

EXPERIMENTAL EVALUATION OF AGRICULTURAL BIOMASS-BASED REDUCTANT FOR SUSTAINABLE FERROALLOY SMELTING

Sewela SAKUNEKA, Michel WA KALENGA, Willie NHETA

Mineral Processing and Technology Research Centre, Department of Metallurgy, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, South Africa, sewela.sakuneka@gmail.com, michelk@uj.ac.za, wnheta@uj.ac.za

<https://doi.org/10.37904/metal.2025.5157>

Abstract

The South African ferroalloy industry faces increasing environmental pressures to transition toward sustainable metallurgical practices. Traditional smelting relies heavily on fossil-based reductants and fluxing agents, contributing significantly to carbon emissions. This study investigates the capabilities of macadamia nutshell biochar as an alternative reductant in ferromanganese production. High-grade manganese ore was crushed and pulverized to ~75 µm. Its mineralogy was analyzed through X-ray diffraction (XRD), while scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray fluorescence (XRF) characterized its chemical composition. Macadamia nutshells were pyrolyzed at 700 °C for 45 minutes under an argon atmosphere to produce biochar, which was characterized using proximate and ultimate analysis. Reduction experiments were performed in an alumina tube furnace at 1300 °C under argon using a graphite crucible to assess the biochar's effectiveness as a reductant. Preliminary results showed great that the use of macadamia biochar as an alternative reductant to produce high carbon ferromanganese production can be effective if thoroughly investigated. Also, the raw macadamia nutshell conversion to biochar was successful with fixed carbon reaching 85.97%.

Keywords: Biomass, macadamia nutshells, pyrolysis, metal recovery, ferromanganese

1. INTRODUCTION

The production of Mn-ferroalloys is closely linked to high CO₂ emissions due to the use of fossil carbon reductants [1]. Metal production accounts for 40% of industrial greenhouse gas emissions, consumes around 10% of the world's total energy, involves the extraction of approximately 3.2 billion tons of minerals, and generates billions of tons of by-products annually [2]. Research on the environmental benefits of using macadamia nutshells as a reductant in smelting operations has emerged as a critical area of interest due to the significant contributions of metallurgical industries to global CO₂ emissions and energy consumption [3]. Over recent decades, the field has evolved from exploring traditional fossil-based reductants toward integrating biomass-derived materials, including agricultural residues, as sustainable alternatives [4]. This shift is driven by the urgent need to mitigate climate change impacts, with steel production accounting for approximately 7% to 9% of global anthropogenic CO₂ emissions [5]. The practical significance lies in reducing greenhouse gas emissions while maintaining industrial efficiency, as well as promoting circular economy principles through waste valorization [6]. Despite advances in biomass utilization, knowledge gaps remain regarding the efficacy and environmental performance of specific biomass wastes like macadamia nutshells compared to traditional reductants [7]. The integration of such biomass materials into existing smelting processes faces technical and supply chain challenges [8].

Pyrolyzed macadamia nut shells can produce biochar with a high surface area, which effectively adsorbs CO₂, thus mitigating emissions during smelting processes. The use of biomass in metallurgical processes can also facilitate the recovery of heavy metals, reducing the environmental impact of waste materials [9]. This study

aims to assess the feasibility of using macadamia nutshell biomass as an alternative reductant for ferromanganese smelting.

2. EXPERIMENTAL WORK

2.1. Materials

The ferromanganese ore used in this was provided by the metallurgy laboratory at the University of Johannesburg. The ore was originally sourced from N'chwaning in the Northern Cape region of South Africa. The macadamia nutshells were sourced from the Tzaneen region of South Africa.

2.2. Equipment

The pyrolysis and reduction experiments were conducted in a horizontal alumina tube furnace. The furnace was operated under an inert environment created by connecting the furnace to an argon gas cylinder. Alumina crucibles were used for the pyrolysis experiments while graphite crucibles were used for the reduction experiments.

