

Introduction: In the last decades, iron ore has been widely investigated and employed as an oxygen carrier in chemical looping combustion process thanks to its low cost and because it is present in abundance on Earth. Biomass can be employed in ironmaking, because it is able to reduce natural hematite (Fe_2O_3) to metallic iron (Direct Reduction Iron, DRI), with the advantage of low ash production and high reactivity and, is of great significance in achieving carbon neutrality [1,2].

Aim of the work: The present work addresses the interactions between biomass and iron in a different perspective: in particular, the effects of biomass pyrolysis on iron ore reduction are investigated. Iron ores are natural minerals widely used in the context of steel industry; their use in combination with biomass is recently gaining interest for also wide range of renewable energy processes, from green steel-making to chemical looping combustion and gasification.

Results and discussion: In the present work thermochemical reactions of mixtures of a lignocellulosic biomass, *Miscanthus Giganteus* (MIS), and of a natural hematite, Khumani Iron Ore (KIO), $90 \mu\text{m} < d < 200 \mu\text{m}$, are investigated. Experiments have been carried out in a thermogravimetric apparatus upon heating up to 1000°C in N_2 and in H_2 enriched atmospheres with different biomass to iron ore weight ratios. The main gaseous products have been monitored on-line by gas analyzers, while the physicochemical and structural properties of the solid products have been investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

Miscanthus Giganteus

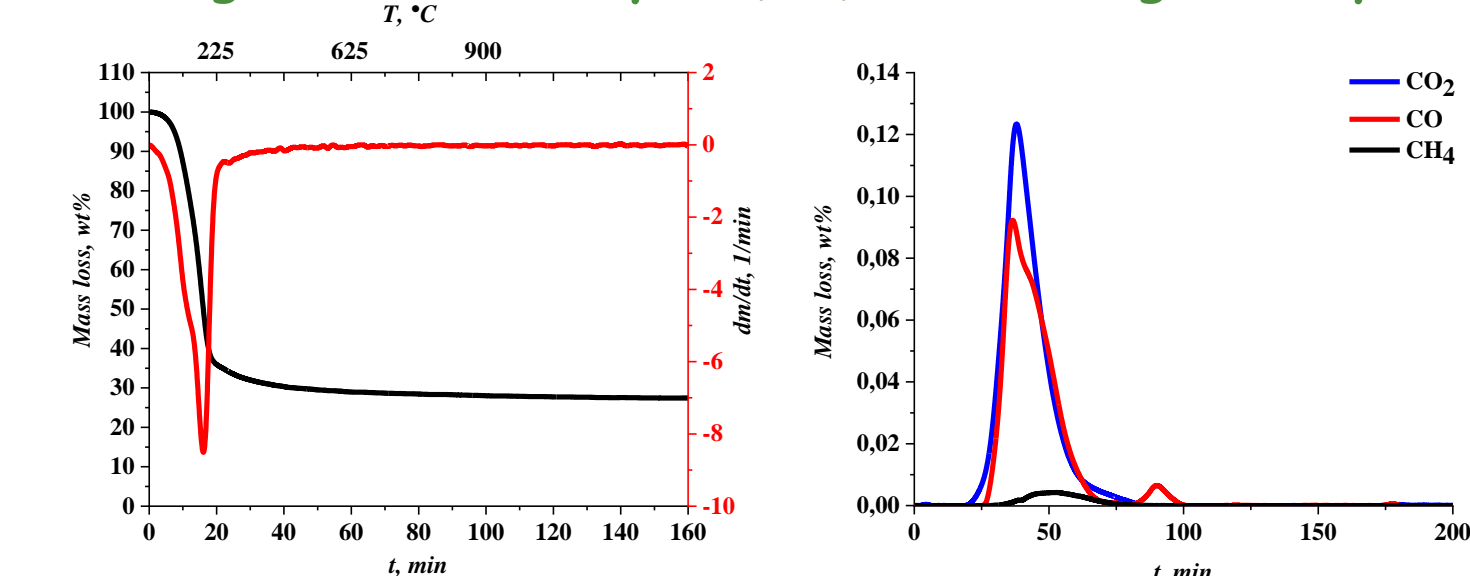
CHN content determination.

