



Evaluation of Biochar from Palm Oil Waste as a Carbon Sink and as Sustainable Cement Replacement in Building Materials

Aan Mohammad Nusrat Aman

Department of Civil Engineering

Faculty of Science and Engineering

Thesis submitted to University of Nottingham Malaysia for the degree of
Doctor of Philosophy

January 2025

Abstract

Over the years, there has been a high demand of concrete in the construction industry due to its strength and durability. However, the production of cement, a key component of concrete, has caused high carbon dioxide emissions, negatively affecting the environment. To address this issue, recent research has explored sustainable supplementary cementitious material such as biochar, which offers increased strength and enhanced properties for concrete and mortar composites. This research focuses on the usability, efficiency, and sustainability of palm oil waste biochar as a cement replacement for carbon sequestration. The selected biochar palm kernel shell and empty fruit bunch were produced through pyrolysis. By recycling palm oil waste and converting it into biochar for construction, this approach promotes sustainable practices within the palm oil industry. This study investigates both the optimisation of biochar production through pyrolysis and its utilisation as a supplementary cementitious material. Response surface methodology was used to optimise pyrolysis parameters. The optimised pyrolysis parameters are 409°C, 15°C/min, 120 minutes for palm kernel shells and 455°C, 15°C/min, 20 minutes for empty fruit bunch. Cement replacement from 1 to 8% was casted with biochar mortar composites and mechanically tested through compressive strength, density, porosity, water absorption and flexural strength to understand the behaviour of biochar with cement. Mortar composites with 4% empty fruit bunch biochar pyrolysed at 455°C were found to be the optimum percentage with improved mechanical properties. Concrete composites with 4% biochar were compared and evaluated by the same mechanical tests. The concrete composites with 4% palm kernel shells pyrolysed at 409°C proved to be the optimum mix.

The carbon dioxide sequestration potential of the biochar, biochar concrete and the mortar composites were tested and analysed. The results show that palm kernel shell biochar, which was pyrolysed at 409°C had the highest carbon dioxide sequestration potential. Both biochar mortar and concrete composites also showed potential, but this was mainly due to physical adsorption rather than chemical adsorption within the tested time frame. Finally, to assess the environmental impact, life cycle assessment was conducted for the biochar mortar and concrete composite using the OpenLCA software. All composites showed a decrease in environmental impact compared to the control. The composite with 4% empty fruit bunch pyrolysed at 500°C had the lowest

impact of 17.2% for mortar and 38.1% for concrete in reference to the control. Based on the combined evaluation of enhanced mechanical properties and carbon sequestration potential, the optimised biochar from both biomass sources, palm kernel shells and empty fruit bunch are proposed as an effective sustainable replacement of cement. The approach by this research determines the importance and feasibility of using a specific type of biochar as a carbon sink and as a supplementary cementitious material. The findings highlight that the utilisation of palm oil waste biochar as a supplementary cementitious material will enhance mechanical properties, promote waste management and additionally reduce the use of landfill.

Acknowledgements

First of all, I would like to express my sincere gratitude to my main supervisor Dr Anurita Selvarajoo. I am grateful for her guidance throughout this research, her constant feedback, her valuable advice and her patience. It has been an honour to work with her during this PhD journey. I would also like to thank my co-supervisor Dr Lau Teck Leong for his support and guidance throughout this research. His helpful comments and suggestions during our meetings were valuable and are greatly appreciated. I am also grateful for the help of the laboratory technicians from the departments of Civil Engineering and Chemical Engineering.

Finally, I would like to express my sincere gratitude for the love, encouragement and constant motivation from my parents and siblings. I wholeheartedly thank my sisters Asma and Aleen for their unwavering love and support. Their constant presence, encouragement and patience during the difficult and stressful moments of my life have been an invaluable source of strength and comfort.

Publications and Conferences

Journal Publications:

- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L.; Chen, W.-H. Optimization via response surface methodology of palm kernel shell biochar for supplementary cementitious replacement Chemosphere Volume 313 2023, 137477. <https://doi.org/10.1016/j.chemosphere.2022.137477>
- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L.; Chen, W.-H. Biochar as Cement Replacement to Enhance Concrete Composite Properties: A Review. Energies 2022, 15, 7662. <https://doi.org/10.3390/en15207662>
- **Aman, A.M.N.**, Selvarajoo, A., Chong, S. et al. Comparative life cycle assessment of pervious concrete production in Malaysia with natural and recycled aggregate. Innov. Infrastruct. Solut. 2022, 7, 211 <https://doi.org/10.1007/s41062-022-00801-3>

Conference Proceedings:

- **Aman, A. M. N.**, Selvarajoo, A., Lau, T. L., & Chen, W. Comparison of Optimized Production of Palm Oil Waste Biochar with Response Surface Methodology for Cement Replacement Application. *E3S Web of Conferences* 2024, 589, 03007. <https://doi.org/10.1051/e3sconf/202458903007>

Conferences:

- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L: Palm Oil Waste Biochar as Cement Replacement In: 2nd International Conference on Water and Environment for Sustainability and 7th Postgraduate Colloquium for Environmental Research 2024 (ICWES-POCER 2024), Kuala Lumpur, Malaysia, April 2024
- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L: Title: Palm Oil Waste Biochar as Cement Replacement. In: 3rd World Conference on Byproducts of Palms & their Applications, Riyadh, Saudi Arabia (ByPalma), 5-8 December 2023
- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L: Adaptation of Different Types of Biochar on Wastewater Treatment: A Review. In: 1st International Conference on Water and Environment for Sustainability (ICWES), Kuala Lumpur, Malaysia, December 2022
- **Aman, A.M.N.**; Selvarajoo, A.; Lau, T.L: Utilization of palm kernel shell for supplementary cementitious replacement. In: 6th Postgraduate Colloquium for Environmental Research (POCER), Langkawi, Malaysia June 2022

Contributed:

- Evaluating the Efficacy of Palm Kernel Shell Biochar for Enhanced Wastewater Treatment in Sewage Systems, Afzaal Mohamed Marikkar, Anurita Selvarajoo, Fang Yenn Teo and **Aan Mohammad Nusrat Aman**, 8th International Conference on Environment 2024 (ICENV 2024), Penang Island, Malaysia from December 17th to 18th, 2024.
- Comparison of Optimized Production of Palm Oil Waste Biochar with Response Surface Methodology for Cement Replacement Application **Aan Mohammad Nusrat Aman**, Anurita Selvarajoo, Teck Leong Lau, Wei-Hsin Chen International Conference on Green Environmental Engineering and Technology (IConGEET) 29 - 30 August 2024
- Bali, Indonesia Selvarajoo, A. & **Aman, A.M.N.**, 2023. Improving biochar properties by pyrolysis of palm biomass for use as cement-based materials. *International Conference on Solid Wastes 2023: Waste Management in Circular Economy and Climate Resilience (ICSWHK2023)*, Hong Kong, 31 May – 3 June 2023.
- Selvarajoo, A., Sugumaran, H.D.M., Teo, F.Y. & **Aman, A.M.N.**, 2022. Waste as an alternative green building material. *8th International Conference on Climate Change (8TH-ICCC)*, Bangkok, Thailand, 17–18 November 2022.
- Song, E.X., Selvarajoo, A., **Aman, A.M.N.**, Teo, F.Y. & Koppula, P., n.d. Performance of biochar in bioretention systems for removal of mixed contaminants: a review. *Larhyss Journal*.

Awards:

- Gold Award for Sustainable Innovation 2022 by the Universiti Tun Hussein Onn Malaysia: Utilisation of Palm Kernel Shell Biochar as Supplementary Cementitious Material
- Silver Award in Invention, Innovation and Technology Exhibition ITEX 2023: Green Biochar Composites

List of Abbreviations

SCM	Supplementary Cementitious Material
PKS	Palm Kernel Shell
EFB	Empty Fruit Bunch
RSM	Response Surface Methodology
CCD	Central Composite Design
ANOVA	Analysis of variance
TGA	Thermogravimetric Analysis
BET	Brunauer-Emmett-Teller
PDS	Particle Size Distribution
FTIR	Fourier Transform Infrared Spectrometry
FESEM	Field Emission Scanning Electron Microscope
EDX	Energy-dispersive X-ray spectroscopy
DOH	Degree of Hydration
CH	Calcium Hydroxide
CSH	Calcium Silicate Hydrate
CC	Calcium Carbonate
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
EI	Environmental Impact
wt	Weightage

Table of Contents

Abstract	i
Acknowledgements	iii
Publications and Conferences	iv
List of Abbreviations	vi
Table of Contents	vii
List of Figures	xii
List of Tables	xv
Chapter 1 Introduction	1
1.1 Research Background	1
1.2 Problem Statement	2
1.3 Research Novelty	3
1.4 Research Aim and Objectives	4
1.5 Research Scope	4
1.6 Thesis Outline	5
Chapter 2 Literature Review	8
2.1 Biochar Production	8
2.2 Palm Oil Waste	10
2.3 Response Surface Methodology	11
2.4 Applications of Biochar in Building Materials	14
2.4.1. Water Absorption	22
2.4.2 Static Modulus of Elasticity	24
2.4.3 Compressive Strength	24
2.4.4 Flexural Strength	27
2.4.5 Tensile Strength	28
2.5 Characterisation of Biochar as Cement Replacement	28

2.6 Carbon Sequestering Potential of Biochar	32
2.7 Life Cycle Assessment Studies on Biochar and Concrete	34
2.8 Summary	39
Chapter 3 Optimisation of Palm Oil Waste Biochar Production.....	41
3.1 Methodology	41
3.1.1 Biomass Collection and Sample Preparations	41
3.1.2 Slow Pyrolysis	42
3.1.3 Response Surface Methodology	43
3.1.4 Biochar Analysis.....	45
3.1.4.1 Field Emission Scanning Electron Microscope—Electron Dispersive X-ray Microscope.....	46
3.1.4.2 Thermogravimetric Analysis	47
3.1.4.3 Particle Size Distribution	48
3.1.4.4 X-Ray Diffraction Analysis	49
3.1.4.5 Fourier Transform Infrared Spectroscopy	49
3.1.4.6 Water Absorption.....	50
3.1.4.7 Brunauer-Emmett-Teller.....	51
3.2 Results and Discussion	51
3.2.1 Palm Kernel Shell Biochar.....	51
3.2.1.1 Optimisation.....	51
3.2.1.2 Biochar Yield	59
3.2.1.3 Elemental Analysis	60
3.2.1.4 Biochar Thermal Stability.....	61
3.2.1.5 Biochar Morphology	64
3.2.2 Empty Fruit Bunch Biochar	66
3.2.2.1 Optimisation.....	66
3.2.2.2 Biochar Yield	72

3.2.2.3 Elemental Analysis	73
3.2.2.4 Biochar Thermal Stability	74
3.2.2.5 Biochar Morphology	77
3.2.3 Optimal Biochar Characterisation.....	78
3.3 Summary of Findings.....	83
Chapter 4 Palm Oil Waste Biochar as a Cement Replacement	84
4.1 Methodology	84
4.1.1 Mortar Mix Preparation	84
4.1.2 Concrete Mix Preparation	85
4.1.3 Physicochemical Properties	86
4.1.4 Compressive Strength	87
4.1.5 Flexural Strength.....	87
4.1.6 Capillary Water Absorption.....	87
4.1.7 Porosity	88
4.2 Results and Discussion	89
4.2.1 Optimisation of Cement Replacement	89
4.2.1.1 Effect of Cement Replacement with Compressive Strength.....	89
4.2.1.2 Relation of Compressive Strength with Other Mechanical Properties	93
4.2.2 Biochar Concrete Composites.....	98
4.2.2.1 Impact of Biochar Type with Compressive Strength.....	98
4.2.2.2 Impact of Biochar Type with Other Mechanical Properties	102
4.2.3 Chemical Properties of Biochar Composites	105
4.2.3.1 Functional Groups.....	105
4.2.3.2 Crystalline Structure	107
4.2.3.3 Thermal Analysis	109
4.2.3.4 Microscopic Viewing.....	112
4.3 Summary of Findings.....	113

Chapter 5	Carbon Sequestration of Biochar Composites	115
5.1	Carbon Sequestering Potential.....	115
5.2	Methodology	115
5.3	Results and Discussion	118
5.3.1	Palm Oil Waste Biochar.....	118
5.3.1.1	Thermal Analysis	118
5.3.1.2	Functional Groups.....	120
5.3.1.3	Crystalline Structure	122
5.3.1.4	Microscopic Viewing.....	123
5.3.2	Biochar Concrete and Mortar Composites.....	125
5.3.2.1	Mass Change.....	125
5.3.2.1	Phenolphthalein Test.....	128
5.3.2.3	Thermal Analysis	129
5.3.2.4	Functional Groups.....	131
5.3.2.5	Crystalline Structure	133
5.3.2.6	Microscopic Viewing.....	134
5.4	Summary of Findings.....	136
Chapter 6	Life Cycle Assessment of Biochar Composites.....	138
6.1	Methodology	138
6.1.1	Goal and Scope	139
6.1.2	Life Cycle Inventory and Assumptions	141
6.1.3	Life Cycle Impact Assessment.....	145
6.1.4	Open LCA Software	146
6.2	Results and Discussion	147
6.2.1	Environmental Impact Assessment.....	147
6.2.2	Individual Process Impact Analysis.....	149
6.3	Summary of Findings.....	156

Chapter 7	Conclusions.....	157
7.1	Research Conclusions	157
7.2	Research Limitations and Future Recommendations	158
	References.....	160
	Appendices.....	182
	Appendix A: Compressive and Flexural Strength of Literature Studies	182
	Appendix B: Basic Organic Functional Group Chart	185
	Appendix C: Trial Mixes of Biochar Composites	186
	Appendix D: Slump Test Results.....	188
	Appendix E: Water Absorption Results of Biochar Composites.....	190
	Appendix F: Design of Experimental Set up	193
	Appendix G: LCA Results	194

List of Figures

Figure 1.1 Thesis outline connecting objectives.....	7
Figure 2.1 Biomass categories used as a supplementary cementitious material based on the literature collected.....	15
Figure 2.2 Detailed map describing factors influencing biochar and cement composite properties.....	29
Figure 2.3 Breakdown of the process of biochar production from the source (biomass) to product (biochar) and its subsequent applications in building materials.....	31
Figure 2.4 Compressive strength of biochar mortar and concrete composites reported in previous studies.....	32
Figure 2.5 Flexural strength of biochar mortar and concrete composites reported in previous studies.....	32
Figure 3.1 Air drying of (a) PKS and (b) EFB.	42
Figure 3.2 Preparation of samples (a) PKS raw, (b) PKS milled, (c) EFB raw and (d) EFB milled.	42
Figure 3.3 Slow pyrolysis experimental set up, consisting of nitrogen cylinder Tubular furnace and the flask outlet.	43
Figure 3.4 Visual comparison of PKS and EFB samples before and after pyrolysis, illustrating the transformation of biomass into biochar.(a) and (b) palm kernel shell, (c) and (d) empty fruit bunch.	43
Figure 3.5 Visual comparison between the (a) original particle size and the (b) powdered form of palm kernel shell after grinding.	46
Figure 3.6 FESEM-EDX FEI Quant400F.....	47
Figure 3.7 STA6000 PerkinElmer TGA-DSC.....	48
Figure 3.8 Heavy duty sieve shaker used for sieving.	48
Figure 3.9 Panalytical X'Pert Pro USA XRD equipment.....	49
Figure 3.10 Frontier FT-IR/FIR PerkinElmer.....	49
Figure 3.11 Biochar water absorption experimental set up (a) measuring cylinder with stirrer, (b) measuring cylinder with biochar stirrer and plastic cover and (c) vacuum pump with conical flask, filter funnel and biochar with filter paper.	50
Figure 3.12 BET Micrometric ASAP2020 USA Equipment.....	51

Figure 3.13 3D representation of responses by the RSM for PKS biochar. (a) Biochar yield response, (b) C content response, (d) K content response, (e) Si content response.	57
Figure 3.14 Predicted against actual of the PKS biochar RSM model. (a) Biochar yield response, (b) C content response, (c) O content response, (d) K content response, (e) Si content response.....	58
Figure 3.15 Conducted PKS pyrolysis runs (a) biochar yield against temperature, (b) biochar yield against residence time and (c) biochar yield against heating rate.....	60
Figure 3.16 TGA analysis of PKS runs at (a) biochar at 300°C, (b) biochar at 500°C, (c) biochar at 700°C, (d) biochar at all temperatures with raw PKS biomass.	63
Figure 3.17 FESEM images of PKS under different temperatures.....	65
Figure 3.18 Labelled FESEM images. PKS biomass, (b) optimised biochar, (c) biochar at 500°C, (d) biochar at 700°C.....	65
Figure 3.19 3D representation of responses by the RSM for EFB biochar. (a) Biochar yield, (b) C content, (d) K content, (e) Si content.....	70
Figure 3.20 Predicted against actual of the EFB biochar RSM model. (a) Biochar yield, (b) C, (c) O,(d) K, and (e) Si content.	71
Figure 3.21 Conducted EFB pyrolysis runs. (a) Biochar yield against temperature, (b) biochar yield against heating rate and (c) biochar yield against residence time.....	73
Figure 3.22 TGA analysis EFB pyrolysis runs at (a) biochar at 300°C, (b) biochar at 500°C, (c) biochar at 700°C, (d) biochar at all temperatures with raw EFB biomass.	76
Figure 3.23 FESEM images of empty fruit bunch biochar produced at (a) 300°C, (b) 455°C, (c) 500°C and (d) 700°C.....	78
Figure 3.24 Particle Size Distribution of biochar.	80
Figure 3.25 FTIR analysis of biomass and biochar.	82
Figure 3.26 XRD analysis of biochar.	82
Figure 4.1 Preparation of mortar mix (a) materials, (b) mixing process, (c) casting (d) demoulding and labelling of samples.	85
Figure 4.2 Concrete mix preparation (a) materials, (b) concrete mixing process and (c) casted samples.....	86
Figure 4.3 Mortar and pestle to crush the biochar concrete and mortar samples.	86
Figure 4.4 Biochar mortar composites casted for 40 × 40 × 160 mm.	87
Figure 4.5 Compressive Strength of biochar mortar composites (a) 7 days curing and (b) 28 days curing.	90

Figure 4.6 Mechanical properties with 28 days compressive strength of biochar mortar composites (a) density, (b) porosity, (c) 72 hr water absorption and (d) 28-day flexural strength.....	94
Figure 4.7 Slump of biochar concrete composites with 4% of each biochar type.....	99
Figure 4.8 Compressive Strength of biochar concrete composites (a) 7 days curing and (b) 28 days curing.	100
Figure 4.9 Mechanical properties of biochar concrete composites (a) density, (b) porosity, (c) 72 hr water absorption and (d) flexural strength.	104
Figure 4.10 FTIR analysis of (a) biochar mortar composites and (b) biochar concrete composites.....	106
Figure 4.11 XRD analysis of (a) biochar mortar composites and (b) biochar concrete composites.....	108
Figure 4.12 TGA analysis of (a) biochar mortar composites and (b) biochar concrete composites.....	110
Figure 4.13 Degree of hydration of (a) mortar samples and (b) concrete samples....	111
Figure 4.14 FESEM image of control samples (a) mortar and (b) concrete. 4% of 409°C PKS with (c) mortar composite and (d) concrete composite. 4% of 455°C EFB with (e) mortar composite and (f) concrete composite.....	113
Figure 5.1 Experimental setup of the carbon sequestering studies. (a) Trial round of experimental setup. Set up for (b) biochar samples, (c) mortar samples, and (d) concrete samples.....	117
Figure 5.2 Professional 14" masonry saw.....	117
Figure 5.3 Thermal analysis of biochar samples post carbonation.	119
Figure 5.4 FTIR analysis of biochar samples after the carbonation test.....	121
Figure 5.5 XRD analysis of biochar samples after the carbonation test.	122
Figure 5.6 FESEM images of biochar samples post carbonation test. (a) 409°C PKS, (b) 500°C PKS, (c) 455°C EFB and (d) 500°C EFB.	123
Figure 5.7 FESEM-EDX of biochar samples post carbonation test. (a) 409°C PKS and (b) 455°C EFB.	124
Figure 5.8 Mass change before and after the carbonation test of (a) mortar samples and (b) concrete samples.	127
Figure 5.9 Phenolphthalein test on samples post carbonation test.....	128
Figure 5.10 TGA post carbonation test of (a) mortar samples and (b) concrete samples.	130