2.3. Methodology

The manganese ore was crushed and further pulverized to $\sim 75\ \mu\text{m}$. The ore mineralogy was analyzed using XRD whereas SEM/EDS and XRF were used to determine the chemical composition. This was done to identify the presence of environmentally significant metals. The macadamia nutshells underwent pyrolysis in a horizontal tube furnace under an argon atmosphere at $700\ ^\circ\text{C}$ for 45 minutes. The alumina crucibles were filled each with 15 g of the raw macadamia nutshell sample and then placed in the furnace's cold zone for 5 minutes prior to pushing it into the hot zone to prevent thermal shock. The schematic of the experimental setup is shown in **Figure 1**. Argon gas was allowed to flow through the furnace to create an inert atmosphere at a rate of 8 ml/min.

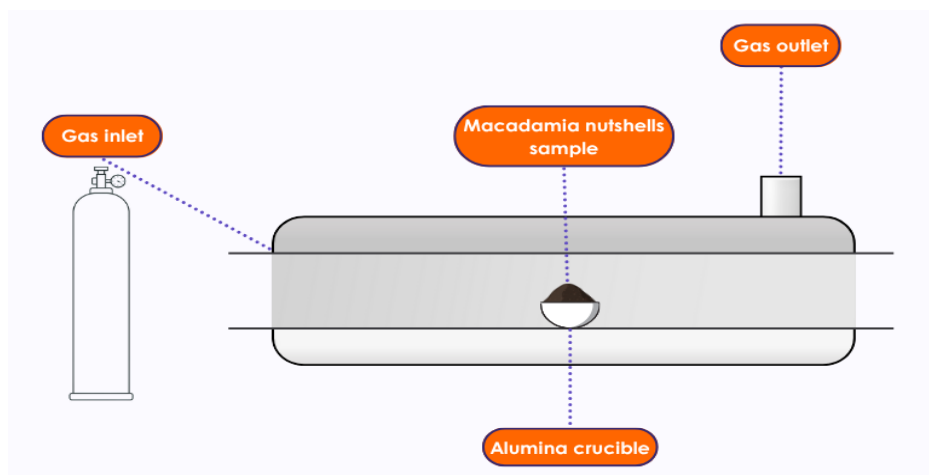


Figure 1 Schematic diagram of the tube furnace used in the experiments

Proximate analysis of macadamia biomass determined ash, inherent moisture, volatile matter, and fixed carbon (by difference). Ash was measured using the ISO method at $550\ ^\circ\text{C}$ (organic) and $950\ ^\circ\text{C}$ (inorganic) for 2 hours. Moisture was determined by drying at $105\ ^\circ\text{C}$ for 1 h 20 min, while volatile matter was assessed at $950\ ^\circ\text{C}$ for 7 min in a covered crucible. Gross calorific value was obtained with a combustion calorimeter, and total sulphur content was analyzed at $1150\text{--}1151\ ^\circ\text{C}$. For reduction experiments, a graphite crucible was weighed before and after each run to check interactions with the ore. Ferromanganese ore was milled with macadamia nutshell biochar for a homogeneous feed, then heated at $1300\ ^\circ\text{C}$ for 2 h in an alumina tube furnace under argon. The sample cooled for ~ 1 h under argon before removal and was transferred to a desiccator. Brief exposure to air during transfer may have caused partial re-oxidation, potentially affecting analysis results.

3. RESULTS A DISCUSSION

3.1. Materials

3.1.1. *Ferromanganese ore*: the chemical composition for the ferromanganese ore used in these experiments are provided in **Table 1** below. The ferromanganese ore sample contains magnesium oxide (MgO) and calcium oxide (CaO) in varying proportions. The presence of these oxides indicate that the ore is basic which could have an influence on the slag basicity which is crucial for the slag fluidity and metal separation. The high manganese content classifies the ore as a high-grade ferromanganese ore, valuable for the production of manganese alloys.

Table 1 Chemical composition of ferromanganese ore

Sample A									
Compound	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl	K ₂ O	CaO
(wt%)	0.03	0.41	0.24	3.02	0.07	0.42	0.02	0.12	7.15
Compound	Cr ₂ O ₃	MnO	Fe ₂ O ₃	NiO	CuO	ZnO	SrO	BaO	
(wt%)	0.08	74.77	12.45	0.08	0.03	0.03	0.50	0.57	

The mineralogy of the ferromanganese ores used in these experiments are provided in **Figure 2** below.