Standardized Analyses of Miscanthus

Miscanthus	wt (%)
C_{daf}	43.3
H_{daf}	5.81
N_{daf}	0.27
O^*	50.69

*Calculated by difference

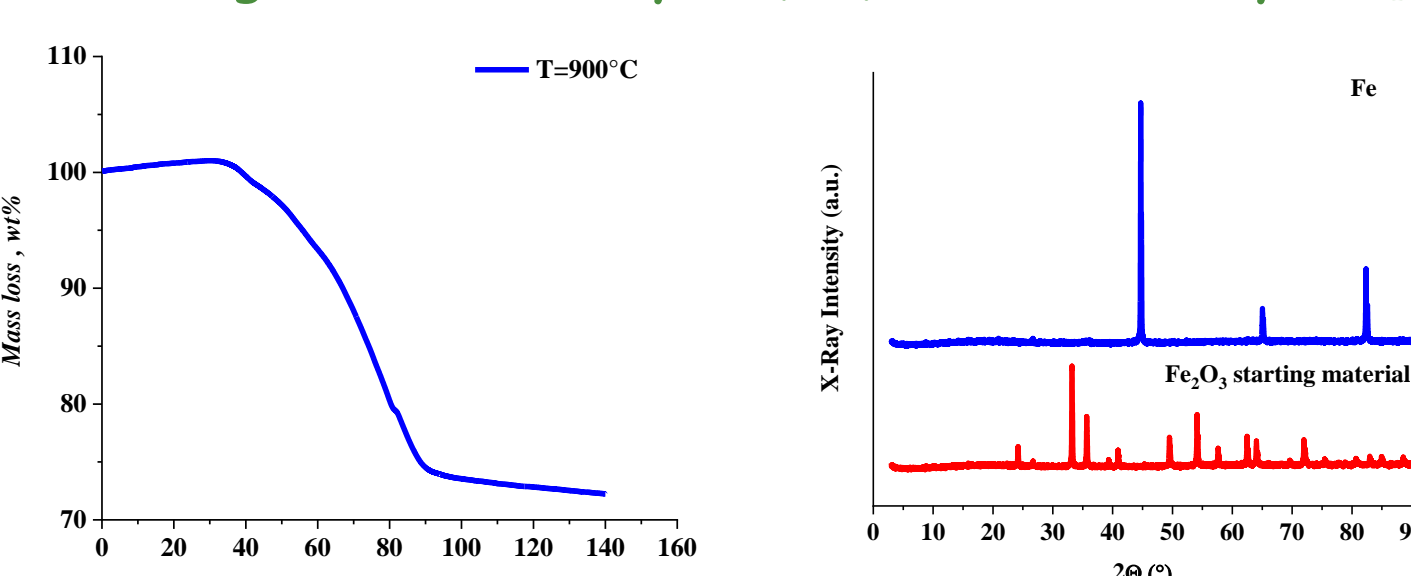
Thermogravimetric analysis (TG) with ABB gas analysers.



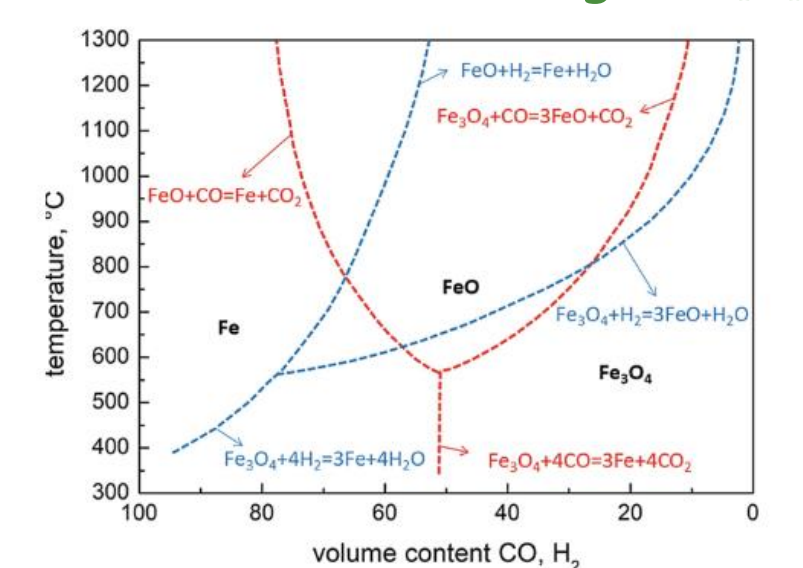
XRF characterization

Elements	Area (%)
Fe	89.9
Si	5.1
Al	2.7
K	0.45
Mg	0.45

Thermogravimetric analysis (TG) and XRD analyses [3].