Figure 5.11 FTIR analysis post carbonation of (a) mortar composites and (b) and concrete composites.	132
Figure 5.12 XRD analysis post carbonation of (a) mortar composites and (b) and concrete composites.	134
Figure 5.13 FESEM images of samples after the carbonation test, (a) mortar control, (b) concrete control, (c) 409°C PKS mortar, (d) 409°C PKS concrete, (e) 455°C EFB mortar and (f) 455°C EFB concrete.	135
Figure 6.1 The different stages of the life cycle assessment process.....	138
Figure 6.2 (a) Concrete LCA system boundary, (b) Mortar LCA system boundary.	140
Figure 6.3 Environmental impact categories for scenarios 2, 3, 4 and 5 of biochar (a) concrete composites and (b) mortar composites.	148
Figure 6.4 Global warming potential (a) concrete composites and (b) mortar composites.	149
Figure 6.5 Environmental impact categories of ingredients and phases for biochar (a) concrete composites' and (b) mortar composites.....	150
Figure 6.6 Environmental impact categories of cement, transport and pyrolysis for concrete composites.	152
Figure 6.7 Environmental impact categories of cement and pyrolysis for (a) concrete composites and (b) mortar composites.	153
Figure 6.8 Environmental impact categories of pyrolysis for (a) concrete composites and for (b) mortar composites.....	155

List of Tables

Table 2.1 Thermochemical conversions with yields of products.	9
Table 2.2 Categorisation of biomass and biochar analysis according to their properties.	10
Table 2.3 Research summary utilising EFB and PKS products from pyrolysis.	11
Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties.	17
Table 2.5 Environmental impact categories and their significance (Guinée, 2001; GaBi Handbook, 2012).....	38

Table 3.1 Parameters of the response surface methodology model.....	44
Table 3.2 Pyrolysis parameters of biochar produced.....	45
Table 3.3 RSM runs for palm kernel biochar.	54
Table 3.4 ANOVA of the palm kernel shell biochar yield, C, O, K and Si content....	55
Table 3.5 RSM runs for empty fruit bunch biochar.....	66
Table 3.6 ANOVA of the empty fruit bunch biochar yield, C, O, K and Si content...	68
Table 3.7 Biochar properties and characteristics.	79
Table 4.1 YTL Cement Type II properties.	85
Table 4.2 Compressive strength after 28 days curing of mortar composites with different supplementary cementitious material.....	93
Table 4.3 Compressive strength after 28 days curing of concrete composites with different supplementary cementitious material.....	102
Table 5.1 Proximate analysis post carbonation of biochar samples.	120
Table 6.1 Labelling of the different scenarios and the quantity of materials used. ...	141
Table 6.2 Processes in each scenario.	141
Table 6.3 LCI collected for cement, fine and coarse aggregate, transport truck and concrete plant.	143
Table 6.4 LCI collected for pyrolysis at each temperature and landfill site.	144
Table 6.5 Distances calculated for concrete LCA.	145
Table 6.6 CML 2 baseline 2000.....	146

Chapter 1 Introduction

1.1 Research Background

Countries in Asia are constantly developing and leading to a drastic increase in demand for building materials such as concrete, as it is widely available, inexpensive and high strength compared to other materials (Mohamad et al., 2021). This leads to an increase in the production of raw materials such as cement and the mining of aggregates, which contributes to higher carbon emissions caused by these processes. Sources indicate that Malaysia accounted for up to 0.8% of global greenhouse gas (GHG) emissions in 2020 (United Nations Development Programme, 2021). The country also reported annual carbon dioxide emissions of 256.05 million tonnes in 2021 (Friedlingstein, 2021), emphasising that these figures come exclusively from the burning of fossil fuels and cement production. Cement is the main component of concrete; it provides strength and binds fine and coarse aggregates together when mixed with water. This has led to increased research into supplementary cementitious materials such as fly ash, silica fume, rice husk ash, granulated blast furnace slag and biochar (Ahmed et al., 2021; Mohamad et al., 2021; Suarez-Riera et al., 2020; Syahida Adnan et al., 2021).

Biochar is a carbon-rich sustainable material produced by thermochemical conversion of biomass, animal waste, municipal solid waste and other organic materials in a low-oxygen environment (Kant Bhatia et al., 2021). Due to its unique properties, such as high surface area, high porosity, functional groups, high cation exchange capacity and chemical stability, this makes biochar suitable for various applications, it has attracted the attention of researchers. Biochar is also an advantageous sustainable material due to its quick and easy production, eco-friendly nature, reusability and cost efficiency (Loy et al., 2021; K. Sahoo et al., 2021; Yaashikaa et al., 2020; Zhu et al., 2022). It has been utilised for many applications, such as wastewater treatment (Fang et al., 2020; Huggins et al., 2016; Michalak et al., 2019; Xiang et al., 2020), chemical recovery (F. Yang et al., 2019), agriculture (Ding et al., 2016; Liang et al., 2006; S. S. Sahoo et al., 2021; Spokas, 2010), carbon sequestering (Dissanayake et al., 2020; Xie et al., 2016) and anaerobic digestion (Duan et al., 2023; Lü et al., 2015; Zhao et al., 2021). Recent research has shown that biochar can be used as a supplementary cementitious material (SCM) for sustainable concrete production using different types of biochar materials

such as wood waste, rice waste and food waste (Asadi Zeidabadi et al., 2018; Gupta and Kua, 2018a; Suarez-Riera et al., 2020; Wang et al., 2020a). The use of biochar has proven to be very effective in agriculture sector and has led to the establishment of associations such as the Biochar Malaysia Association (“Biochar Malaysia Association,” 2023). Biochar is referred to as "carbon gold" by the International Biochar Initiative (“International Biochar Initiative,” 2024), which promotes the research and commercialisation of biochar for soil fertility and climate change mitigation in agricultural systems.

The Malaysia Palm Oil Council has reported that Malaysia is one of the largest palm oil exporters in the world; therefore, palm oil mills generate a significant amount of waste. Palm oil mills generate waste by-products during the processing of Fresh Fruit Bunches (FFB). From 20.80 tonnes of FFB, approximately 4.4 tonnes (22%) of Empty Fruit Bunches (EFB) and 1.10 tonnes (5.5%) of Palm Kernel Shells (PKS) are produced as waste (MPOC, 2023). Sources from the local oil mill (Seri Putra Oil Mill Banting, Selangor) and others (FELDA Sungai Tinggi, Selangor, Hyper Fusion Mill Gua Musang, Kelantan and Kilang Kelapa Sawit Bukit Pasir Sdn. Bhd. Muar, Johor) indicate that the waste, if not disposed of in landfills, is used as fuel for steam generation in boilers to generate electricity (Abdullah et al., 2013). Various research initiatives have explored using these wastes as biochar for power generation in direct carbon fuel cells (Jafri et al., 2020), biodiesel production (Quah et al., 2020), and agricultural promotion (Wan Mahari et al., 2020a).

This research investigates the use of PKS and EFB biochar as a cement replacement for carbon dioxide sequestration in mortar and concrete composites. In addition, the mechanical strength and chemical properties of the optimised mixtures of biochar mortar and concrete composite are investigated. Finally, life cycle assessments for the biochar composites were carried out to advance the research and assess the environmental impact.

1.2 Problem Statement

Carbon Dioxide is one of the major greenhouse gases that contributes significantly to global warming. From the construction industry high carbon dioxide emissions are usually generated from cement production. Increasing research into sustainable building materials is driven by this issue and has prompted researchers to investigate

materials that are abundant in their respective regions and that can help in reducing the carbon footprint in the construction industry. As Malaysia is one of the largest exporters of palm oil, significant amounts of waste are generated, prompting numerous industries to investigate the utilisation of this waste. The main types of waste include empty fruit bunch and palm kernel shells, which are being investigated to mitigate the increase in landfill sites and minimise the release of toxic gases when used as fuel for steam boilers. One area of interest in this research is the thermochemical conversion of palm oil waste into biochar, a carbon-absorbing and chemically stable material. Biochar has attracted considerable attention in agriculture and numerous studies have led to its use in industry and the establishment of large-scale biochar production plants.

Adding biochar to building materials is one way to reduce carbon emissions while reducing the amount of cement used. The resulting mixture would also be able to absorb carbon dioxide. Research is currently being carried out into various methods of using biochar as a building material. It aims to develop sustainable building materials while promoting waste management. In addition, further research is needed to evaluate biochar as a cement replacement, including its life cycle, while ensuring that it fulfils acceptable mechanical and chemical properties within the established standards. This research can help in the development of mortar and concrete mixes for low strength structural applications. Moreover, studying the life cycle of the material can promote the use of biochar not only for agricultural purposes but also for building materials.

1.3 Research Novelty

The literature indicates that biochar from palm kernel shells and empty fruit bunches has not been used as a cement replacement within the 1 to 8% range. From the literature it was comprehend that minor percentages of biochar have shown improvement in mechanical properties. This research proposes an alternative waste management method for the palm oil industry by utilising palm oil waste biochar palm kernel shell and empty fruit bunch as cement replacement, addressing the usability of these materials. In addition, the usage of response surface methodology, to produce biochar as a cement replacement is explored. In this research, carbon sequestering evaluation is conducted after the mix has attained its target properties, focusing on efficiency rather than using carbonisation as a curing method. Life cycle assessment of the optimised biochar mortar and concrete composite mixes is proposed to enhance the sustainability and reduce the environmental impact. To summarise, the approach in this research aims

determine the importance and feasibility of using a specific type of biochar as both a carbon sink and as a supplementary cementitious material.

1.4 Research Aim and Objectives

The aim of this research was to design an environmentally beneficial mortar and concrete composite using optimised biochar from palm oil waste with the ability to sequester carbon.

The objectives of the research were:

1. To optimise the pyrolysis parameters for biochar production intended to be used as a cement replacement, using response surface methodology with two different biomass have been selected palm kernel shell and empty fruit bunch.
2. To evaluate, compare and optimise the effect of different percentages of cement replacement on the mechanical properties of biochar mortar composites.
3. To investigate the mechanical properties of biochar concrete composites using optimum percentage of cement replacement.
4. To evaluate the potential of carbon sequestration by the optimised biochar, mortar and concrete composites, to determine which type of biochar is most efficient in sequestration.
5. To assess and analyse the environmental impact of the concrete and mortar composites to determine the most sustainable type of biochar as a cement replacement.

1.5 Research Scope

This research explored the usability, efficiency and sustainability of palm oil waste biochar as a cement replacement in mortar and concrete composites. The specific palm oil waste materials investigated are palm kernel shell and empty fruit bunch. Biochar production is optimised using response surface methodology for each palm oil waste separately. The optimisation focused on three pyrolysis parameters temperature, heating rate and residence time. These parameters were interchanged through ranges that have been adopted from the literature. To optimise the pyrolysis parameters the responses that were maximised were biochar yield, carbon, potassium and silicon content and the oxygen content minimised. This was done to result in biochar with high yield, chemical stability and carbon sequestering capabilities.

To evaluate the usability of the palm oil waste biochar as a cement replacement, both mortar and concrete composites were tested for physical and mechanical properties. These include the hardened density, compressive strength, porosity, water absorption and flexural strength. However, the durability of the mixes has not been investigated. The cement has been replaced from 1 to 8% with different types of biochar for mortar composites. Different biochar consists of the optimised pyrolysis parameters from palm kernel shell and empty fruit bunch and pyrolysis parameters adopted from the literature. That leads to using four different types of biochar in this research. The most effective replacement percentage from the mortar results was further applied and studied in concrete composites.

The efficiency of the palm oil waste biochar is then explored through carbon dioxide sequestration. This research investigated the capabilities of biochar separately and biochar mortar and concrete composites to sequester carbon dioxide. Carbon sequestration is tested after the composites have been water cured and attained their desired properties. Therefore, the carbon curing has not been considered for this research. The sustainability aspect of the researched biochar is then investigated through life cycle assessment combining the biochar production, the disposal of palm oil waste to landfill and the production of concrete. The assessment was then conducted to acknowledge which of the biochar mortar or concrete composites has the lowest negative environmental impact compared to the conventional mix used without biochar.

1.6 Thesis Outline

The thesis is composed of 7 chapters, which can be outlined below and Figure 1.1 demonstrates the thesis outline with the objectives:

- Chapter 1 Introduction: Introduces the research background and the novelty of the current research problem and states the objectives of this research underlying the aim.
- Chapter 2 Literature Review: Covers the review of the biochar production processes and applications with response surface methodology. In-depth review of different types of biochar and its effects of the mechanical and chemical properties for each mortar or concrete composites is included. Additionally, the life cycle assessment and carbon sequestration studies done for biochar and

together with biochar mortar and concrete composites are mentioned and elaborated.

- Chapter 3 Optimisation of Palm Oil Waste Biochar Production: This chapter covers the first objective of this research which states and explains the methodology used to produce biochar from both materials (palm kernel shell and empty fruit bunch) through pyrolysis and response surface methodology. Optimised pyrolysis parameters have been explained with different biochar analysis conducted to understand the physiochemical properties of the material prior to use as cement replacement. The optimised biochar is further analysed to predict its behaviour before its use for the next objective.
- Chapter 4 Palm Oil Waste Biochar as a Cement Replacement: This chapter deals the second and third objective of this research which uses biochar as a cement replacement. The optimised biochar of each material was used as cement replacement with different percentages (1-8%) to form biochar mortar composites. Each mix was compared and evaluated through mechanical tests to determine which percentage replacement is the most efficient and sustainable. The optimised percentage replacement was then casted to concrete composites with all different biochar materials that have been produced.
- Chapter 5 Carbon Sequestering of Biochar Composites: This chapter covers the fourth objective of this research that discusses the carbon dioxide sequestering potential. The methodology of the carbon sequestering studies for the biochar, mortar and concrete composites are stated. Different physiochemical analysis are conducted on the samples after the carbon sequestering experiment.
- Chapter 6 Life Cycle Assessment of Biochar Composites: This chapter covers the final objective of this research. With the results of the optimum cement replacement, the life cycle assessment are conducted on biochar mortar and concrete composites to conclude the most effective and sustainable biochar to be used as a building material.
- Chapter 7 Conclusion: Summarises the results of each stage of the research and suggests future recommendations.

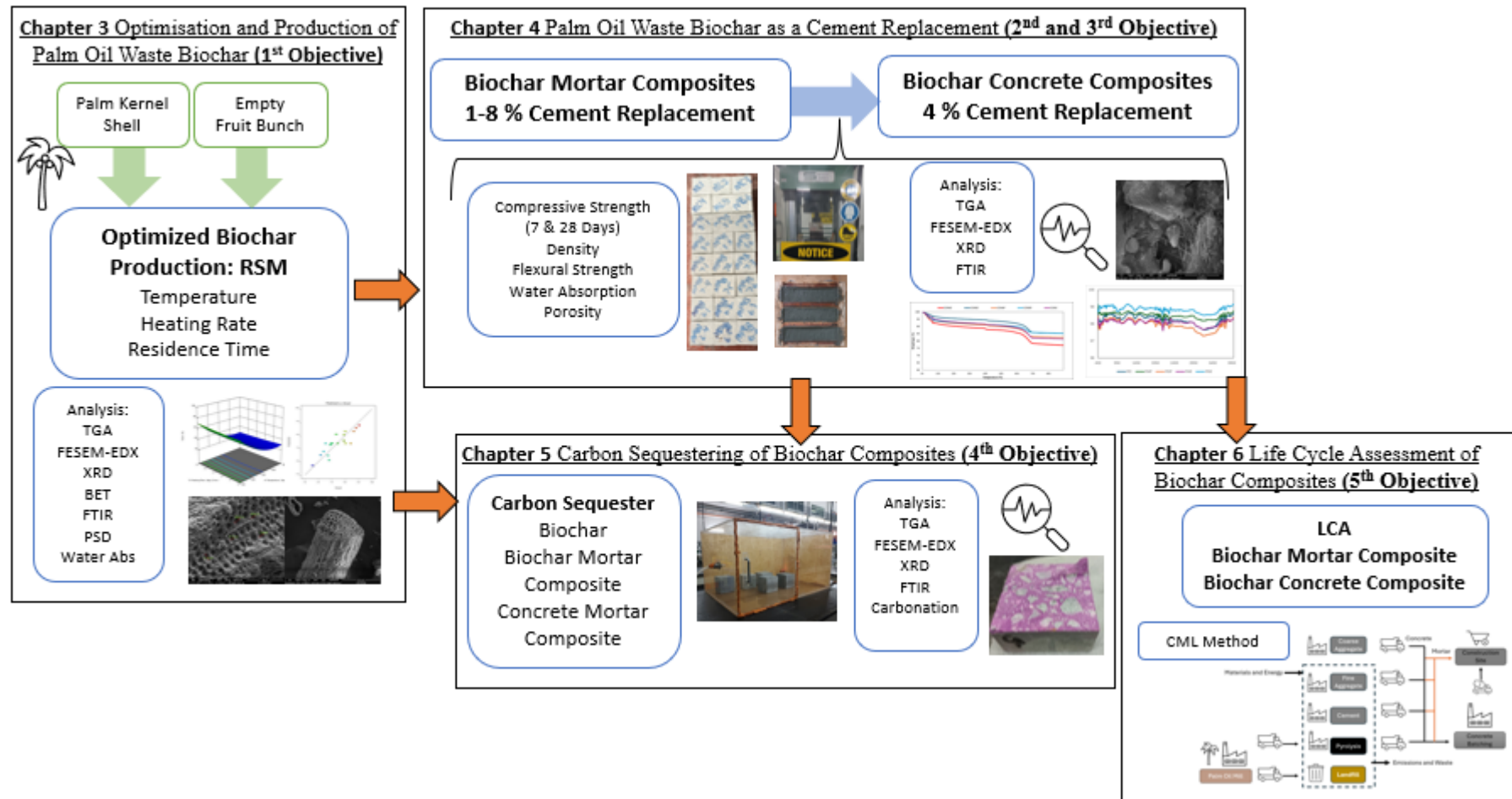


Figure 1.1 Thesis outline connecting objectives.

Chapter 2 Literature Review

This chapter contains the literature review of the topics related to the research conducted for this thesis. It begins with an overview of the production of biochar and the factors that influence its physical and chemical properties. It discusses various methods of managing the waste generated in the palm oil industry. The benefits of using response surface methodology in the production of biochar for this research are also discussed. The chapter then looks at the various applications of biochar in the construction industry and its effects on the mechanical properties of composite materials. The relationship between the composition of biochar and its mechanical properties are then examined in detail. Finally, the possibilities of carbon sequestration by biochar and life cycle assessment studies of biochar and biochar composites are discussed.