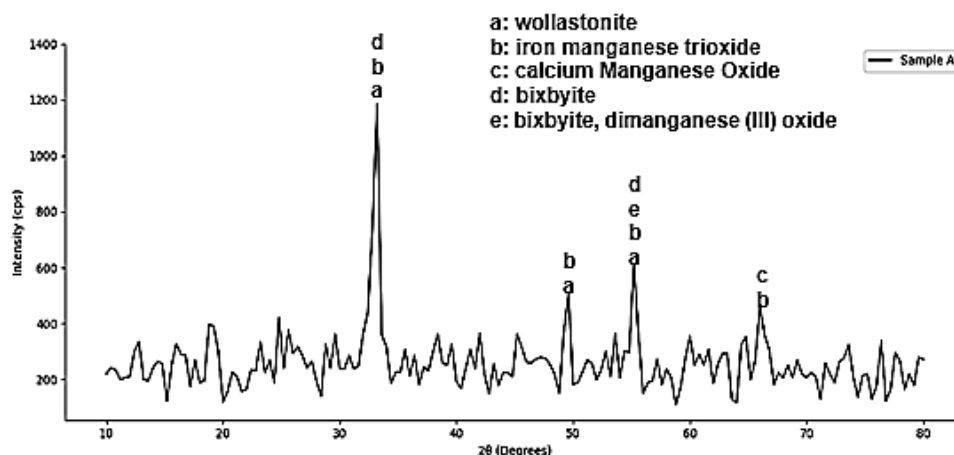


Figure 2 XRD plot of manganese ore

The SEM images revealed irregularly shaped, angular particles as a result of crushing. The sample display relatively larger and denser particles. The bright regions observed in the sample correspond to metal-rich or denser oxide phases while the darker regions likely represent lower-density oxides and gangue, These morphological differences reflect the heterogeneous nature of the ore.

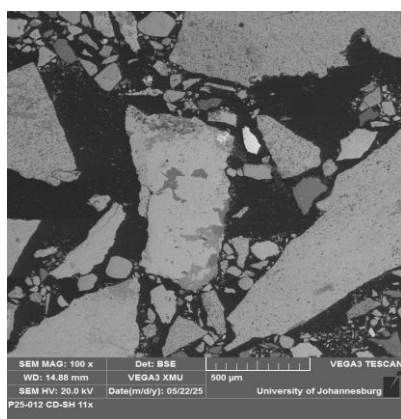


Figure 3 SEM of the ferromanganese ore

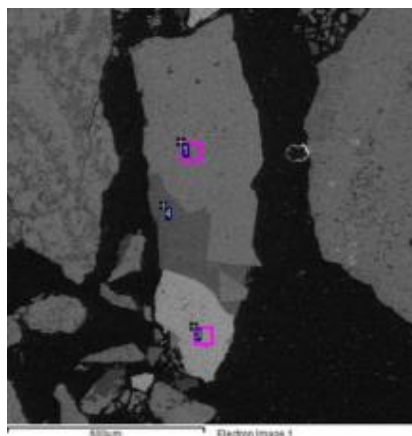


Figure 4 SEM-EDS of the ferromanganese ore

Table 2 Analysis of the spectra (wt%)

Formula	Element	Spectrum		
		1	3	4
Mn	Mn	24.97	24.97	24.97
Fe	Fe	6.37	6.37	6.37
CaO	Ca	0.27	0.27	0.27
SiO ₂	O	68.39	68.39	68.39

3.1.2. *Raw macadamia nut shell biomass and biochar*: **Tables 3** and **4** present the proximate and ultimate analysis of the biomass at 700 °C. The macadamia nutshell biomass showed low ash and volatile matter with a high fixed carbon content, indicating good carbonization and thermal stability. Moisture remained consistently low, confirming effective drying. The high calorific value highlights its strong energy potential, while the low sulfur content makes it suitable for cleaner metallurgical applications with minimal SO₂ emissions. This makes the biomass suitable for cleaner metallurgical operations.