Baur-Glaessner diagram [4].



Fe-O-H₂ and Fe-O-C system including the Boudouard equilibrium for 1 bar and a carbon activity of 1.

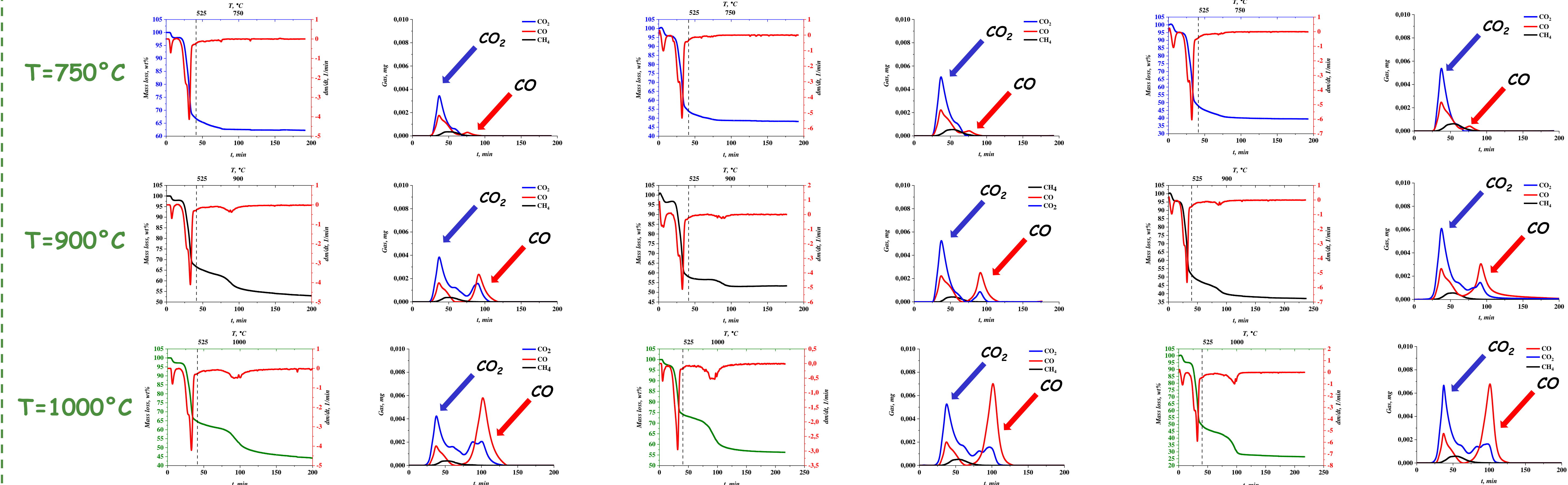
Miscanthus Giganteus-Khumani Iron Ore Formulations

Different Miscanthus and Iron ore weight ratios were investigated at different temperatures.

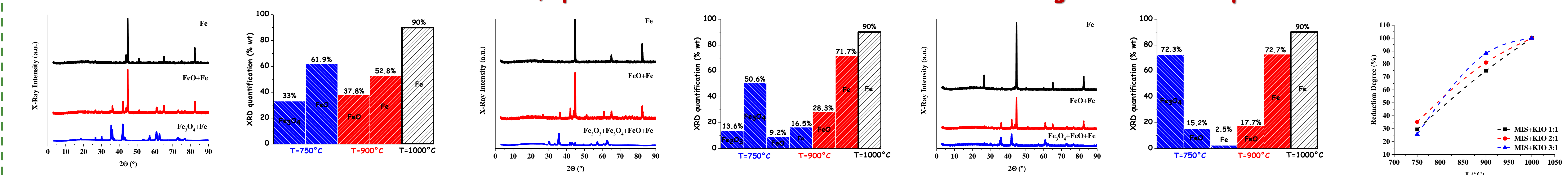
1:1 wt%

2:1 wt%

3:1 wt%



XRD characterization, quantification and calculation of reduction degree versus temperature