2.1 Biochar Production

The conversion of biomass into fuels through thermochemical processes results in a variety of products, each with different applications and benefits. The most popular processes for converting biomass to biochar are gasification, pyrolysis, torrefaction, flash carbonisation and hydrothermal carbonisation (Danish et al., 2021; Kant Bhatia et al., 2021; Yaashikaa et al., 2020). Table 2.1 provides an example of each thermochemical conversion and its product yield. The table shows the different temperatures used in each study, as well as the type of material and the residence time, that is the time interval in which the temperature is maintained. With these parameters, Table 2.1 shows the yield for each product: biochar, bio-oil and syngas. In the following section, the pyrolysis process is discussed in more detail as it is the most commonly used method (Danish et al., 2021; Yaashikaa et al., 2020). The biomass used for these processes consists of cellulose, hemicellulose and lignin components. These components are thermally decomposed during pyrolysis. Yaashikaa et al., (2020) studied multiple processes to determine which is most favourable in terms of cost, ease of preparation, and maximum yield. There are two known methods for pyrolysis: fast pyrolysis and slow pyrolysis, which differ in terms of heating rate, temperature, residence time and pressure. In general, fast pyrolysis is used when the maximum yield is desired in the form of a liquid product, while slow pyrolysis is carried out when the maximum yield is desired in the form of a solid product, that is biochar (Al Arni, 2018).

Al Arni, (2018) conducted an experimental study to compare the two types of pyrolysis with bagasse, which is a by-product of extracting sugar from sugarcane. The authors kept all experimental conditions and processes constant with the exception of residence time and heating rate. They wanted to investigate the effects of changing these parameters on the yield of the products. The study confirmed that slow pyrolysis is preferable when biochar is the desired product. This is due to the fact that further decomposition of the organic matter increases, leading to an enlargement of the pores and higher volatile matter release, which would favour the yield of bio-oil (Tomczyk et al., 2020).

During the thermochemical transformation of biomass in the absence of oxygen, it undergoes chemical and physical changes. During this transformation process, pores are formed by the release of volatile substances and a carbon skeleton of the material is created. The most common changes are loss of mass, formation of pores, increase in carbon content, decrease in oxygen content, change in functional groups, surface area and change in crystalline structure. It was found that the yield (Selvarajoo, 2021) and surface area (Selvarajoo and Oochit, 2020) of the resulting biochar, as well as its stability in terms of the oxygen-to-carbon ratio (Bong et al., 2022), strongly depend on the pyrolysis temperature. Table 2.2 summarises the types of characterisation analyses that have been performed in recent research on biochar (Akhtar and Sarmah, 2018a; Akinyemi and Adesina, 2020; Gupta and Kua, 2018a; Khushnood et al., 2016).

Table 2.1 Thermochemical conversions with yields of products.

Technique	Temperature (°C)	Biomass	Residence Time (min)	Yield of Biochar (%)	Yield of Bio-Oil (%)	Yield of Syngas (%)	Reference
Pyrolysis	390–980(slow)	Sugarcane	60	30–33	19–27	26–37	(Al Arni, 2018)
	380–780 (fast)	Sugarcane	20	27–28	38–47	11–21	(Al Arni, 2018)
	550 (fast)	Palm Kernel Shell	N/A	35.46	23.8	14.54	(Kim Hoang Pham et al., 2024)
Hydrothermal carbonization	220	Rice husk	60	68–76	N/A	N/A	(Ding et al., 2022)
Gasification	550–920	Wood	30	11–16	N/A	≈80	(Klinghoffer et al., 2015)
Torrefaction	200–300	Olive stone	30–120	40–90	8–49	0.3–10	(Ismail et al., 2021)

Table 2.2 Categorisation of biomass and biochar analysis according to their properties.

Analysis Method	Purpose
Proximate	Determination of moisture content, volatile matter and ash content.
Ultimate	Determination of C, H, N, O, H/C and O/C contents.
SEM (Scanning Electron Microscopy)	Biochar and biomass morphology (pore size) characterization.
BET (Brunauer–Emmett–Teller)	Determination of surface area, pore volume and mean pore diameter.
FTIR (Fourier Transform Infrared Spectrometry)	Determination of functional groups.
XRD (X-ray Diffraction)	Assessment of the presence of various crystalline materials.
TGA (Thermogravimetric Analysis)	Determination of thermal stability.
NMR (Nuclear Magnetic Resonance)	Determination of structural composition.
EDX (Energy-dispersive X-ray spectroscopy)	Determination of elemental composition.
PIDS (Polarized-Intensity Differential Scattering)	Determination of particle size distribution (PSD).
ICP-MS (Mass Spectrometry with Inductively Coupled Plasma)	Elemental and isotopic inorganic analysis.
EDS (Electron-Dispersive Spectroscopy)	Determination of elemental composition.
PDS (Particle Size Distribution)	Determination of the size of the majority of particles.

2.2 Palm Oil Waste

It has been reported that Malaysia is the second largest producer and exporter of palm oil in the world, accounting for 25.8% and 34.3% of global production and export respectively by 2021 (MPOC, 2023). A considerable amount of waste is therefore produced during the extraction of palm oil. Solid waste includes palm kernel shells (PKS) and empty fruit bunches (EFB). Palm kernel shells are the shell fractions that are produced when the nuts are crushed in the palm oil mill. It was reported that Malaysia exported almost 1 million megatonnes of PKS to the world in 2020 (MPOC, 2023). PKS has various uses; it can be used in industrial boilers, furnaces, as a catalyst for biofuel production (Bazargan et al., 2015) and in water treatment (Baby et al., 2019). In Malaysia, it has been used as a solid fuel in the steam boilers of palm oil mills for several years. This fuel produces steam to drive turbines and generate electricity for the mills, forming an energy self-sufficient process (MPOC, 2023).

Recent research has experimented with the incorporation of palm kernel shells into concrete mixes. It has been used as a substitute for coarse aggregates (Azunna, 2019), lightweight aggregate (Ogundipe et al., 2021) and as a partial cement replacement with eggshell powder (Vasudevan and Marimuthu, 2021) as well as being blended with rice husk ash (RAHEEM et al., 2021) and used for clay production (Bediako et al., 2016). The use of PKS has also been extended by converting it into biochar through thermochemical conversion. This conversion, which takes place in the absence of air,

changes the physicochemical properties of the biomass and enables further applications such as electricity generation in direct carbon fuel cells (Jafri et al., 2020), biodiesel production (Quah et al., 2020), and agricultural enhancement (Wan Mahari et al., 2020a).

A study by Omar et al., (2011) investigated the properties and moisture content of EFB and reported that EFB is a good candidate for the production of biochar due to its combustion, thermal and dielectric properties. EFB biochar is widely used as an absorbent for wastewater treatment and for the uptake of soil contaminants (Lee et al., 2014; Salleh et al., 2012; Samsuri et al., 2013; Sari et al., 2014). In another study, microwave pyrolysis was performed on pellets and short-fibre EFB to produce bio-oil for power generation (Md Said et al., 2022). The use of raw EFB has also been investigated for the production of fuel pellets when mixed with tea waste (Pua et al., 2020). EFB has shown the potential for further modification when converted into biochar, as a study by Mubarak et al., (2016) found that magnetic biochar has a higher yield, surface area and porosity. Table 2.3 cites research papers that have analysed PKS and EFB pyrolysis products have been used for different objectives, emphasising their importance and versatility in the industry.

Table 2.3 Research summary utilising EFB and PKS products from pyrolysis.

Biomass	Pyrolysis Conditions	Country	Objective	Reference
Empty Fruit Bunch	505°C, N ₂	Malaysia	Solid Fuel	(Idris et al., 2020)
	600-1200 W, Vacuum 400-1000°C, N ₂		Absorbent	(Mubarak et al., 2016)
Palm Kernel Shell	290–380°C (auger), 520°C, (fluidized bed)	Korea	Maximum Bio-oil Extraction	(Oh et al., 2016)
	750 W, 35 min, Vacuum	Malaysia	Fertilizer	(Wan Mahari et al., 2020b)
	500–700 W, 5–15 min, Vacuum		Fuel	(Ge et al., 2020)
	550–750 W, 30 min, Vacuum		Fertilizer	(Nam et al., 2018)
	250–750°C, 1 hour, N ₂	China	Multipurpose (Fuel, Carbon Sequestering, Catalyst, Absorber)	(Ma et al., 2017)

2.3 Response Surface Methodology

In order to improve the utilisation of biomass waste and reduce costs and time, the Response Surface Methodology (RSM) was used to optimise the production of biochar.

Optimisation is a method to determine the best solution in relation to certain quality criteria and leads to an improved performance of the designed system. RSM is a mathematical and statistical tool that provides an effective method for optimising process parameters with a minimum number of experiments (Bezerra et al., 2008; Singh Pali et al., 2023). In a study by Yadav et al., (2019), RSM was used to obtain rice husk biochar with a higher calorific value, higher energy density and higher energy yield using different process parameters, namely heating rate, temperature and residence time. By using RSM, it determines the significance of the interactions between temperature and time, temperature and heating rate, and time and heating rate. And concluded that temperature and time had the greatest influence on the yield and quality of the biochar. Similarly, Yadav and Jagadevan, (2021) investigated the fluoride absorption capacity of rice husk biochar and concluded that it was strongly influenced by all three parameters. The authors also considered the fuel properties of biochar and reported that its use was strongly influenced by temperature alone. Shubhi Gupta et al., (2022) conducted an optimisation study using both RSM and artificial neural networks (ANN) to produce biofuel from pine needles by pyrolysis. The authors varied the pyrolysis temperature, heating rate and inert gas flow rate and concluded that a combined approach of both optimisation methods could better model the pyrolysis of pine needles. Furthermore, the results showed that the yield was strongly influenced by the temperature, while the flow rate had the least effect on the product yield.

In another study, the experimental conditions for achieving maximum bio-oil yield through fast pyrolysis using RSM were optimised on the basis of the Central Composite Design (CCD) (Kiliç et al., 2014). In this study, the temperature, heating rate and nitrogen gas flow rate were varied. The study concluded that a three-factor experimental design the CCD is an effective method for investigating the influence of pyrolysis parameters. Temperature was identified as the most important factor, followed by heating rate and gas flow rate. Using optimisation by the same design, the CCD another study investigated the microwave-induced co-pyrolysis of EFB and tire tread to enhance the yield and quality of bio-oil (Idris et al., 2020). The optimisation showed that a feedstock ratio of 65% EFB, a reaction temperature of 505°C and an activated carbon loading of 65% resulted in the highest bio-oil yield (40.0 wt%) and energy recovery (59.0%). While the resulting oil exhibited desirable diesel-like properties, its

high acidity poses a challenge for direct use as a fuel, although catalytic processes can mitigate these issues.

Another RSM study was conducted on the use of carbonised coconut shell as a solid catalyst for biodiesel production (Endut et al., 2017). The factors considered in this study included carbonisation temperature and time and sulphonation temperature and time, with biodiesel yield being the target product. The authors demonstrated that the carbonisation temperature strongly influenced the reaction, confirming that the properties of the biochar are significantly affected. In another study, the production of biochar from EFB and PKS was optimised, investigating nitrogen flow rate, heating rate, pyrolysis temperature and time, with the responses being biochar yield and higher calorific value (Lee et al., 2020). The aim was to optimise the parameters for biochar production to achieve the highest yield and energy content while considering the cost of bioenergy production.

An investigation by Ferreira et al., (2020), the RSM was used to optimise biofuel production from EFB by varying temperature and nitrogen. In other studies, temperature, heating rate and residence time were considered as factors to optimise biochar for lead removal (Zhou et al., 2020), to promote methane production (Duan et al., 2023), and to improve fluoride absorption (Yadav and Jagadevan, 2021). Another study by Li et al., (2023) determined the optimal pyrolysis temperature for the chemical glucose-histidine, which is used as a flavouring agent in the food industry, by using multiple responses for a more efficient optimisation process. These studies show the importance of saving time and material to obtain the most effective product through RSM.

Rajendiran et al., (2023) studied the production of biochar from banana waste was optimised using three production parameters temperature, heating rate and retention time to produce biochar that is potentially suitable for various applications, like to improve soil pH, soil water retention, fertiliser and carbon sequestration. A study, on biochar production was combined with biomass treatment to produce a chemical adsorbent to treat cadmium pollution in agriculture using banana waste (Ding et al., 2023). Olive mill waste was used in another research experimenting with temperature and pressure using a factorial design of RSM to understand the effects of these factors on biomass pyrolysis using thermogravimetric analysis (TGA) (Manyà et al., 2013).

The pyrolysis of lignin was investigated in a separate study focussing on the temperature, heating rate and loading mass of the material (Jung et al., 2016). Similarly, another study investigated temperature and heating rate as well as an additional mixing ratio of the quantities of materials used, in particular algae and lentil husks. This study concluded that temperature had the greatest influence on the results, although the focus was on bio-oil yield (Kazemi Targhi et al., 2022). An experiment conducted by Hussain et al., (2023) in India optimised the temperature, retention time and slurry concentration for the production of biochar and bio-oil using *Citrus maxima* peel waste. The study found that the model can be used for lab-scale applications for peel waste. Many of the studies that were mentioned have emphasised the most important pyrolysis parameters: Temperature, heating rate and residence time. By recognising the importance of these factors, research can be more effectively directed towards exploring materials for different applications.

2.4 Applications of Biochar in Building Materials

Recent studies have shown that biochar enhances certain attributes in concrete when used as a cementitious material. For example, biochar as a cementitious material enhances chemical stability and storage potential, promotes low conductivity, and can be used as an internal curing agent, filler material, and carbon absorbent (Gupta and Kua, 2018a; Suarez-Riera et al., 2020). In previous research, biochar has been employed to develop building materials such as natural inorganic clay composites, red clay binders, bituminous materials, tunnel lining, underground construction and geopolymers.

Table 2.4 summarises the experimental procedures conducted in previous studies using biochar as a supplementary cementitious material (SCM), including the biomass material, the pyrolysis temperature, the percentage of biochar added, the ratio of concrete mixture (sand, aggregate, and water ratios), the properties tested of the biochar, the optimal amount of biochar added to the concrete or mortar mix, and the properties of composites enhanced by the addition of biochar. All these studies are discussed further with respect to the water absorption abilities, static modulus of elasticity, compressive, flexural and tensile strength of the tested samples. The summary of these previous studies can provide insights for future research regarding which tests and types of analysis should be conducted to obtain enhanced biochar composites. Researchers can utilise this summarised data to guide their selection of concrete or mortar mixtures

aimed at achieving improved strength, as well as to explore additional enhancements or to compare with new data obtained from investigating the use of different biomass in concrete and mortar. Table 2.4 also highlights if the biochar percentage was added to the total amount of cement or replaced a percentage of cement. Figure 2.1 shows the types of biomasses that have been used as SCM in previous studies, with the aim of encouraging further research on materials that have not yet been extensively investigated, such as marine biowaste (3%). As indicated by the pie chart, the majority of studies have utilised wood waste (30%). As research with wood biomass consistently demonstrate improvements, as shown in Table 2.4.

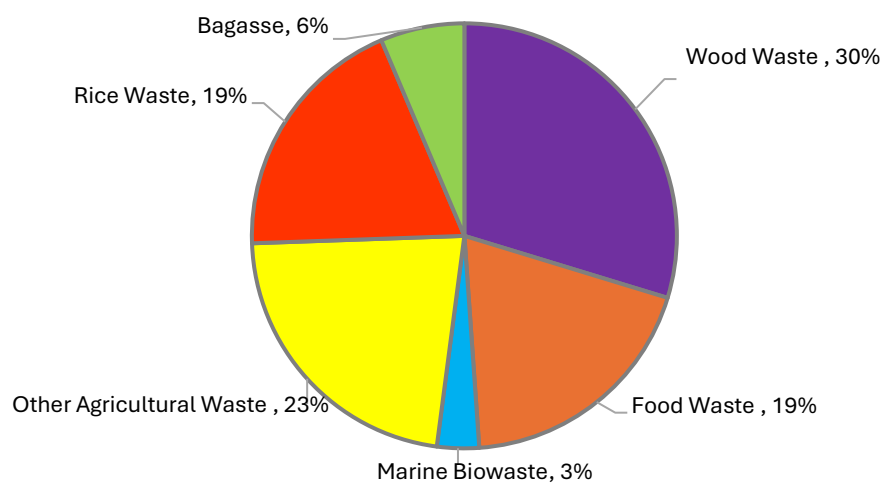


Figure 2.1 Biomass categories used as a supplementary cementitious material based on the literature collected.

A study conducted by Qin et al., (2021a) and Tan et al., (2022) are distinctive from other studies, as the authors investigated biochar as a cementitious material for pervious concrete. As pavement concrete is exposed to direct sunlight, they also tested the solar reflectance and evaporation cooling effect of their samples, indicating that increased biochar content reduces albedo, which is the amount of light reflected. Most studies listed in Table 2.4 optimised biochar cement ratios as low as 0.1% or 1% (Akhtar and Sarmah, 2018; Akinyemi and Adesina, 2020; Ding et al., 2022; Gupta and Kua, 2018; Maljaee et al., 2021; Wang et al., 2020). However, Yang and Wang, (2021) used higher biochar contents of 2% and 5%. Similarly, Asadi Zeidabadi et al., (2018) investigated 5% to 10% biochar addition. Yang and Wang, (2021) conducted an investigating biochar concrete composite using ultrasonic pulse velocity (UPV). They concluded that an increase in biochar decreases the UPV, indicating that the presence of biochar causes a decrease in the concrete's density and elastic properties, in agreement with the results

reported by (Praneeth et al., 2020a). Khushnood et al., (2016) investigated the average modulus of rupture of concrete with the addition of biochar derived from peanut and hazelnut shells; most of the tested concrete composites exhibited increased bending strength with increased biochar addition. Gupta et al., (2021) investigated the performance of biochar mortar composite exposed to sodium chloride and sodium sulphate solutions. Mortar composites containing 1–2 wt% wood waste biochar was found to be 8–11% stronger than the control after exposure to NaCl for 120 days. Furthermore, mortar composites with wood waste and rice husk biochar exposed to sodium sulphate solution exhibited an increase in compressive strength of 14–17% after 120 days of exposure to reaction products in the pore spaces of the composite (Chen et al., 2022a). Ofori-Boadu et al., (2017) investigated the influence of swine waste biochar on the early ageing properties of hardened cement paste. The authors reported that biochar reduced low ability by promoting porous and negatively charged carbonaceous surfaces, leading to the adsorption of capillary water. The initial setting time was also reduced as a result of the reaction between the biochar and cement.

Chapter 2 Literature Review

Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties.