Table 3 Proximate and ultimate analyses of the raw macadamia nutshells

Parameters (wt% as received)					
Proximate Analysis				Ultimate Analysis	
Ash (%)	Volatile Matter (%)	Inherent Moisture (%)	Fixed Carbon (%)	Total Sulphur (%)	CV (kJ/g)
0.45	73.05	6.43	20.08	0.31	18.9

Table 4 Proximate and ultimate analyses of the macadamia nutshell biomass

Parameters					
Proximate Analysis				Ultimate Analysis	
Ash (%)	Volatile Matter (%)	Inherent Moisture (%)	Fixed Carbon (%)	Total Sulphur (%)	CV (kJ/g)
2.36	10.90	0.86	85.97	0.09	32.70

The proximate analysis of macadamia nutshell biochar in **Table 4** revealed a fixed carbon content of 85.97%. This value lies within the typical fixed carbon ranges reported for conventional coke used in metallurgical applications specifically. Ferromanganese or ferroalloy production standards often cite fixed carbon levels of 86 to 88% [10], and general industrial coke specifications report fixed carbon typically between 87 to 91%. The proximity of the biochar's fixed carbon content to these benchmarks suggests it may serve as a prospective alternative reductant, meeting essential carbon quality requirements of metallurgical coke.

Figures 5 and **6** present the SEM-EDS results. Three spectra of the biochar were analyzed, and the chemical composition of the macadamia nutshell biochar were generated in **Table 5**.

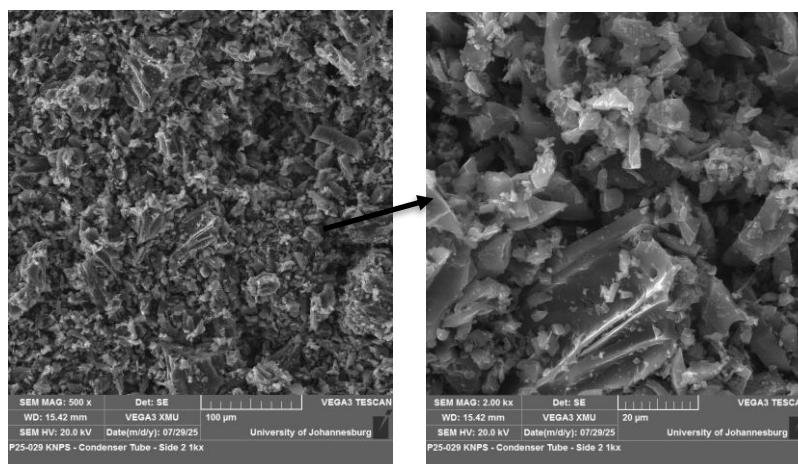


Figure 5 SEM images macadamia nutshell biochar

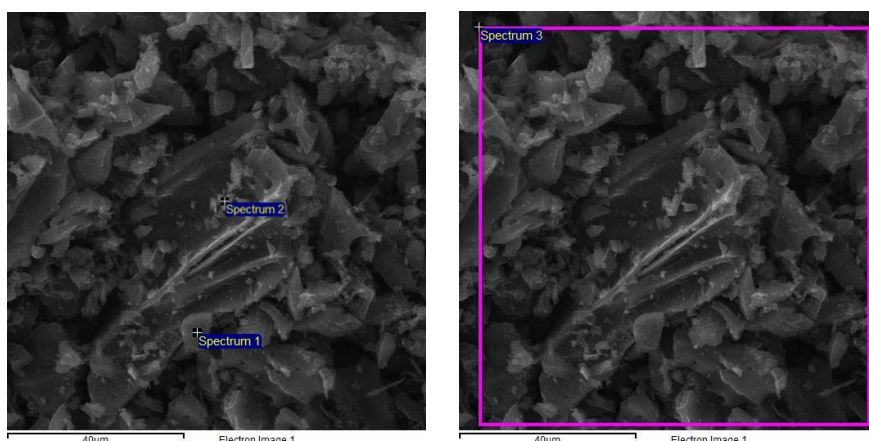


Figure 6 SEM-EDS of biochar

The dominance of carbon in the elemental spectrum of the biochar presented in **Table 5** below suggests excellent potential as a reductant. The low ash and sulfur contents, confirmed through proximate and ultimate analysis, make it particularly desirable for clean smelting applications, as it would produce fewer impurities and less harmful emissions compared to conventional reductants.