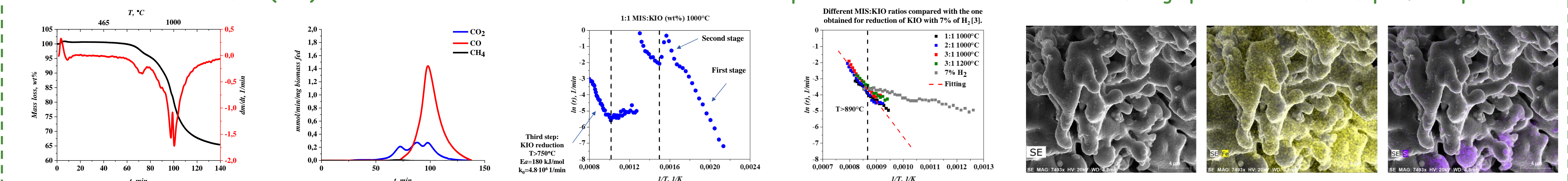


Role of biochar in KIO reduction, reduction rate and morphological investigation

3:1 CHAR:KIO (wt%) 1000 °C

Arrhenius plots

SEM micrographs and EDX metal maps of KIO particles



Conclusions: different weight ratios between biomass/iron ore and temperatures have been explored. In particular, by increasing the amount of biomass and temperature a high percentage of metallic iron was obtained. Based on mass balances, two different regions of temperatures have been identified: a) at $T < 500^\circ\text{C}$ the mass loss is due to pyrolysis of biomass, b) at $T > 500^\circ\text{C}$ the mass loss increases with the MIS:KIO ratio. The mass loss cannot be attributed only to reduction of Fe_2O_3 , but also biomass gasification occurs. This is evident in the appearance of remarkable CO peaks above 900°C . It is shown that kinetics of biomass pyrolysis at $T < 500^\circ\text{C}$ is not influenced by the presence of KIO. Kinetics of KIO reduction has been obtained fitting the mass loss data above 750°C . These results suggest that the co-conversion approach described herein has potential applications in the fast-growing field of chemical looping and ironmaking technologies. Further work will be carried out to investigate also the potential of this approach for tailoring carbonaceous chars for catalysis and environmental applications.

Acknowledgements: Antonio Fabozzi acknowledges funding from the European Union - NextGenerationEU under the National Recovery and Resilience Plan (PNRR), Mission 04 Component 2 Investment 3.1, Project "ECCSELLENT - Development of ECCSEL-R.I. Italian facilities: usEr access, services and IoNg-Term sustainability" Code: IR0000020 - CUP F53C22000560006. iENTRANCE@ENL - Infrastructure for ENergy TRAnSition and Circular Economy @ EuroNanoLab" - Code IR0000027 - CUP B33C22000710006 - European Union - NextGenerationEU under the National Recovery and Resilience Plan (PNRR), Mission 04, Component 2, Investment 3.1. The authors acknowledge Luigi Stanzione and Andrea Capuzzo for CHN and XRF analysis.

References: [1] Abi B., A. "Influence of combined catalysts on the catalytic pyrolysis process of biomass: A systematic literature review." Energy Conversion and Management 309 (2024): 118437. [2] Fabozzi, A., Cerciello F., & Senneca O. "Reduction of Iron Oxides for CO₂ Capture Materials." Energies 17.7 (2024): 1673. [3] Cerciello, F., Fabozzi, A., Yannakis, C., Schmitt, S., Narin, O., Scherer, V., & Senneca, O. (2024). Kinetics of iron reduction upon reduction/oxidation cycles. International Journal of Hydrogen Energy, 65, 337-347. [4] Cavaliere, P. "Smelting Reduction: Most Efficient Technologies for Greenhouse Emissions Abatement." Clean Ironmaking and Steelmaking Processes: Efficient Technologies for Greenhouse Emissions Abatement (2019): 377-417.