Biomass	BC ^a Analysis	Temp ^b (°C)	BC (%) (Add/Rep)	Optimum BC	Ratio			Conclusions of Biochar Behaviour	Reference
					S:C ^c	A:C ^d	W/C ^e		
Wood Waste									
Saw Dust	C: 62.25% O:25.60% K: 0.42% Si: 0.40% 2–400 nm pores	300	2 (Add)	2%	2.75:1	N/A	0.4	- Compressive strength: Inc^f by 26% (72 MPa) of Pre-soak BC500. - Degree of hydration: Inc by 5% (67%) of pre-soak BC500. - Hardened density porosity: Dec^g by 17% (≈0.83 mm) of pre-soaked 500BC. - Flexural strength: Inc by 6% (≈13 MPa) of pre-soak BC500. - Split tensile strength: Inc by 12% (≈4.7 MPa) of pre-soak BC300_M. - Sorptivity: Inc by 33% (0.64 × 10⁻² mm/s^{0.5}) of pre-soak BC500. - Depth of water penetration: dec by 68% (≈7 mm) of pre-soak BC500. - Investigation of curing: moist curing preferable.	Gupta and Kua, 2018a)
	C: 87.13% O: 7.21% K: 0.42% Si: 0.45% 2–400 nm pores	500					0.25		
							0.4		
							0.22		
Mason Pine	Yield 30% 152 m ² /g 0.036 cm ³ /g	500	1 (Add)	1%	1:1	N/A	0.3	- Compressive strength: Inc by 8.9% (≈73 MPa) with 700-1 and 6% (≈71 MPa) with 500-1. - Hydration process: Inc by 12% (≈235 J/g) with 700-5. - Different curing methods: concrete mix with CO₂ curing most favourable.	Wang et al., 2020a)
	Yield 25% 388 m ² /g 0.057 cm ³ /g	700	2(Add)						
			5(Add)						
			1(Add)						
Eucalyptus plywood	BET: 250 m ² /g C: 85.13% Si: 0.4%	500	2(Add)	6.5%	N/A	5:1	0.35	- Compressive strength: Inc by 30% (≈12.3 MPa) with 6.5% of BC. - Splitting tensile strength: Inc by 25% (2 MPa) with 3.2% of BC. - Solar reflectance: Dec by 17% (0.138) with 3.2% of BC. - Water absorption: Inc by 32% (≈3.7%) with 3.2% of BC. - Water permeability: Inc by 4% (≈5.2 mm/s) with 3.2% of BC. - Porosity: Inc by 14% (33%) of 3.2% of BC.	Qin et al., 2021a)
			3.2 (Rep)						
			6.5 (Rep)						
			9.5 (Rep)						
Wood chips	pH: 10.22 BET: 28.06 m ² /g	700	2 (Add)	2%	3:1	N/A	0.5	- Flexural strength: Dec by 2% (4.54 MPa) with 2% BC. - Fracture energy: Inc by 36% (0.071 N/mm²) of 2% used as filler.	Suarez-Riera et al., 2020)

Chapter 2 Literature Review

Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties. (continued)

Biomass	BC ^a Analysis	Temp ^b (°C)	BC (%) (Add/Rep)	Optimum BC	Ratio			Conclusions of Biochar Behaviour	Reference
					S:C ^c	A:C ^d	W/C ^e		
Wood Chips	Size: 63.5 µm	500	1.0 (Add)	1%	3:1	N/A	0.42	• Compressive strength: Dec by A1 to 89 MPa, B1 to 43 MPa, C1 to 67 MPa. • Flexural strength: Inc by B1 sample to 4.5 MPa. • Fracture energy: Inc by C1 to 110 N/m.	Sirico et al., 2020a)
			2.5 (Add)		N/A	3.4:1	0.55		
			1 (Add)						
			2.5 (Add)						
			1 (Add)						
Wood Waste	d ₅₀ : 9.13 µm	500	1 (Rep)	3%	0.56	5:1	0.35	• Compressive Strength: Inc of 8.4% by S-2 • Flexural Strength: Inc of ~3.6% by S-1 • Density: Inc of ~1% by S-2 • Porosity: Dec of ~4.2% by S-2 • Water Absorption: Inc of 50% by S-4 • Evaporation of Cooling Effect: Inc of 13% by S-2 • CO₂-emission: Dec of 14.1% CO₂eq by S-2	Tan et al., 2022)
			3 (Rep)						
			5 (Rep)						
			8 (Rep)						
Agriculture Waste									
Olive Tree	C: 76.7% O: 12.93% pH: 8.28 0.326 m ² /g 1.7 g/cm ³	500	2 (Add)	OTB-5%	2.5	N/A	0.45	• Setting time: Dec by 15min by 5% OTB • Porosity: Dec of 27.8% by 2% OTB • Capillary Absorption: Dec of 27.3% by 2% OTB • Compressive Strength: Inc of 12.5% by 5% OTB • Flexural Strength: Inc of 24.5% by 5% SON in 56 days.	Kalderis et al., 2024)
			5 (Add)						
Commercial	C: 69.1% O: 5.84% pH: 8.7 0.178 m ² /g 2 g/cm ³	N/A	2 (Add)	OTB-5%	2.5	N/A	0.45	• Compressive Strength: Inc of 12.5% by 5% OTB • Flexural Strength: Inc of 24.5% by 5% SON in 56 days.	Kalderis et al., 2024)
			5 (Add)						
Sugarcane bagasse	N/A	200	2 (Add)	2%	N/A	N/A	0.8	• Thermal properties: dec with 4% of BC by 25% (0.228 W/m.K). • Flexural strength: Inc with 2% BC (2.77 MPa) rather than biomass. • Water absorption: BC has less absorption than biomass; lowest porosity by 2% BC (43.54%). • Modulus of elasticity: inversely proportional to BC content; highest by 2% of BC (1.97 GPa). • Cement hydration: Inc with 2% of BC (≈10.8 mW/g).	Rodier et al., 2019)
			4 (Add)						

Chapter 2 Literature Review

Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties. (continued)

Biomass	BC ^a Analysis	Temp ^b (°C)	BC (%) (Add/Rep)	Optimum BC	Ratio			Conclusions of Biochar Behaviour	Reference
					S:C ^c	A:C ^d	W/C ^e		
Palm Kernel Shell	N/A	700	0.1 (Add)	0.1%	2.35	N/A	0.37	• BC added as aqueous solution with Triton X-100. • Compressive Strength: Dec by 42% by 0.1% BC • Density: Dec by 9% by 0.1% BC • Carbonation test proved 0.5 and 0.33 exhibited high carbonation.	Flórez et al., 2019)
			0.33 (Add)						
			0.5 (Add)						
Areca Nut Husk	C: 78.98% O: 16.04% D50: 1.4 µm 4.34 m ² /g	300	2 (Rep)	AB-500 2%	2.5:1	N/A	0.4	• Compressive Strength: Inc of 34% by AB 500 2% • UPV: Inc of 7.9% by AB 500 2%	Manjunath et al., 2024)
	C: 83.56% O: 13.60% D50: 1.1 µm 44.07 m ² /g	400	2 (Rep)						
	C: 85.12% O: 12.69% D50: 0.7 µm 112.38 m ² /g	500	2 (Rep)						
Corn Stover	C: 44% Si: 23.51% Fe: 8.03% 7.101 m ² /g	500	1 (Rep)	Su-BCC-2%	N/A	N/A	0.4	• Chemical Reagents added: Su-BCC showed optimal results. • Setting Time: Dec by the Inc of BC • Compressive Strength: Inc of ~21% by 2% Su-BCC • CO₂ Abs: Highest by OH-BCC • LCA: Dec of 4% by BCC-2%.	Ye et al., 2024)
	17.467 m ² /g		2 (Rep)						
	9.753 m ² /g		2 (Rep)						
	26.661 m ² /g		2 (Rep)						
	15.446 m ² /g		2 (Rep)						
	11.913 m ² /g		2 (Rep)						
	C:45.06% With Fly Ash	550	2 (Add)	4%	N/A	N/A	N/A	• Compressive strength: Inc by 6.6% (40.5 MPa) of 6% M20 BC, by 7% (37.5 MPa) of 4% M40 BC and by 2.7% (37 MPa) of 2% M50 BC. • Carbon sequestering: Inc with 4.6% (0.477 CO₂ equivalents/Kg of block making) for 6% of M20.	Praneeth et al., 2020a)
			4 (Add)						
			6 (Add)						
Rice husk	N/A	550	2 (Rep)	2%	2.5:1	N/A	0.5	• Ultrasonic pulse velocity: 2% with BC-like control ≈4490 m/s. • Workability: dec by 2.5% (195 mm) and 10% (180 mm) of 2% and 5% BC. • Compressive strength: dec by 5.5% (42.07 MPa) of 5% BC. • Degree of hydration: dec by 2.3% (88.7 DOHth%) and 5.4% (85.9 DOH%) of 2% and 5% of BC. • Chloride diffusivity: Inc to 12.36 × 10⁻¹² m²/s by 5% of BC. • Electrical resistivity: Inc by 13% (9.10 KΩ.cm) of 5% BC.	Yang and Wang, 2021)
			5 (Rep)						

Chapter 2 Literature Review

Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties. (continued)

Biomass	BC ^a Analysis	Temp ^b (°C)	BC (%) (Add/Rep)	Optimum BC	Ratio			Conclusions of Biochar Behaviour	Reference				
					S:C ^c	A:C ^d	W/C ^e						
Marine Biowaste													
Chitosan (shellfish)	C: 72.9% H: 1.3% N: 6.8%	800	0.1 (Add)	0.1%	N/A	N/A	0.45	• Toughness: Inc to 2.12 J with BC. • Flexural strength: Dec to 2.07 MPa with BC. • Compression strength: Dec to 16.43 MPa with BC.	Nisticò et al., 2020a)				
Combination Waste													
Rice Husk	Si:246.7 mg/g Ca: 4.58 mg/m C: 36.06% O: 49.23%	500	0.1(Rep)	RH0.1	N/A	6:1	0.32	• Water absorption: Inc by 45% (8%) with RH0.25. • Compressive strength: Dec by 10% (≈34 MPa) with RH0.1. • Splitting tensile strength: Inc by 5% (≈39 MPa) with RH0.1. • Flexural strength: Inc by 23% (≈4.8 MPa) with RH0.1.	Akhtar and Sarmah, 2018a)				
			0.75(Rep)										
			1(Rep)										
Pulp and paper mill sludge	Si: 15.9 mg/g Ca: 49.21 mg/g C: 30% O: 68.5%		0.1(Rep)										
			1(Rep)										
Poultry litter	Si: 29.3 mg/g Ca: 33.3 mg/g C: 19.03% O: 77.63%	450	0.1(Rep)										
			0.75(Rep)										
Mixed sawdust	C: 87% 196.92 m ² /g 0.071 cm ³ /g	500	1 (Add)	1–2 wt% FWBC and MWBC	2.75:1	N/A	0.4			• Compressive strength: Inc by 20% (58.08 MPa) of 1% MWBC. • Flexural strength: Inc by 4.6% (12.80 MPa) of 1% MWBC. • Elastic modulus: Inc by 2.8% (29 GPa) of 1% MWBC. • Split tensile strength: Similar trend to that of flexural strength. • Water sorptivity: Dec by 66% (0.00085 mm/s ^{1/2}) of 1% FWBC; dec by 8% (0.00055 mm/s ^{1/2}) MWBC. • Depth of water penetration: dec by 40% (9.33 mm) of 1% FWBC; dec by 64% (5.50 mm) with 1% MWBC.	Gupta et al., 2018b)		
			2 (Add)										
			5 (Add)										
Food Waste	C: 71% 9.70 m ² /g 0.00288 cm ³ /g							2 (Add)					
Rice waste	C: 66% 35.70 m ² /g 0.016 cm ³ /g							5 (Add)					
Rice husk	37.5 m ² /g		700					5 (Add)	5% Treated RHB & BB			N/A	N/A
		10 (Add)											
		5 (Add)											
Bagasse	52.3 m ² /g			10 (Add)									

Chapter 2 Literature Review

Table 2.4 Summary of various studies on biochar production and characterization, as well as optimum biochar content as cementitious materials and composite properties. (continued)

Biomass	BC ^a Analysis	Temp ^b (°C)	BC (%) (Add/Rep)	Optimum BC	Ratio			Conclusions of Biochar Behaviour	Reference
					S:C ^c	A:C ^d	W/C ^e		
Olive stone	Size: 0.04–40 µm C: 76.60% 1.635 g/cm ³ 3.38 m ² /g	500	0.5 (Rep) 1 (Rep) 2 (Rep) 4 (Rep)	Up to 4% of and Rice Husk	3:1	N/A	0.5	• Workability: Inc by 3.4% (152 mm) of 1% OSB, by 8.8% (160 mm) of 0.5% FWB and 2% (150 mm) of 0.5% RHB. • Compressive strength: Inc by 9% (28.44 MPa) 2% of OSB; Inc by 5.7% (27.53 MPa) and 7% (27.87 MPa) with 1% of FWB and RHB. • Flexural strength: Inc by 8.2% (7.39 MPa) and 4% (7.11 MPa) with 2% of RHB and OSB. • Capillary water absorption: Inc to 5.6% of water absorption by 0.5% FWB; Inc to 5.9% water absorption of 4% OSB.	Maljaee et al., 2021b)
Rice husk	Size: 0.04–40 µm C: 53.07% 1.710 g/cm ³ 9.44 m ² /g		0.5 (Rep) 1 (Rep) 2 (Rep) 4 (Rep) 0.5 (Rep)						
Wood chips	Size: 0.2–100 µm C: 77.23% 1.551 g/cm ³ 4.58 m ² /g		1 (Rep) 2 (Rep) 4 (Rep)						
Coffee powder	C: 82.9% Si: 0.3% K: 9.15%		0.5 (Add) 0.8 (Add) 1 (Add)					• Compression strength: Inc by 72% (57.79 MPa) of PY-CP 0.5%. • Fracture energy: Inc by 72% (0.033 N/mm) of PY-HS 0.8%. • Modulus of rupture: Inc by 46% (4.02 MPa) of PY-HS 0.8%.	Restuccia and Ferro, 2016a)
Hazelnut shells	C: 97.9% Si: 0.11% K: 1.01%		0.5 (Add) 0.8 (Add) 1 (Add)						
Peanut shells	Avg diameter 600 nm C: 93.8% 2.20 g/cm ³		0.025 (Add) 0.05 (Add) 0.2 (Add) 0.5 (Add) 1 (Add)						
Hazelnut shells	Avg diameter 750 nm C: 87.7% 2.35 g/cm ³	850	0.025 (Add) 0.05 (Add) 0.2 (Add) 0.5 (Add) 1 (Add)	0.08% Peanut shells	N/A	N/A	0.35	• Fracture energy: Inc by 70% (1.6 fracture energy/fracture energy of pure cement) of 0.08 wt% HS. • Electromagnetic radiation shielding: Inc by 0.5 wt% of both BC. • Flexural strength: Inc by 80% (5.33 MPa) of 0.08 wt% HS.	Khushnood et al., 2016)
Rice husk	C: 41.01% O: 56.19% Si: 19.24%		2 (Rep) 1 (Rep) 2 (Rep)						
Wood waste	C: 79.86% O: 16.71% Si: 0.15%		1 (Rep)						

^aBC: biochar, ^bTemp: Temperature, ^cS:C: sand to cement ratio, ^dA:C: aggregate to cement ratio, ^eW/C: water to cement ratio, ^fInc: Increase, ^gDec: decrease, ^hDOH: degree of hydration

2.4.1. Water Absorption

Water absorption of concrete is determined by measuring the amount of water that penetrates the samples, which depends on the pore volume of concrete. The presence of macropores in a concrete mix increase with increasing biochar content. It is known that macropores strongly influence the permeability properties of cementitious mixtures, resulting in high sorption capacity and penetration depth (Akhtar and Sarmah, 2018b; Gupta and Kua, 2018a). Asadi Zeidabadi et al., (2018) also found that water absorption rate in cement mortar cast with 1% biochar was significantly reduced by 41% when using biochar samples that had previously been soaked in water. This led to a reduction in porosity due to the compaction effect on the mortar paste. The authors also suggested that mortar with soaked biochar has better durability as it protects the mortar sample from foreign liquids. However, the results of a study conducted by Akhtar and Sarmah, (2018a) contradict this statement; the water absorption rate of cement mortar cast with biochar from rice husk and paper mill sludge was similar to that of the control sample. It is hypothesised that the difference between the results of these studies is due to the fact that the biochar used in the latter study was not previously saturated with water. The results of most of the samples prepared by (Maljaee et al., 2021b) confirm this phenomenon, apart from the samples cast with 0.5% olive stone biochar and 4% forest wood biochar. The tests conducted by Qin et al., (2021a) using plywood as biomass for biochar confirmed that the addition of biochar had no effect on the water permeability and porosity of concrete.

Gupta and Kua, (2018a) reported that fine biochar particles increased the compactness of hardened mortar by blocking macropores, which increased the strength of the samples. The authors also reported that biochar had no significant effect on the drying rate and dimensional change of the mortar. On the other hand, another study proved that biochar improved the overall hydration of cement by regulating the moisture effect, but neither accelerated nor retarded the hydration process (Wang et al., 2020a), as studied by the isothermal calorimetry results. A further investigation used the tea bag method to determine the water absorption capacity of biochar samples before casting concrete composites (Gupta and Kua, 2018a). The authors reported that the absorption capacity in water and cement filtrate did not vary significantly, implying that biochar can maintain its absorption potential in a high-pH solution. They also conducted tests to determine the water sorptivity of the samples, which is a measure of the tendency of

a porous material to absorb water through capillary suction. Their results showed that the higher the biochar dosage, the more water was absorbed by the samples. These results demonstrate that the sorptivity feature of biochar reduces the amount of free water in the mortar mix by absorption, which means that a smaller amount of evaporable water escapes from the capillary pores. This finding is in agreement with the results of a study by Maljaee et al., (2021b), who further prepared samples with varying water–cement ratios, concluding that the strength of the mix was significantly increased with the addition of biochar produced at 500°C compared to biochar produced at 300°C, with water–cement ratios of 0.45 and 0.50, respectively.

When biochar is mixed with mortar paste, its water-binding properties reduce the local water-to-cement ratio. Choi et al., (2012) tested the water-retention effects of hardwood biochar and reported that mortar mixes with biochar exhibited a lower moisture evaporation rate than the control samples. The authors also noted that mixes with biochar required more water to achieve the desired workability. Another study reported that the retained water was later used to cure the mortar, suggesting that biochar particles act as a self-curing agent (Gupta et al., 2018b). The authors conducted tests to determine the permeability of the biochar added to the mortar and found that in all their samples, the permeable void content was lower than that of mortar without the addition of biochar. The percentage of biochar content indicates the proportion of pores responsible for absorbing and storing water. Maljaee et al., (2021a) reported that the water retention capacity of biochar promoted the internal curing of mortar and early-age hydration. Asadi Zeidabadi et al., (2018) confirmed that the larger the surface area of the biochar, the higher the water requirement. To maintain the water-to-cement ratio, superplasticisers were added to control the required slump values. A study on cementitious composites with biochar from rice husk and wood waste was conducted to investigate the hydration kinetics (Gupta et al., 2021b). The authors reported that the addition of 1–2 wt% biochar derived from rice husk and wood waste significantly reduced water permeability compared to the control mortar, as reflected by a 15–18% increase in the strength of the cement mortar after 7, 42, and 120 days. The authors also found that the addition of 1 wt% of both types of biochar increased the hydration rate due to the high specific surface area and smaller particle size of the biochar compared to that of cement.