Table 5 Analysis of the spectra (wt%)

Formula	Element	Spectrum		
		1	2	3
CaCO ₃	C	92.53	94.76	92.74
SiO ₂	O	6.74	4.56	6.48
MgO	Mg	0.07	0.14	0.07
K ₂ O	K	0.58	0.12	0.56
CaO	Ca	0.09	0.12	0.15

3.1.3. Reduced product:

The reduced ferromanganese product showed bright metallic regions, confirming metallic phase formation. Increased Fe and decreased O indicated successful carbothermic reduction by macadamia nutshell biochar (**Table 6**), producing Mn and Fe, though some residual carbon suggested incomplete reduction. SEM revealed metallic droplets surrounded by slag remnants containing Si, Al, and Ca oxides (**Figure 9/ Table 7**). Oxygen detected in the product was attributed to partial re-oxidation during handling despite argon cooling. The graphite crucible exhibited negligible mass loss (0.068 g), confirming minimal interaction with the feed.

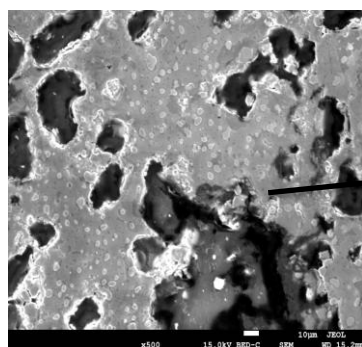


Figure 7 SEM of the reduced product

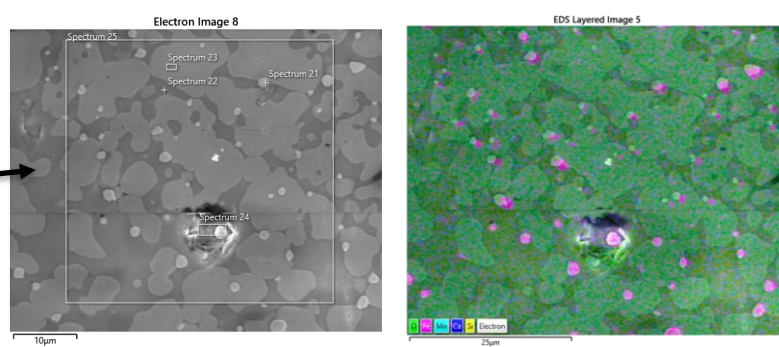


Figure 8 SEM-EDS of the reduction product

Table 6 Analysis of the spectra (wt%)

Formula	Element	Spectrum		
		21	24	25
O	O	7.3	11.1	34.6
Mn	Mn	12.4	34.5	51.0
SiO ₂	Si	1.1	4.5	5.7
CaO	Ca	0.9	16.3	5.7
Fe	Fe	77.8	29.1	3.0

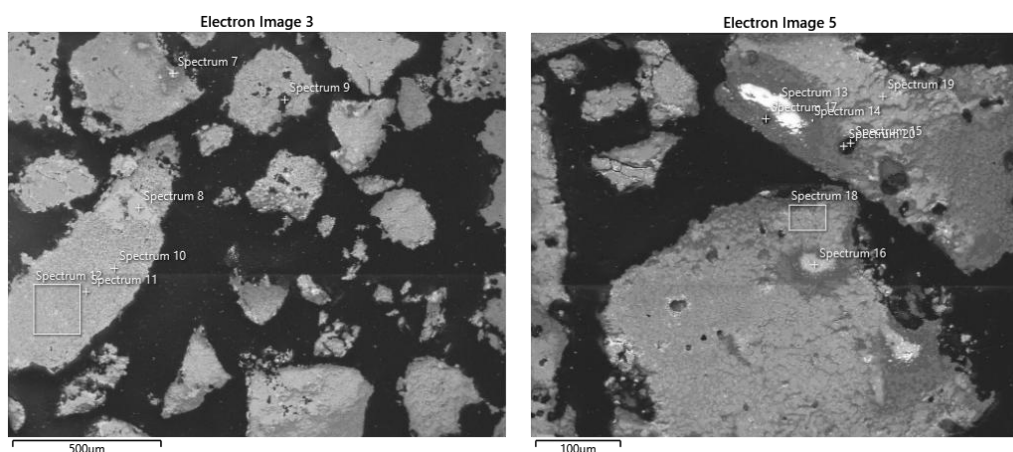


Figure 5 SEM-EDS of slag spectra

Table 2 Analysis of the spectra (wt%)

