost identical basis of the exponential term, thus suggesting that both parameters reach the asymptotic value at the same fixed carbon-to-volatile matter ratio. Specifically, the asymptotic value is reached at a ratio of about 5, which means that biochar matrices with an higher fixed carbon-to-volatile would not be properly valorized through bio-CCAs and could be instead utilized in other impact mitigation pathways, i.e., through their direct introduction inside the iron and steel processes as fossil carbon substitutes.

4. Conclusions and developments

The proper valorization of biomass from the furniture, transportation, agricultural and municipal residue industries is becoming increasingly important in the transition of carbon from fossil to biogenic. In this regard, understanding the maximum quality threshold of each carbon matrix for which effective valorization is lost in one process and can be routed to another pathway requiring higher quality turns out to be of vital importance for an optimization of material flows. In this study, the ability to model the reduction behavior of bio-CCAs with respect to the fixed carbon-to-volatile matter ratio of biochar proved effective in understanding the maximum level at which it is preferable to redirect biochar to other valorization pathways, such as direct introduction within metallurgical furnaces. Nevertheless, further investigation is needed to validate the reliability of the model within the fixed carbon-to-volatile matter ratio of 0.66-6.65, which is currently under study.

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