As demonstrated by the experiments discussed above, the sorptivity attribute of biochar is a crucial aspect to consider when it is used as a cement replacement. These experiments also show that the water retention capacity of biochar is dependent on the type of biomass from which it is derived, as each biomass reacts differently when converted into biochar at the same temperature in terms of pore formation and particle surface area. Furthermore, when using the same biomass but converting it into biochar at different temperatures, the higher the temperature, the larger the pore volume. The presence of pores increases the water retention capacity of biochar, promoting the internal self-curing of concrete composites. Many studies have aimed to standardize the water-to-cement ratio with the use of superplasticizers to explore how various properties of biochar influence the mechanical characteristics of concrete composites. Alternatively, when using novel biochar as a cement replacement, this research also aims to gain a comprehensive understanding of the potential and behaviour of biochar. This could be achieved by the standardisation of the water-to-cement ratio, as demonstrated by several other studies referenced in Table 2.4.

2.4.2 Static Modulus of Elasticity

The modulus of elasticity is important because it shows the ability of concrete to resist deformation due to stresses. Gupta et al., (2018b) determined the average static modulus of mortar mix samples cast with biochar from food waste, rice waste and wood waste. The highest modulus of elasticity of the mortar mix samples was found for the cast samples with 1% biochar from wood waste, although the difference was insignificant compared to the control sample. Rodier et al., (2019) investigated the modulus of elasticity of concrete composites containing biochar derived from sugarcane and found that the modulus of elasticity decreased with increasing biochar content. These results indicate that biochar concrete composites can be further investigated for use in earthquake-resistant structures, as flexibility increases with a low modulus of elasticity. As the biochar content increases, the desirable properties of concrete composites decrease. As shown in Table 2.4, most reported optimum biochar contents are below 6%.

2.4.3 Compressive Strength

The compressive strength of a concrete sample is one of the most important properties to be determined. The range of loads that a concrete mix can withstand determines

whether it can be used for structural purposes or other purposes like pavement. Gupta and Kua, (2018a) found that the addition of 1–2 wt% BC 300 and BC 500 (biochar produced by pyrolysis at 300°C and 500°C respectively) to concrete composites increased the strength of the samples on days 7 and 28 of testing. The maximum measured increase in strength of BC 500 on day 7 was 35%, but on day 28 it was only 16% compared to the control samples. A biochar content of more than 1–2 wt% of the total cement amount reduces the compressive strength of the mixture, independent of the pyrolysis temperature. It is hypothesised that the reduction in compressive strength is related to the low density and high porosity of the mortar mix, as the results for both BC 300 and BC 500 showed a negative correlation between porosity and compressive strength. An early increase in strength on day 7 was also observed in by other studies (Gupta and Kashani, 2021; Manjunath et al., 2024). These results suggest that the strength of concrete mixtures decreases with increasing biochar content, similar to the results reported in relation to other properties. Maljaee et al., (2021b) compared the effects of increasing the proportion of biochar from olive stone, forest wood and rice husk from 0.5 to 4% and reported that the compressive strength of all samples increased after 28 days of curing, except for those cast with 2% and 4% biochar from forest wood. This could be due to the fact that the particle size of the forest wood, which is much coarser than cement particles, increases porosity and thus reduces compressive strength. Yang and Wang, (2021) conducted tests on samples cast with 5% biochar on day 3 and 28, respectively, and reported a decrease in strength of 12.8% and 5.5%. This is due to increased biochar content in the mix.

Another study reports that 1% biochar increases the compressive strength of concrete samples by 8.9% (Wang et al., 2020a). Biochar pyrolysed at 700°C improved the compressive strength of the concrete sample more than that pyrolyzed at 500°C, which can be attributed to its high porosity and large surface area that facilitates cement hydration. These results contradict the findings of a study by Gupta and Kua, (2018a), emphasising the importance of biomass selection. In one study, food waste, rice waste and wood waste were used converted into biochar, with each biochar added separately to compare the effects on the compressive strength (Gupta et al., 2018b). The mortar composite with 1% wood waste exhibited 20% higher compressive strength after 28 days due to the high-water absorption and retention capacity of the biochar, which reduced the amount of free water in the mortar composite, resulting in rapid curing of

the samples. Asadi Zeidabadi et al., (2018) added 5% and 10% of both treated and untreated biochar to the composite samples. They concluded that 5% biochar from rice husk was appropriate and improved compressive strength due to its filling effect in the early stages and pozzolanic reaction in the later stages. The authors also indicated that the biochar pretreatment improved the compressive strength of samples cured for 28 days by 36% compared to samples with untreated biochar. In addition, silica fume with biochar was also added to mortar mix (Gupta and Kua, 2020). The addition of 10% silica fume led to an increase in 28-day compressive strength of 18–20% compared to the control. The authors attributed this result to the pozzolanic effect, which was enhanced by the addition of silica fume, ultimately leading to increased hydration and late strength development. Sirico et al., (2020a) reported a decrease in compressive strength of concrete cast with 1% biochar but an increase in flexural strength. Although most studies (Akinyemi and Adesina, 2020; Gupta and Kua, 2018a; Wang et al., 2020a) reported an increase in compressive strength of with 1% biochar, which is consistent with the physical and chemical properties of biochar concrete, the actual extent of improvement is highly dependent on the biomass used to produce the biochar as well as the pretreatment conditions.

Liu et al., (2022) investigated the increase in compressive strength and crack resistance of cement composites with bamboo biochar. The results showed that the addition of biochar increased the compressive strength of the samples due to filling and self-curing effects, with an optimum dosage of 1–3 wt% biochar recommended. In a study where cement was replaced with biochar from peanut shell waste, the addition of 1 wt% and 3 wt% increased the compressive strength of the samples at an early stage by 18–20% compared to normal mortar (Gupta and Kashani, 2021). In the same study, the addition of 3% biochar and 20% fly ash to the cement mix together and separately improved the 7-day strength by 19% compared to the addition of only 20% fly ash. Choi et al., (2012) used biochar derived from hardwood; a proportion of up to 5% increased the compressive strength of the cement mix to 46.5 MPa compared to the control (43.7 MPa at day 28). However, the authors found that the use of biochar in proportions of 10%, 15% and 20% decreased the strength of the samples. These results are consistent with most of the reported optimal biochar contents listed in Table 2.4. The highest amount of optimal biochar was suggested with 6.5% of eucalyptus wood produced at

500°C (Qin et al., 2021a) and lowest 0.08% of peanut shells produced at 850°C (Khushnood et al., 2016).

2.4.4 Flexural Strength

Gupta and Kua, (2018a) reported that no significant improvements in flexural strength were observed in tests, but that increasing the biochar dosage slightly improved flexural strength due to the formation of air voids in the tensile plane, which is attributed to the fine particle size and porous nature of the biochar additive. They also found that mortar with pre-soaked and dry biochar had the highest flexural strength. Akhtar and Sarmah, (2018a) reported that replacing 0.1% of the total cement amount with biochar from poultry litter, rice husk and paper mill sludge improved the flexural strength of the samples by up to 20% compared to the control. Maljaee et al., (2021b) reported similar improvements in flexural strength and compressive strength. However, the sample containing 4% forest wood biochar exhibited increased porosity in the tensile plane, which resulted in increased cracking under tensile loading compared to the samples containing olive stone and rice husk biochar. In a study on the replacement of sand with biochar from poultry litter at a dosage of 10 to 40% of the total weight in cement, the authors investigated the mechanical strength, and durability samples (Praneeth et al., 2021). The results showed that the flexural strength of the composite with 20% biochar was improved by 26% compared to the control. In addition, a reduction in the thermal conductivity and density of the cement composites was observed.

Suarez-Riera et al., (2020) conducted tests to investigate the use of biochar for two applications: as a filler in concrete mixes and as a cement replacement. Their results showed that when biochar was used as a cement replacement, the flexural strength decreased slightly by 2%. However, when used as a filler and premixed with a water superplasticiser solution, an increase of more than 15% was observed. In the same study, the authors determined the fracture energy of the mortar mixes and reported a higher increase when biochar was used as a filler than a cement replacement. The fracture energy was determined to confirm the increase in ductility in the presence of biochar in the composite. This study emphasised that the effects on flexural strength depended on the biomass from which it was obtained (Suarez-Riera et al., 2020). This observation is consistent with the results of a study by Khushnood et al., (2016), who compared biochar composites with hazelnut and peanut shell biochar. Their results show that peanut shell biochar has better mechanical strength due to its lower density. However,

Gupta et al., (2018b) reported that the addition of biochar had no significant effect on the flexural strength and splitting tensile strength of composites, regardless of the type of biomass used. Only samples cast with 1% biochar from wood waste showed a slight improvement. Most of the studies discussed here have also proven that increasing the biochar content in the mortar or concrete mix ultimately leads to a decrease in flexural strength (Gupta et al., 2018b; Khushnood et al., 2016; Maljaee et al., 2021b; Sirico et al., 2020a). In addition, the flexural strength of composites is also highly dependent on the type of biomass used to produce the biochar.

2.4.5 Tensile Strength

Asadi Zeidabadi et al., (2018) reported that concrete samples cast with 5% treated bagasse biochar showed an increase in tensile strength by 78%, while samples cast with treated rice husk ash showed a decrease in tensile strength. This is due to the increase in the porous micro-aggregate structure of the rice husk ash particles, which weakens the concrete matrix and thus reduces the splitting tensile strength. In a study by Akhtar and Sarmah, (2018a), it was found that 0.1 wt% rice husk content is the most appropriate ratio to promote splitting tensile strength but has a negative effect on compressive strength due to the irregular pore structure. On the other hand, in a study conducted by Gupta et al., (2018b), no significant increase in splitting tensile strength was observed in samples containing food waste and rice waste biochar, except for one sample containing 1% wood waste biochar, which is probably due to the biochar particles acting as a self-curing agent.

2.5 Characterisation of Biochar as Cement Replacement

The characterisation and analysis of biomass to be used for the production of biochar is crucial for the determination of elemental composition, surface functional groups, thermal stability and structure. It must be determined whether a biomass is suitable for the intended use. Maljaee et al., (2021a) have conducted extensive research on the various biomass factors that affect biochar, as shown in Figure 2.2. This information can support future research in the selection of biomass to produce biochar as SCM. Figure 2.2 also shows the pyrolysis conditions, that is the production temperature, heating rate, residence time and properties of the biochar that affect the properties of the cement composite.

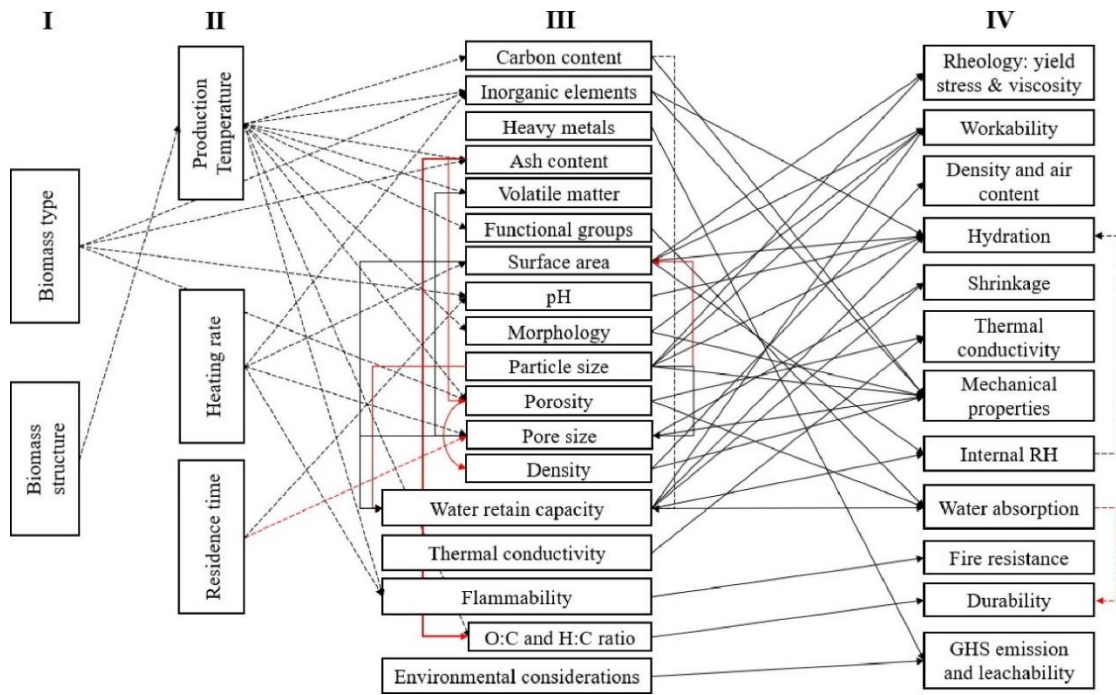


Figure 2.2 Detailed map describing factors influencing biochar and cement composite properties.

*Reprinted with permission from Ref. (Maljaee et al., 2021a) Note: I: biomass factors, II: pyrolysis production, III: biochar properties, VI: cement composite properties. Red lines represent inverse effects.

It is known that the pretreatment of biomass prior to pyrolysis influences the properties of biochar. Yaashikaa et al., (2020) reported that high moisture content in the biomass is an important factor for the formation of biochar, that is the higher the moisture content, the more energy and the higher the temperature required for pyrolysis. Therefore, less heat and energy are required, making it economically feasible. In addition, shredding the biomass, immersing it in a dilute acid solution and burning it reduces the moisture content, which increases the yield of biochar. The physicochemical properties of biochar can be further improved after production by treatment with acids, alkalis or oxidising agents, and the surface of the biochar can be modified by acid treatment. The following chapter emphasised that the use of biochar produced from waste could increase the efficiency of the circular economy, which could lead to the selection of biomass for biochar-concrete composites to enable economic concrete production. Figure 2.1 gives an indication of which biomasses should be investigated further.

Analysing the biomass is also necessary to detect impurities. As described by You et al., (2018), biochar may contain harmful components during pyrolysis or gasification

that originate from the use of contaminated biomass. Asadi Zeidabadi et al., (2018) pointed out the importance of the presence of amorphous silica in biochar, which improves the mechanical strength of concrete composites when it reacts with calcium hydroxide (CH) to form calcium silicate hydrates (C-S-H), as also reported by (Maljaee et al., (2021b). Maljaee et al., (2021a) reported that even the shape of the biochar particles has an influence on the properties of the mortar. Additionally, even the shape of the biochar particles has an influence on the properties of the mortar. When biochar particles have an angular shape, they restrict the movement of the hardened cement paste, which leads to a reduction in the spreading diameter during the slump test. Also Dixit et al., (2019) concluded that when comparing coarse, medium and fine biochar as a cement replacement, the fine biochar came closest to the control. The characteristics highlighted in the study include the ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C), which determine the aromaticity and maturation of biochar, which in turn is related to the properties that make biochar an efficient additive in cement mortar. In addition, the decomposition of cellulosic components in biochar during pyrolysis can ensure the long-term durability of biochar's properties in cementitious composites.

In a study by Ye et al., (2024), biochar-cement composites were modified with different chemicals, each of which promoted cement hydration without altering the original biochar properties. These samples include Al-BCC, a biochar modified with aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and calcium chloride (CaCl_2), Si-BCC modified with sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$), OH-BCC with sodium hydroxide (NaOH) and Su-BCC with citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and tetraethyl orthosilicate ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$). It was also found that a 2% addition of Su-BCC provides the best mechanical performance and adequate environmental compatibility. Each property of biochar adds an aspect that is desirable for a composite cement mix, as shown in Figure 2.3. Recent research (Table 2.4) has shown that the use of biochar as an SCM at an optimal concentration increases strength. In addition, numerous experimental studies have been conducted to determine the preferred properties of biochar required to improve strength. Although it has been demonstrated that the performance of biochar is primarily dependent on the type of biomass, it is clear that some properties must be matched to achieve the desired properties of the resulting biochar. A summary of the research conducted on this topic is shown in Figure 2.3. It shows which properties can be altered and made to obtain the biochar-concrete or mortar composites with the

desired properties. In addition, the properties of biochar that can be altered to improve biochar cement mix composites. For example, if the desired biochar composite requires high durability and increased cement hydration, a high cellulose content would be required in the biochar material.

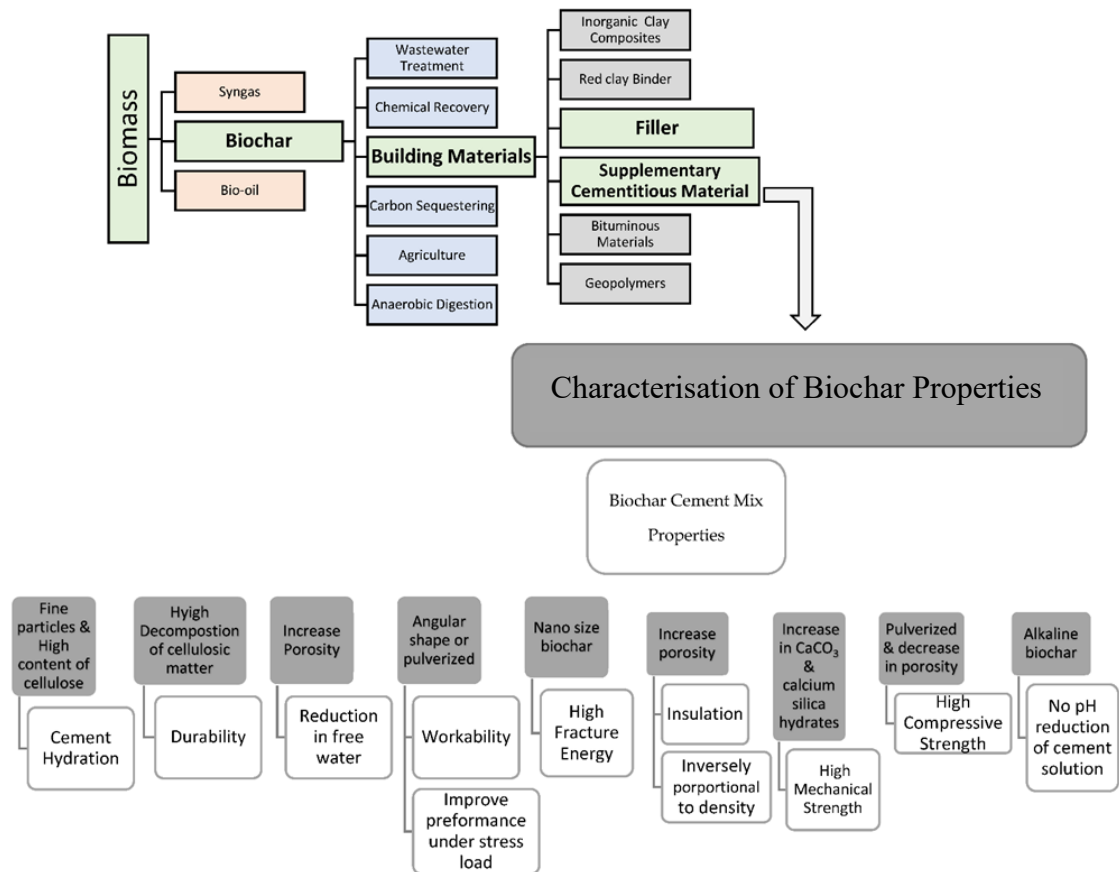


Figure 2.3 Breakdown of the process of biochar production from the source (biomass) to product (biochar) and its subsequent applications in building materials.

Figures 2.4 and 2.5 illustrate the summary of data obtained in this literature review in relation to the research papers mentioned in Table A.1 in Appendix A and show the trend of the most commonly used biochar production temperatures and biochar composites compared to control samples. Figures 2.4 and 2.5 can be used as a guide for future research. As it can be seen from the graph, most studies have used a temperature of 500°C for biochar production, with most samples showing higher compressive and flexural strength compared to the control samples. This information can serve as a basis for further testing of biochar concrete or mortar composites containing biochar produced at temperatures close to 500°C. As increasing the temperature further to

700°C or 800°C would require the use of more energy in the production of the biochar batch.