Formula	Element	Spectrum		
		7	16	19
O	O	48.7	52.4	46.6
Mn	Mn	-	16.5	3.7
Al ₂ O ₃	Al	3.7	1.1	4.0
SiO ₂	Si	15.9	15.2	17.4
CaO	Ca	27.9	14.4	26.9
MgO	Mg	3.7	0.3	1.3

4. CONCLUSION

The findings of this study underscore the viability of macadamia nutshell biochar as a sustainable reductant in the production of ferromanganese. The experimental data reveals that its attributes such as high fixed carbon content, low ash and sulfur levels, and calorific value position the biochar as a promising alternative to traditional metallurgical coke. The successful carbothermic reduction processes observed, along with the formation of metallic manganese and iron, affirm its effectiveness in carbothermic reduction process. Although conducted for orientation of the investigation at 1300 °C, a further and thorough research is scheduled to assess the process in the temperature range of the coke bed zone.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Department of Metallurgy at the University of Johannesburg for providing laboratory access, resources and technical support.

REFERENCES

- [1] TANGSTAD, M., TRANELL, G.M. *Reducing CO₂ emissions from the ferro-alloy and silicon production*. The Australasian Institute of Mining and Metallurgy. Aug 21, 2024, 13 p.

- [2] RAABE, D. The materials science behind sustainable metals and alloys. *American Chemical Society*. Mar. 08, 2023. doi: [10.1021/acs.chemrev.2c00799](https://doi.org/10.1021/acs.chemrev.2c00799).
- [3] EL-TAWIL, A.A., AHMED, H.M., ÖKVIST, L.S., BJÖRKMAN, B. Self-reduction behavior of bio-coal containing iron ore composites. *Metals* (Basel), Jan. 2020, ol. 10, no. 1, doi: [10.3390/met10010133](https://doi.org/10.3390/met10010133).
- [4] SUOPAJÄRVI, H., PONGRÁCZ, E., FABRITIUS, T. The potential of using biomass-based reducing agents in the blast furnace: A review of thermochemical conversion technologies and assessments related to sustainability. 2013. doi: [10.1016/j.rser.2013.05.005](https://doi.org/10.1016/j.rser.2013.05.005).
- [5] GUITAR, M.A., THOME, A., BRITZ, D. How green will the green-steel production be? *Springer Nature*. Dec. 01, 2025. doi: [10.1007/s43621-025-01254-1](https://doi.org/10.1007/s43621-025-01254-1).
- [6] LONTOC, M.J. et al. From waste to sustainable energy: Harnessing organic by products in developing eco-briquettes. 2024. [Online]. Available from: www.multiresearchjournal.com.
- [7] DiGIOVANNI, C., LI, D., NG, K.W., HUANG, X. Evaluation of biochar and coke blends for slag foaming applications in electric arc furnace steelmaking. *Steel Research International*, Jan. 2025, vol. 96, no. 1, doi: [10.1002/srin.202400518](https://doi.org/10.1002/srin.202400518).
- [8] DiGIOVANNI, C., LI, D., NG, K.W., HUANG, X. Ranking of injection biochar for slag foaming applications in steelmaking. *Metals* (Basel), Jun. 2023, vol. 13, no. 6. doi: [10.3390/met13061003](https://doi.org/10.3390/met13061003).
- [9] GRIESSACHER, T., ANTREKOWITSCH, J. Utilization of biomass at the recycling of heavy metal containing wastes. *Waste Biomass Valorization*, Sep. 2012, vol. 3, no. 3, pp. 369–374, doi: [10.1007/s12649-012-9126-6](https://doi.org/10.1007/s12649-012-9126-6).
- [10] KIEUSH, L. et al., “A comprehensive review of secondary carbon bio-carriers for application in metallurgical processes: Utilization of torrefied biomass in steel production. Dec. 01, 2022, MDPI. doi: [10.3390/met12122005](https://doi.org/10.3390/met12122005).