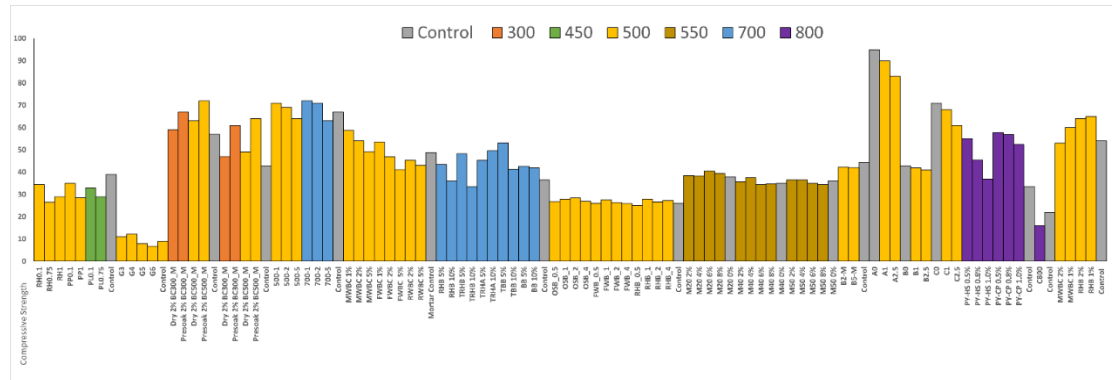


Figure 2.4 Compressive strength of biochar mortar and concrete composites reported in previous studies.

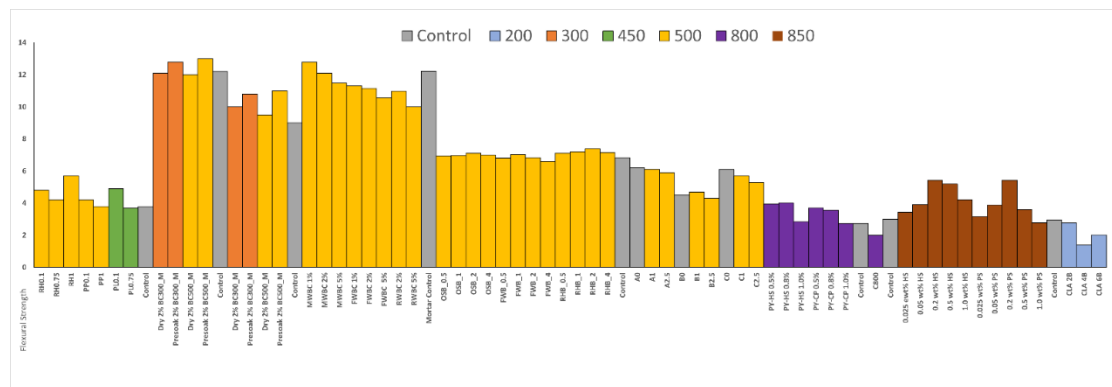


Figure 2.5 Flexural strength of biochar mortar and concrete composites reported in previous studies.

2.6 Carbon Sequestering Potential of Biochar

Previous research has shown that carbon sequestration can be achieved through the carbonisation of concrete, but only for concrete without reinforcement due to the risk of corrosion (Gupta and Kua, 2018a; Xuan et al., 2016). Maljaee et al., (2021a) reported that the chemical and physical properties of biochar remained unchanged after CO₂ saturation, although they led to a reduction in strength when mixed with mortar. Praneeth et al., (2020a) investigated the carbon-binding capabilities of concrete composites containing biochar from maize straw. Their test samples were subjected to mineral carbonisation for two hours after demoulding to improve CO₂ uptake and carbon sequestration. The test results indicated that post-carbonisation and further formation of calcium carbonate (CaCO₃) in the biochar-containing composites were responsible for an increase in strength. A study conducted by Wang et al., (2020a) has

shown that curing with carbon dioxide is more effective than curing with air for biochar concrete composite samples. Curing with carbon dioxide is an environmentally friendly method for accelerating cement reactions in composite mixes, such as hydration and strength development (Qin et al., 2021a; Wang et al., 2020a). Souradeep Gupta et al., (2022a) investigated carbon sequestration in foamed mortar by adding biochar from wood waste through accelerated carbonisation with a 2% CO₂ concentration. According to thermogravimetric analysis, the carbon dioxide uptake of foamed mortar with silica fume and fly ash was 30% after 28 days, higher than the 3% reported for the control without biochar.

In another study, Gupta, (2021) investigated the effects of the accelerated carbonation technique of cement composites with the addition of biochar and silica fume on carbon sequestration, strength and hydration. After carbon mineralisation, the cement blocks showed similar carbon sequestration to the control sample and the mix with silica fume after 28 days of carbonisation. For the sample produced with carbon sequestered biochar, the CO₂ equivalent for carbonised and non-carbonised biochar cement was 6–7% lower than the control without biochar. Gupta et al., (2021a) also investigated the addition of fly ash and biochar to improve CO₂ uptake and carbonate mineralisation in cement mortar. The authors reported that the replacement of 23% fly ash and biochar in cement improved the ability to sequester carbon through mineralisation by 7–13% compared to the control.

Since there has been limited research on carbon sequestration by biochar-cement composites, research on the literature can be shifted to studies that have looked at the carbon sequestration capabilities of biochar alone. Dissanayake et al., (2020) concluded that the volume of micropores and the presence of basic functional groups play a crucial role in the carbon dioxide adsorption capacity of biochar. Accordingly, biochar can be modified by chemical and physical treatments, such as activation conditions with steam or ammonia. With the help of these pretreatments, the carbon adsorption capacity of biochar is expected to remain effective when blended with concrete components. Gupta et al., (2018c) recommended the use of unsaturated biochar as supplementary cementitious material to sequester carbon, as designed biochar can trigger carbonisation that weakens strength development. Fawzy et al., (2021) emphasized that the production, use and storage of biochar is highly carbon-negative, resulting in an estimated sequestration of 0.3–2 gigatons of CO₂ per year by 2050. Again highlighting

that the development of an industrial biochar production system would be beneficial for the removal of carbon from the atmosphere.

2.7 Life Cycle Assessment Studies on Biochar and Concrete

Biochar is an environmentally friendly material that is used to solve many environmental problems, such as reducing greenhouse gas emissions, wastewater treatment and soil remediation (Yaashikaa et al., 2020). It is also known that biochar can remove pollutants due to the presence of functional groups such as hydroxyl and carboxyl groups. Gupta and Kua, (2018a) reported that the conversion of wood waste into biochar increases the value of wood waste compared to its displacement to landfill sites. This would definitely have a positive impact on the environment, as landfilling of wood waste has been shown to cause toxic emissions in life cycle assessment (LCA) studies (Fawzy et al., 2021). To mitigate the impact of landfilling, a study was conducted in China on plywood frames that could no longer be reused so were then used as biomass for biochar production (Qin et al., 2021a). In addition, the biomass from food waste could eventually be utilised as an economic resource as there is no cost for collection (Akinyemi and Adesina, 2020; Khushnood et al., 2016).

Gupta et al., (2018c) reported that the use of wood waste in composite cement mixtures is sustainable and cost-effective mixes. Gupta and Kashani, (2021) used peanut shells processed into biochar from local waste and replaced small amounts of cement, which significantly improved the hydration, setting and strength development of the tested mixtures. These results could promote the use of recycled waste. In addition, the use of biochar could reduce the CO₂ equivalent of cement mortar and cement-fly ash mortar due to the reduction in cement demand and the negative net CO₂ equivalent of biochar production. LCA has shown that biochar has the potential to reduce net greenhouse gas emissions by 870 kg CO₂-equivalent per tonne of dry feedstock, depending on the type of feedstock and preparation method, of which 62–66% is due to carbon storage and sequestration by the biomass feedstock of biochar (Jiang et al., 2021).

Studies using waste materials to produce biochar suggest that this process could reduce landfill emissions and increase the value of the waste produced (Gupta et al., 2018a; Gupta and Kua, 2018a; Mensah et al., 2021; Suarez-Riera et al., 2020; Yaashikaa et al., 2020), which in turn reduces the environmental impact. According to Gupta and Kua, (2018a), the estimated price of using biochar in mortar is similar to that of control. In

order to assess the economic benefits, it is advisable to determine the environmental impact through a life cycle assessment and life cycle costs (LCC). Campos et al., (2020) investigated biochar as a partial replacement for Portland cement and concluded that the mix with the shortest path for the use of biochar reduces the environmental impact compared to a conventional concrete mix without biochar. A techno-economic analysis (TEA) and cradle-to-grave LCA study was conducted for biochar produced with portable systems from forest waste and applied to the ground, confirming its environmental benefits and economic feasibility (Sahoo et al., 2021). All portable systems studied, such as the Oregon stove and the air curtain burner, showed a negative impact on global warming, which also emphasises that the use of forest residues can contribute to the mitigation of forest fires.

A study by Zhu et al., (2022) examined several life cycle assessments of pyrolysis of various agricultural residues and concluded that biochar consistently provides an effective carbon substitute for soil improvement, energy sources and carbon offsets. The authors emphasised the importance of regionalising the context and application to better understand the impact of biochar on emissions and distances covered. Similarly, Roberts et al., (2010) compared the LCA pyrolysis of different agricultural residues for soil improvement, at a temperature of 450°C. Their design allowed the gases to flow into a thermal oxidiser for clean combustion, with the heat generated drying the biomass before pyrolysis. They reported that yard waste from biomass produced the highest net greenhouse gas emission reduction (-885 kg CO₂-eq/t) but required a significant energy input (+3507 MJ) for production. In addition, Chew et al., (2023) integrated the life cycle assessment with the green house gas emissions (GHG) protocol to assess the use of EFB and oil palm trunks as fuel in Malaysia and Indonesia. They reported carbon emissions of 534.7–732.3 kg CO₂-eq/tonne of pellets during fuel combustion and identified hotspots in washing plants (169.2–439.0 kg CO₂-eq/tonne of pellets) and burners (87.1–214.5 kg CO₂-eq/tonne of pellets). The study found that the production of pellets from EFB could reduce landfill waste by 62-74.1%, with oil palm stem pellet production having lower emissions (46.8% less) compared to EFB pellet production, indicating its potential as a low-carbon fuel.

Other LCA studies have increasingly focussed on the environmental impacts associated with concrete production, particularly greenhouse gas emissions and energy efficiency. The LCA study conducted by Gursel and Ostertag, (2016) in Singapore examined the

impact of sourcing concrete materials such as cement and aggregates imported from various countries in Asia. Their results showed that using materials from the closest country, Malaysia, led to an 11% reduction in global warming potential (GWP) for high-strength concrete. They also found that Malaysian cement production was the most energy efficient among Japan, China, Taiwan and Malaysia, resulting in lower CO₂ emissions. Another study analysed the GWP of green concrete using rice husk ash in the USA and compared nine different concrete mixes (Gursel et al., 2016). The control mix without additives had the highest GWP at 544 kg CO₂ equivalent/m³, mainly due to transport and cement production. When rice husk ash, fly ash and limestone powder replaced 40% of the cement, the GWP dropped significantly to 284 kg CO₂-equivalent/m³, illustrating the potential environmental benefits of using alternative materials.

Life cycle assessments and cost-benefit analyses were carried out for biochar-enriched concrete. Biochar was used as an aggregate in combination with other SCMs, resulting in a significant reduction in CO₂ emissions and demonstrating the successful production of carbon-negative concrete with overall economic benefits (Chen et al., 2022c). Concrete with biochar and metakaolin proved to be the most promising mix, binding 59 kg CO₂ sequestered per tonne and achieved a potential total gain of 35.4 USD m⁻³. Tests with concrete have proven that it can reduce pollution by absorbing NO₂ due to the reaction with highly alkaline cement hydrates such as calcium hydroxide and CSH. Krou et al., (2013) reported that the addition of activated carbon to concrete used for road tunnels and car parks can significantly increase the absorption of NO₂. The authors demonstrated that conventional concrete can absorb NO₂ to a significant extent, leading to the formation of nitrite salts in the alkaline aqueous solution covering the hydrates. They reported that conventional concrete absorbed $7.4 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$ after 20 hours of exposure, while the activated carbon concrete absorbed $1.7 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$. Another study also investigated the entrapment of NO_x, but with cement pastes. Horgnies et al., (2012) and reported that the absorption varied depending on the temperature and carbonisation of the cement paste and that the addition of activated carbon increased NO₂ absorption. Colangelo et al., (2018) conducted a life cycle assessment in Italy that analysed the environmental impact of different alternative concrete mixes using construction waste, incinerator bottom ash, marble sludge and blast furnace slag as a substitute for aggregates. Their findings emphasised a consistent

observation across all LCA studies: cement production consistently resulted in higher CO₂ emissions compared to aggregates, highlighting the need for alternative materials to reduce environmental impact. A recent study by Wijeyawardana et al., (2024) presented a novel approach using cement modified with biochar for water treatment. Their LCA assessed various biochar sources, including rice husks and sawdust, and concluded that this combination has a greater overall negative impact on the environment compared to the use of pure biochar. This finding suggests that while innovative approaches to the use of cement and biochar composites can be promising, careful consideration of their environmental impact is critical.

It has been analysed and highlighted that the current LCAs for concrete mainly focus on energy consumption and greenhouse gas emissions, overlooking other important environmental aspects such as volatile organic compounds (VOCs), heavy metals and toxic emissions from additives and SCMs (Gursel et al., 2014). Many studies also use national averages, which does not reflect local conditions and technologies that can strongly influence the environmental impact of concrete production in certain areas. Furthermore, dismissing certain LCA components as insignificant ignores their potential cumulative impacts. Even small percentages of energy consumption or emissions can add up to significant impacts when considered on a global scale (Gursel et al., 2014).

Overall, the studies discussed illustrate the importance of LCA in identifying sustainable practises in concrete production and use. By examining different materials and local sourcing strategies, the researchers continue to improve our understanding of how to minimise the environmental footprint of cement production for concrete. When conducting an LCA study, it is important to consider the different environmental impact categories analysed and their respective importance. The following categories in Table 2.5 fall under the CML 2 Baseline 2000 methodology. These impacts are summarised under common categories used for the assessment of climate change and ecotoxicity impacts (GaBi Handbook, 2012; Guinée, 2001).

Table 2.5 Environmental impact categories and their significance (Guinée, 2001; GaBi Handbook, 2012).

Environmental Impact Categories	Significance
Abiotic depletion	The abiotic depletion potential includes all natural resources, such as fossil energy carriers, crude oil, and mineral raw materials. Abiotic resources are defined as non-renewable raw materials derived from non-living sources. This impact category assesses the depletion of global non-renewable resources, which are defined as those requiring at least 500 years to regenerate. It evaluates both the overall availability of natural elements and the availability of fossil energy carriers. It is measured in units of mineral consumption which is kilograms of antimony (Sb) equivalents (kg Sb-eq).
Acidification	Air pollutants are converted into acids, acidifying the soil and water. This leads to a drop in the pH value of rainwater and fog. The gases that contribute to this category are sulphur dioxide and nitrogen dioxide. Acidification has direct and indirect harmful effects, such as the leaching of nutrients from the soil or damage to building materials, such as increased decomposition rates of metals and natural stones. It is expressed in sulphur dioxide equivalents (SO ₂ -Eq).
Eutrophication	Eutrophication is the accumulation of nutrients in aquatic or terrestrial areas. Air pollutants contribute to eutrophication. The consequences of eutrophication of water bodies are a lack of oxygen, resulting in methane and hydrogen sulphide, which lead to the destruction of the ecosystem. In addition, the eutrophication of soils leads to an increased nitrate content in groundwater, which also finds its way into drinking water. A reaction product of nitrate is toxic to humans. It is calculated in phosphate equivalents (PO ₄ -Eq).
Global warming (GWP100)	The GWP is mainly associated with greenhouse gas (GHG) emissions, such as carbon dioxide and methane. These greenhouse gases absorb heat in the atmosphere, more specifically in the troposphere, which warms the Earth's surface. The GWP is calculated in carbon dioxide equivalents (CO ₂ -Eq), which means that the global warming potential of an emission is given in relation to CO ₂ .
Human toxicity	The human toxicity signifies the evaluation of negative effects that substances can have on human health. It examines potential health risks associated with exposure to toxic materials, taking into account factors such as the duration and frequency of exposure. It is often quantified in terms of equivalents to reference substances like 1,4-Dichlorobenzol. Understanding human toxicity is crucial for informing regulations and safety measures to protect public health from harmful exposures.
Marine aquatic ecotoxicity	The marine aquatic ecotoxicity signifies the analysis of how pollutants affect marine ecosystems and organisms. It focuses on the detrimental impacts that toxic substances can have on marine life, including various species of fish, invertebrates, and aquatic plants found in ocean environments. The impact is measured by examining the concentration of pollutants in marine habitats and their effects on marine organisms, in equivalents to reference substances 1,4-Dichlorobenzol. This assessment is vital for the conservation of marine biodiversity and the overall health of ocean ecosystems.

Environmental Impact Categories	Significance
Fresh water aquatic ecotox.	Fresh water aquatic ecotoxicity evaluates the effects of pollutants on freshwater ecosystems such as rivers, lakes and wetlands. It focuses on the toxicity of substances to freshwater organisms, including fish, amphibians and aquatic vegetation. It is determined by analysing how pollutants affect life in these ecosystems. This assessment is crucial for the protection of freshwater resources, which are essential for drinking water supply, agriculture and ecological balance. It is measured, in equivalents to reference substances 1,4-Dichlorobenzol.
Terrestrial ecotoxicity	The terrestrial ecotoxicity investigates how pollutants affect terrestrial ecosystems, including soil organisms and terrestrial plants. It considers the effects of toxic substances on soil health, plant growth and wildlife in terrestrial environments. It is assessed based on the exposure of terrestrial organisms to contaminants. Understanding terrestrial ecotoxicity is important for maintaining soil quality, agricultural productivity and the integrity of ecosystems that support biodiversity and human livelihoods. It is quantified, in equivalents to reference substances like 1,4-Dichlorobenzol.
Photochemical oxidation	Photochemical oxidation signifies a process in the atmosphere where ozone is produced through complex chemical reactions involving sunlight, nitrogen oxides, and hydrocarbons. While ozone protects the stratosphere, it is harmful at ground level, contributing to summer smog that can damage vegetation and pose health risks to humans. High concentrations of ozone are typically found in warm, dry, and stagnant air, particularly in areas with low levels of nitrogen oxides and carbon monoxide, such as forests. The potential for ozone formation is quantified in ethylene equivalents (C ₂ H ₄ -eq.), highlighting the influence of weather and local conditions on actual ozone concentrations.

2.8 Summary

The literature discussed in this chapter begins with an introduction to various processes and factors that determine biochar production. It then examines the abundance of palm oil waste generated in Malaysia and its utilisation in various industries. Highlighting different uses of PKS and EFB. However, the applications of these palm oil waste biochar as a supplementary cementitious material remains unexplored. The benefits of RSM for biochar production for various applications are covered. The literature emphasised the importance of interchanging the pyrolysis parameters such as temperature, heating rate and residence time. These were then adopted for this research. Nevertheless, the use of RSM with these three parameters together were not studied in the existing literature for the purpose of using biochar as a cementitious material. This then leads to the main section where the use of biochar as a building material is discussed in detail. Table 2.4 shows a summary of the valuable experimental research that has been carried out using biochar as a cement replacement or additive. The

temperatures used for production of these biochar was noted and the range from 200-800°C was then adopted for the biochar optimisation process for this research. In addition, the cement replacement percentages from 1-8% was also comprehended from the literature and then used in this research. The majority of studies have focused on the addition of biochar rather than its use as a cement replacement. Therefore, this research emphasises the importance and sustainability benefits of replacing of cement with biochar. The effects of biochar on mechanical properties such as water absorption, static modulus of elasticity, compressive strength, flexural strength and tensile strength are discussed based on previous experiments with different types of biochar. The section characterisation of biochar as a cement replacement then shows the understanding and linkage of the biochar properties studied to the various effects on concrete or mortar composites. The carbon sequestration potential of biochar and life cycle assessment studies of biochar and concrete are discussed. Despite the progress in this field, the literature reveals significant gaps related to comparative biochar performance, optimised production for cement applications, post-curing carbon sequestration, and life cycle assessments all of which are addressed in this research.

Chapter 3 Optimisation of Palm Oil Waste Biochar Production

This chapter discusses on optimising pyrolysis parameters of palm oil waste biochar production. The response surface methodology (RSM) was used for the optimisation process. Following the biochar production, analysis was conducted on the biochar, regarding yield, carbon content, chemical composition, crystalline structure, functional groups, morphology, thermal stability, and particle size distribution. The content of this chapter covers the first objective of this research, in which two sets of optimised pyrolysis parameters were found for palm kernel shell and for empty fruit bunch.

3.1 Methodology

3.1.1 Biomass Collection and Sample Preparations

Palm kernel shell (PKS) and empty fruit bunch (EFB) were collected from a local palm oil mill, Seri Putra Oil Mill Banting, Selangor. In the mill, both waste are mostly used as fuel for the steam boilers. Around 30 kg of PKS and 40 kg of EFB were collected from the mill. Upon collection, both wastes were washed and rinsed with tap water to remove contaminants. Like oil and dust that has been settled on the surface of the PKS and EFB during the extraction of the palm oil. They were then air dried for approximately 48 hours as shown in Figure 3.1. After being air dried, they are kept in the oven at 80°C. Moisture content was measured and ensured to be less than 10% before stored for the pyrolysis experiment. Low moisture content requirement would aid in energy efficiency and ensure a complete pyrolysis of the material (Ferreira et al., 2020). As drying of biomass would take additional energy to the pyrolyzing the biomass. The dried sample was milled using a rotor beater mill (Retsch SM100) and sieved to the sizing of 1.18 mm to 2 mm. PKS was sieved using a mechanical sieve shaker. While the EFB was sieved manually by covering the sieves with a lid and shaking it in circular motion to avoid the formation of clumps since it's a fibrous structure. Sieved samples were then covered and stored under dry environment. Figure 3.2 (a) – (c) illustrate the raw and the milled PKS and EFB, which have been later sieved and used for pyrolysis.

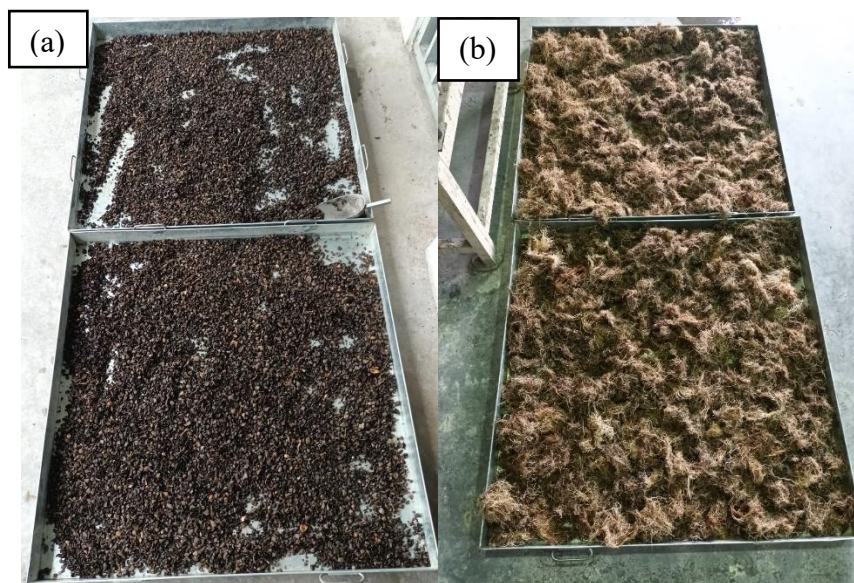


Figure 3.1 Air drying of (a) PKS and (b) EFB.

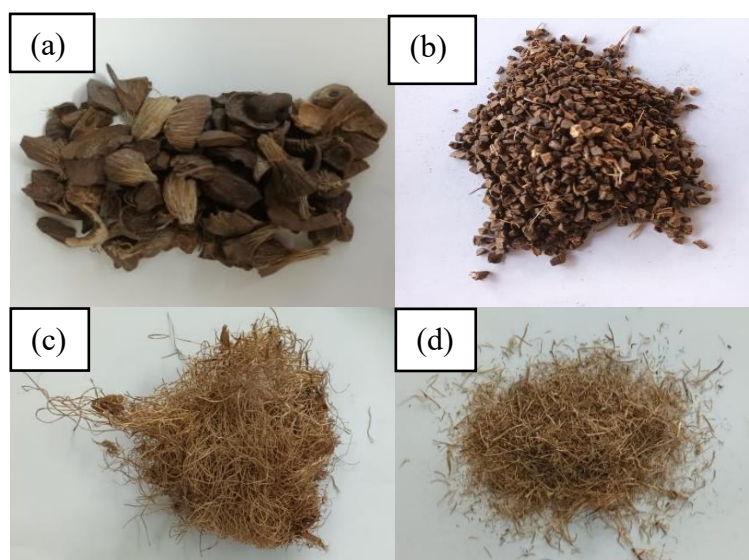


Figure 3.2 Preparation of samples (a) PKS raw, (b) PKS milled, (c) EFB raw and (d) EFB milled.

3.1.2 Slow Pyrolysis

The experiment was conducted with a long tubular furnace (Carbolite CTF 12/100/900). Sieved sample was placed on a metal plate and inserted into the centre of the furnace. The experimental setup, shown in Figure 3.3, includes the tubular furnace, nitrogen inlet and flask outlet which ensure controlled pyrolysis conditions. The inlet of the furnace was connected to a nitrogen cylinder with a tube to prevent biochar oxidation. The nitrogen flow was kept steady for all the experiments at 30 ml/min. The outlet of the furnace was connected to a conical flask filled with tap water to form a closed system and allow

the bio-oil to settle. Syngas and volatile vapours were allowed to escape through the flask's outlet. Around 30 g of PKS and 12 g of EFB sample were used for each pyrolysis run. Figure 3.4 shows the samples before and after pyrolysis for PKS and EFB. Equation (3.1) was used to calculate the biochar yield. ($m_{\text{feedstock}}$) representing the mass of the biomass sample and (m_{char}) representing the mass of the resultant biochar. The pyrolysis parameters that have been varied for this research are temperature, heating rate and residence time (the holding time at set temperature), as stated in Table 3.1.

$$y_{\text{mass}}(\%) = \frac{m_{\text{char}}}{m_{\text{feedstock}}} \times 100 \quad (3.1)$$

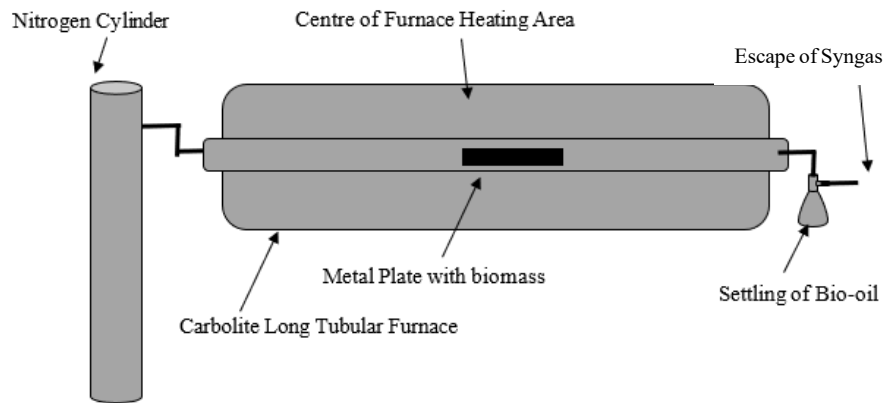


Figure 3.3 Slow pyrolysis experimental set up, consisting of nitrogen cylinder tubular furnace and the flask outlet.

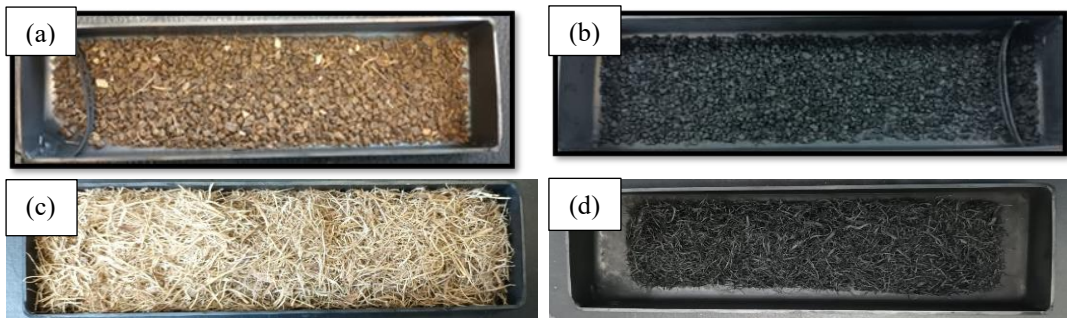


Figure 3.4 Visual comparison of PKS and EFB samples before and after pyrolysis, illustrating the transformation of biomass into biochar. (a) palm kernel shell (b) palm kernel shell biochar, (c) empty fruit bunch (d) empty fruit bunch biochar.

3.1.3 Response Surface Methodology

Optimisation with response surface methodology (RSM) approach has been divided into 6 steps. (1) Selection of independent variables and responses; (2) Selection of experimental design strategy; (3) Execution of experiments and obtaining results; (4) Fitting the model equation to experimental data; (5) Obtaining response graphs and

verification of the model; (6) Determination of optimal conditions (Witek-Krowiak et al., 2014). In this research, three parameters pyrolysis temperature, residence time, and heating rate were varied. Central composite design (CCD) was selected as the response surface design, as it is widely used due to its relatively low experimental runs and its higher accuracy in model prediction, which is highly important for the optimisation process (Singh Pali et al., 2023; Witek-Krowiak et al., 2014). The RSM was conducted by the Design Expert Version 12 software. The CCD method is composed of two-level factorial design ($2n$); it is suitable for fitting first-order and second-degree models. This design is featured with centre point experiments (m) that are augmented with a group of axial points ($2n$). The centre point is marked as 0, whereas the span from factorial point to centre point is marked as +1 or -1. Equation (3.2) was used to calculate the total number of experiments (N), where (n) is the number of parameters and (m) is the centre point. The three parameters for the model are the pyrolysis temperature, heating rate, and residence time. Moreover, the responses chosen for the model are biochar yield, carbon, oxygen, potassium, and silicon content. As calculated by Equation (3.2), 20 experiments were needed to examine the correlation between the responses and the quantitative experimental parameters with 6 centre points, 8 factorial points, and 6 axial points. The experimental error and reproducibility of data could be gathered from the centre points. Table 3.1 provides the coded variables of the three factors. The maximum and minimum values that have been keyed into the model. RSM has calculated the mean and standard deviation of the set of data, as stated in Table 3.1. The standard deviation is low for all factors, indicating that the data points of the runs are not close to the mean value. This RSM model has been used for both materials, PKS and EFB, each going through 20 runs of interchangeable parameters.

$$N = 2^n + 2n + m = 2^3 + 2(3) + 6 = 20 \quad (3.2)$$

Table 3.1 Parameters of the response surface methodology model.

Coded Variable	Parameter	Unit	Input		Coded Level		Mean	Std. Dev
			Min	Max	-1	+1		
A	Temperature	°C	200	800	300	700	500	158
B	Heating Rate	°C /min	2	20	5	15	10	4
C	Residence Time	min	10	155	20	120	70	39

3.1.4 Biochar Analysis

Mass production of the optimised biochar was done for both PKS and EFB. The optimal parameters that were found through RSM optimisation process are 409°C, 15°C/min, 120 mins for PKS, and 445°C, 15°C/min, 20 mins for EFB. These are then further discussed in detail under results Section 3.2. From the literature, it has been concluded that the most common pyrolysis temperature that has been used for biochar production to be utilised as SCM is 500°C (Akhtar and Sarmah, 2018a; Gupta et al., 2018b; Gupta and Kua, 2018a; Maljaee et al., 2021b). An additional mass production of biochar from each biomass PKS and EFB was conducted at 500°C to compare with the optimised biochar of this research. To evaluate the difference in biochar behaviour under different production temperature. Pyrolysis parameters that were used for PKS and EFB were 500°C, 15°C/min, 120 mins, and 500°C, 15°C/min, 20 mins. The heating rate and residence time were matched to the optimal parameters, in order to focus on the effect of temperature change only. Altogether, four types of biochar have been used as stated in Table 3.2 have been used as a cement replacement which will be further discussed in Chapter 4. After pyrolysis, biochar has been pulverised using a stainless-steel electrical grinder and then sealed in plastic zip bags until further analysis and its use for cement replacement. PKS biochar before and after grinding is illustrated in the following Figure 3.5. Following section consists of the analysis conducted on all biochar in order to understand the physiochemical properties, including elemental and chemical composition, morphology, particle size distribution, and absorption characteristics, that would affect the mortar and concrete properties. In addition to this analysis the biochar's density was also measured using the displacement method.

Table 3.2 Pyrolysis parameters of biochar produced.

Pyrolysis Parameter	Unit	Empty Fruit Bunch		Palm Kernel Shell	
		This Research	Literature	This Research	Literature
Temperature	°C	455	500	409	500
Heating Rate	°C /min	15		15	
Residence Time	min	20		120	



Figure 3.5 Visual comparison between the (a) original particle size and the (b) powdered form of palm kernel shell after grinding.

3.1.4.1 Field Emission Scanning Electron Microscope—Electron Dispersive X-ray Microscope

Morphology of the biochar and biomass samples was observed by the Field Emission Scanning Electron Microscope (FESEM). In addition, surface elemental composition was recognised by the Energy Dispersive X-ray spectroscopy (EDX) with the same equipment, which is the FEI Quant400F as shown in Figure 3.6. Elemental analysis conducted recognised the actual elemental composition of the biochar and biomass samples within the range, as it only detects the surface elements on the samples, including impurities in different areas.



Figure 3.6 FESEM-EDX FEI Quant400F.

3.1.4.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) has been conducted using the STA6000 PerkinElmer TGA-DSC shown in Figure 3.7. Thermal analysis was conducted on biomass and the biochar samples to observe the physical and chemical properties of materials, which are measured as a function of loss of weightage at a specific set of temperature rises (Yaashikaa et al., 2020). Approximately 12 mg of the sample was heated under the nitrogen flow from room temperature of around 25°C to 110°C at a rate of 5°C/min and been held at the set temperature for 10 min. Following that, the temperature was increased until the set temperature of 920°C and held for 20 min. The temperature has then been set to cool down to 820°C and switched to oxygen flow at a rate of 50°C/min (Barranco et al., 2007). Proximate analysis can be performed through calculations as shown in Equations (3.3),(3.4),(3.5) and (3.6) which includes the moisture content, volatile matter, ash content and fixed carbon. Moisture content is the change of mass from the starting temperature to the holding temperature of 110°C. Volatile matter is calculated by subtracting the mass at 920°C to 110°C after the holding time of 20 mins. Ash content is the mass of the material left after the cooling down at 820°C. Fixed carbon is calculated by subtracting 100 from the sum of the moisture, volatile and ash content.

$$\text{Moisture Content (\%)} = \text{Weightage Difference}_{(\text{Initial } 30^{\circ}\text{C})} - \text{Weightage Difference}_{(110^{\circ}\text{C})} \quad (3.3)$$

$$\text{Volatile Content (\%)} = \text{Weightage Difference}_{(110^{\circ}\text{C})} - \text{Weightage Difference}_{(920^{\circ}\text{C})} \quad (3.4)$$

$$\text{Ash Content (\%)} = \text{Weightage Difference}_{(820^{\circ}\text{C})} \quad (3.5)$$

$$\text{Fixed Carbon (\%)} = 100 - (\text{Moisture Content} + \text{Volatile Content} + \text{Ash Content}) \quad (3.6)$$



Figure 3.7 STA6000 PerkinElmer TGA-DSC.

3.1.4.3 Particle Size Distribution

Particle size distribution (PSD) of all types of biochar has been conducted through sieve grading from 0.032 mm to 1 mm. BS EN 933-1:2012 standard has been followed for this procedure. The biochar was dried in an oven for 2 hours at 110°C to rid of any moisture clumps and then placed within the sieves on a mechanical shaker as shown in Figure 3.8 for 15 minutes. The sieving was run three times and averaged out.



Figure 3.8 Heavy duty sieve shaker used for sieving.

3.1.4.4 X-Ray Diffraction Analysis

For X-ray diffraction (XRD) analysis, Panalytical X'Pert Pro USA was used, as shown in Figure 3.9. This analysis is used to identify the crystalline phases that provide information about the chemical composition of the material. Results will be obtained in scattering angle (2θ), which is the angle between the incident beam and diffracted beam from the material, and the intensity is determined, which is the strength of the diffracted rays.



Figure 3.9 Panalytical X'Pert Pro USA XRD equipment.

3.1.4.5 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy analysis equipment that was used is Frontier FT-IR. PerkinElmer, as shown in Figure 3.10. The analysis has been conducted on all the biochar samples to identify the surface functional groups which shows, the chemical composition of the samples. The peaks from the analysis graphs of transmittance (%) against wavenumber (cm^{-1}) are matched to a specific functional group as provided in the chart given in the Appendix B.



Figure 3.10 Frontier FT-IR/FIR PerkinElmer.

3.1.4.6 Water Absorption

Water absorption of the biochar was measured by first oven drying 2 grams each sample for 24 hours to get rid of retained moisture by the biochar. Biochar was then kept in a measuring cylinder with distilled water and a stirrer. Measuring cylinder is then covered with plastic and constantly stirred for 24 hours. The setup is shown in Figure 3.11. The mix is then poured on to filter paper and funnelled on a conical flask that is attached to a vacuum pump to aid the filtration process. Biochar filter paper is weighed (m_1), then placed in the oven for 24 hours and measured again (m_2). (m_1) is then subtracted from (m_2) to attain the maximum amount of water absorbed. A percentage of water absorbed is calculated by multiplying the subtracted amount of water absorbed by 100 and divided by the original mass as shown in Equation (3.7).

$$\text{Water Absorption (\%)} = \frac{m_2 - m_1}{m_2} \times 100 \quad (3.7)$$

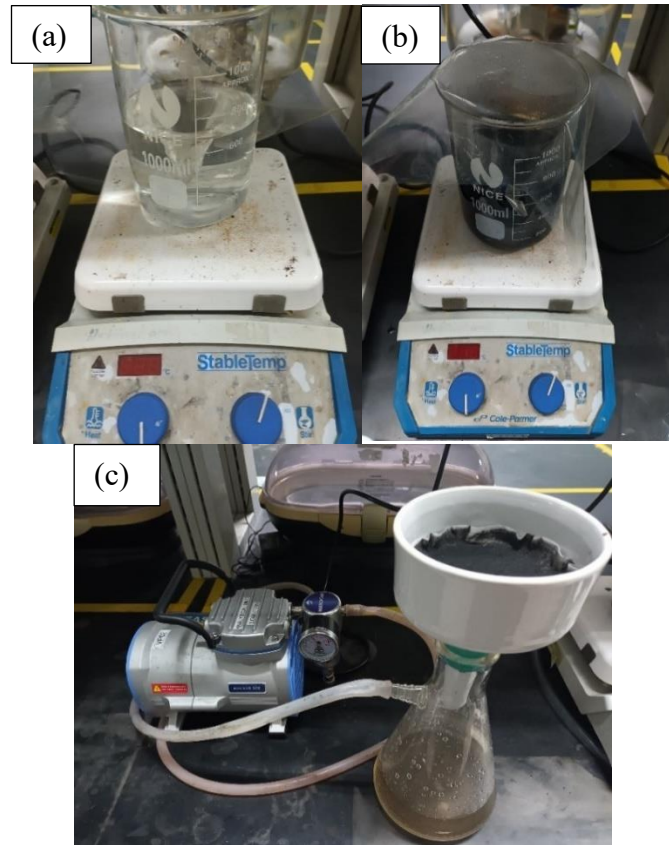


Figure 3.11 Biochar water absorption experimental set up (a) measuring cylinder with stirrer, (b) measuring cylinder with biochar stirrer and plastic cover and (c) vacuum pump with conical flask, filter funnel and biochar with filter paper.

3.1.4.7 Brunauer-Emmett-Teller

Brunauer-Emmett-Teller (BET) analysis is conducted with Micrometric ASAP2020 USA, as shown in Figure 3.12. Analysis was conducted on biochar samples to measure the surface area and pore width, and pore volume of the samples which determines the adsorption capabilities of the material. The material is preheated and degassed for 2 hours at 300°C to desorb any moisture or gases prior to the analysis.



Figure 3.12 BET Micrometric ASAP2020 USA Equipment.

3.2 Results and Discussion

3.2.1 Palm Kernel Shell Biochar

3.2.1.1 Optimisation

Optimisation process is done by setting three pyrolysis parameters (temperature, heating rate and residence time) in range and the responses biochar yield, carbon (C), potassium (K), and silica (Si) as maximum and oxygen (O) as minimum. Prior research has demonstrated that the necessary responses are favourable if biochar is intended for use as an SCM. These advantages include high biochar yield would be beneficial as a high amount of biochar is desired, high carbon content and low oxygen content for chemical stability of biochar, silica and potassium have been known to the pozzolanic effect during cement hydration. Table 3.2 provides all the runs by the RSM with their respective collected through pyrolysis and analysis of the biochar. Equations (3.8)–(3.12) show the mathematical equations for biochar yield, carbon, oxygen, potassium, and silica content modelled by the RSM from the entered data. These equations, indicate the significance of each pyrolysis parameter. In addition to that, with coded equations, linear interaction and quadratic effects of independent variables could be demonstrated.

$$\text{Yield} = 35.1237 - 19.768A + 0.385765B - 2.48875C - 1.8625AB + 2.6125AC + 0.4375BC + 12.9002A^2 + 0.730986B^2 + 1.43309C^2 \quad (3.8)$$

$$C = 80.8563 + 11.3496A - 2.74723B + 0.992995C - 0.1425AB - 0.265AC + 0.315BC - 2.60861A^2 - 1.90543B^2 + 0.54073C^2 \quad (3.9)$$

$$O = 15.1934 - 11.6612A + 1.00077B - 1.65496C - 0.4325AB + 0.4125AC - 1.2025BC + 4.11893A^2 + 1.14637B^2 + 0.549124C^2 \quad (3.10)$$

$$K = 0.294852 + 0.0456A + 0.120746B + 0.0693085C \quad (3.11)$$

$$Si = 0.477172 + 0.018A + 0.0750188B + 0.0601753C - 0.0175AB - 0.1025AC + 0.0775BC - 0.197335A^2 + 0.0975558B^2 + 0.012387C^2 \quad (3.12)$$

A detailed study of biochar mortar and concrete composites was carried out and is summarised in Table 2.4 (Section 2.4.1). It shows that the mechanical properties of the composites are highly dependent on the temperature of the biochar production. The temperature range of 200°C to 800°C was chosen in this study to understand the behaviour of PKS biochar, focussing on the properties that are beneficial for its use as a cement replacement. Experiments at 200°C (Rodier et al., 2019) and 300°C (Boumaaza et al., 2022) were considered previously; therefore, they have been adapted in this research. Even though low-temperature biochar has rarely been considered for cement replacement, this research has incorporated a range of temperatures to observe the resulting changes in biomass behaviour. The investigation of PKS biochar, which is produced at lower temperatures, would clarify why it is not suitable as a cement replacement. Analysis of variance (ANOVA) was conducted to define the significance and the nature of the interactions between the factors and the responses, probability (p-value), Fischer variation (F-value), and correlation effect (R^2). Table 3.3 includes the ANOVA results presented by the model. The R^2 of the biochar yield, C, and O responses are very close to 1, which indicated the model quality is satisfactory and there is a good agreement between the experimental and predicted values, which can be observed in Figure 3.14 (a), (b), and (c). However, the R^2 of the K and Si content is lower than 0.8, which indicates a lower agreement between the experimental and predicted values.

The predicted R^2 of the K, O, C, and biochar yield responses are all in agreement with their respective adjusted R^2 and the difference is less than 0.2. However, the Si response shows a negative predicted R^2 . This indicates that for this response specifically, choosing the overall mean may be better for predicting the response than the current model. The adequate precision R^2 is the measure of the signal ratio of the model. The

adequate precision R^2 of all the responses is greater than 4, which is stated as desirable and that it is an adequate signal. All the response models prove to be significant except Si, as stated in Table 3.3; this could possibly be due to a very low correlation between all the variables as stated in Equation (3.12).

Equations (3.8) – (3.12) state the interaction between the factors individually and in combination for each response A, B, and C representing temperature, heating rate, and residence time. Among the interaction effects in Equation (3.8), the interaction between AB and AC is more significant than BC. Equation (3.9) states that AB and BC are more significant than AB. Moreover, Equation (3.10), AB and AC are very similar in their influence on the response and are both less significant than BC. Equation (3.11) suggests that the B variable, which is the heating rate, is most significant to the response. Equation (3.12) implies that all interaction effects are very low; AB and BC are less influential than AC. Following the data of the 20 runs, the model has produced an optimised run of 409°C, 15°C/min, and 120 min with predicted results of 46.90% yield, 72.55% C, 21.18% O, 0.46% K, and 0.81% Si. The differences between each response that was obtained after running the optimised variables are as stated in Table 3.2, 8.7% yield, 0.82% C, 4.3% O, 0.07% K, and 0.37% Si. By referring to the differences of the predicted result with the experimental results, the validation of the model can be stated. For responses C, O, K, and Si content, it can be reported that the experiment is valid as the percentages are within a precise range. However, the biochar yield response difference is higher than 5%, which is a slightly wider range, indicating a low justification of the model for this specific response.

Figure 3.13 illustrates the visual quadratic interaction amongst variables that were analysed using three-dimensional response surface plots. These figures highlight the relationship between each response with the temperature and heating rate factors. Figure 3.13 (a) and (c) represent the interaction of the parameters with biochar yield and oxygen content, and it can be seen that they both have a similar trend in which the surface plots are sloping downwards as the temperature increases. This trend could be reported as a negative correlation between temperature and both responses, the yield and the oxygen content. From Figure 3.13 (a) and (c), the significant effect on temperature from 400°C for both these responses can be seen. Emphasising that the higher the pyrolysis temperature the lower the yield and oxygen content. The order of significance can be reflected in the equations (3.8) to (3.12).

Table 3.3 RSM runs for palm kernel biochar.

Run	Temperature (°C)	Heating Rate (°C/min)	Residence Time (min)	Yield (%)	C (%)	O (%)	K (%)	Si (%)
1	500	10	70	34.1	80.71	16.99	0.23	0.54
2	500	10	70	35.6	82.62	16.44	0.13	0.31
3	500	10	70	35.6	77.85	13.64	0.51	0.73
4	300	5	20	72.7	67.22	31.34	0.23	0.24
5	300	5	120	60.4	66.53	32.62	0.17	0.25
6	500	10	70	35.1	79.51	9.96	0.64	0.61
7	800	10	70	30.9	93.5	5.96	0.18	0.15
8	500	10	70	34.6	81.99	17.33	0.09	0.21
9	500	10	70	36.6	81.82	16.41	0.43	0.51
10	700	5	120	32.4	89.73	9.76	0.26	0.15
11	500	10	10	37.7	78.9	20.13	0.15	0.29
12	500	2	70	38.1	83.86	15.06	0.14	0.61
13	200	10	70	95.1	58.2	41.15	0.04	0.12
14	500	10	155	34.4	86.22	11.48	0.46	0.84
15	700	15	120	31.4	85.39	9.25	0.45	0.34
16	500	20	70	36.4	66.48	21.7	0.78	1.13
17	700	5	20	32.7	89.05	9.44	0.17	0.5
18	700	15	20	31.6	85.88	11.13	0.4	0.43
19	300	15	20	77.4	62.19	37.37	0.1	0.19
20	300	15	120	68.4	65.19	31.23	0.42	0.56
O ^a	409	15	120	38.2	73.37	25.48	0.39	0.44

O^a: Optimised temperature.

On the other side, the opposite trend is followed with the carbon content and temperature, as observed in Figure 3.13 (b). In Figure 3.13 (d) and (e), no direct correlation can be observed between the parameters and the responses for silicon and potassium. However, through the shape of the surface plots a clear difference between the responses and the parameters can be highlighted. The flat surface from Figure 3.13 (d) indicates the stability of the potassium content and that it is not highly affected by the parameters. The slight upwards tilt in the surface indicates the minimal increase in the content. As in Figure 3.13 (e), the curvature surface is more pronounced for the temperature than the heating rate. As it can be seen that the silicon content only increases up to 500°C and then decreases. Signifying the parameters should be optimised to get a high silicon content. This could also be observed in the graphs represented in Figure 3.14 (d) and (e). Figure 3.14 shows the predicted against the actual that was modelled by the RSM. Figure 3.14 (a), (b), and (c) for yield C and O content all show the points representing the run experiments closely packed within the diagonal central line across the graph. This indicates a close trend and correlation followed by the response between the predicted and actual data.

Chapter 3 Optimisation of Palm Oil Waste Biochar Production

Table 3.4 ANOVA of the palm kernel shell biochar yield, C, O, K and Si content.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks	R ²	
Yield Model	6787.55	9	754.17	141.71	< 0.0001	significant	0.9922	
A	4884.67	1	4884.67	917.86	< 0.0001			
B	2.00	1	2.00	0.3752	0.5538		Adjusted R²	Std Dev
C	71.38	1	71.38	13.41	0.0044		0.9922	2.31
AB	27.38	1	27.38	5.14	0.0467			
AC	54.08	1	54.08	10.16	0.0097		Predicted R²	Mean
BC	1.44	1	1.44	0.2715	0.6137		0.9377	44.56
A²	1707.33	1	1707.33	320.82	< 0.0001			
B²	10.20	1	10.20	1.92	0.1963		Adeq Precision R²	C.V%
C²	20.59	1	20.59	3.87	0.0776		40.1000	5.18
Residual	53.22	10	5.32					
Lack of Fit	49.38	5	9.88	12.88	0.0070	significant		
Pure Error	3.83	5	0.7667					
Cor Total	6840.77	19						
C Model	1910.81	9	212.31	37.75	< 0.0001	significant	0.9714	
A	1610.17	1	1610.17	286.33	< 0.0001			
B	104.88	1	104.88	18.65	0.0015		Adjusted R²	Std Dev
C	11.38	1	11.38	2.02	0.1854		0.9457	2.37
AB	0.1625	1	0.1625	0.0289	0.8684			
AC	0.5618	1	0.5618	0.0999	0.7584		Predicted R²	Mean
BC	0.7938	1	0.7938	0.1412	0.7150		0.8166	78.14
A²	69.63	1	69.63	12.38	0.0055			
B²	68.54	1	68.54	12.19	0.0058		Adeq Precision R²	C.V%
C²	2.95	1	2.95	0.5253	0.4852		20.3054	3.03
Residual	56.24	10	5.62					
Lack of Fit	40.11	5	8.02	2.49	0.1701	not significant		
Pure Error	16.13	5	3.23					
Cor Total	1967.04	19						
O Model	1963.09	9	218.12	32.46	< 0.0001	significant	0.9669	
A	1699.79	1	1699.79	252.92	< 0.0001			
B	13.92	1	13.92	2.07	0.1807		Adjusted R²	Std Dev
C	31.60	1	31.60	4.70	0.0553		0.9371	2.59
AB	1.50	1	1.50	0.2227	0.6471			
AC	1.36	1	1.36	0.2025	0.6623		Predicted R²	Mean
BC	11.57	1	11.57	1.72	0.2188		0.8649	18.92
A²	173.60	1	173.60	25.83	0.0005			
B²	24.81	1	24.81	3.69	0.0836		Adeq Precision R²	C.V%

Chapter 3 Optimisation of Palm Oil Waste Biochar Production

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks	R ²	
C ²	3.05	1	3.05	0.4533	0.5160		19.0842	13.70
Residual	67.21	10	6.72					
Lack of Fit	26.60	5	5.32	0.6552	0.6730	not significant		
Pure Error	40.60	5	8.12					
Cor Total	2030.30	19						
K Model	0.2972	3	0.0991	3.37	0.0448	significant	0.3870	
A	0.0260	1	0.0260	0.8837	0.3612			
B	0.2122	1	0.2122	7.21	0.0162		Adjusted R ²	Std Dev
C	0.0592	1	0.0592	2.01	0.1753		0.2721	0.1715
Residual	0.4706	16	0.0294				Predicted R ²	Mean
Lack of Fit	0.2249	11	0.0204	0.4162	0.8952	not significant	0.0975	0.2990
Pure Error	0.2457	5	0.0491				Adeq Precision R ²	C.V%
Cor Total	0.7678	19					6.2210	57.36
Si Model	0.9640	9	0.1071	2.99	0.0515	not significant	0.7291	
A	0.0041	1	0.0041	0.1131	0.7436			
B	0.0782	1	0.0782	2.18	0.1703		Adjusted R ²	Std Dev
C	0.0418	1	0.0418	1.17	0.3055		0.4853	0.1892
AB	0.0025	1	0.0025	0.0684	0.7990			
AC	0.0840	1	0.0840	2.35	0.1565		Predicted R ²	Mean
BC	0.0480	1	0.0480	1.34	0.2736		-0.3827	0.4355
A ²	0.3985	1	0.3985	11.13	0.0075			
B ²	0.1797	1	0.1797	5.02	0.0490		Adeq Precision R ²	C.V%
C ²	0.0016	1	0.0016	0.0433	0.8394		7.5572	43.45
Residual	0.3581	10	0.0358					
Lack of Fit	0.1726	5	0.0345	0.9301	0.5307	not significant		
Pure Error	0.1855	5	0.0371					
Cor Total	1.32	19						

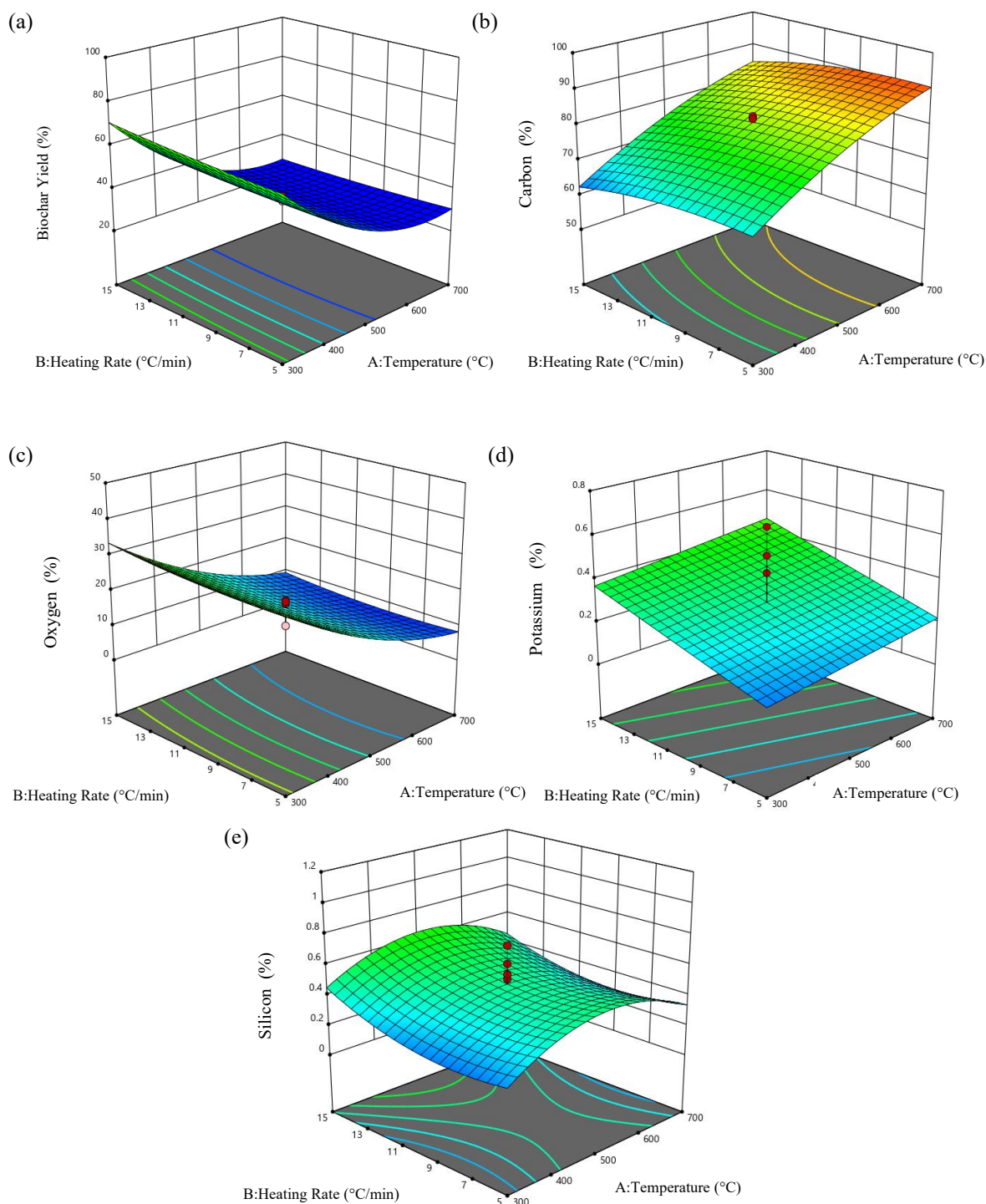


Figure 3.13 3D representation of responses by the RSM for PKS biochar. (a) Biochar yield response, (b) C content response, (d) K content response, (e) Si content response.

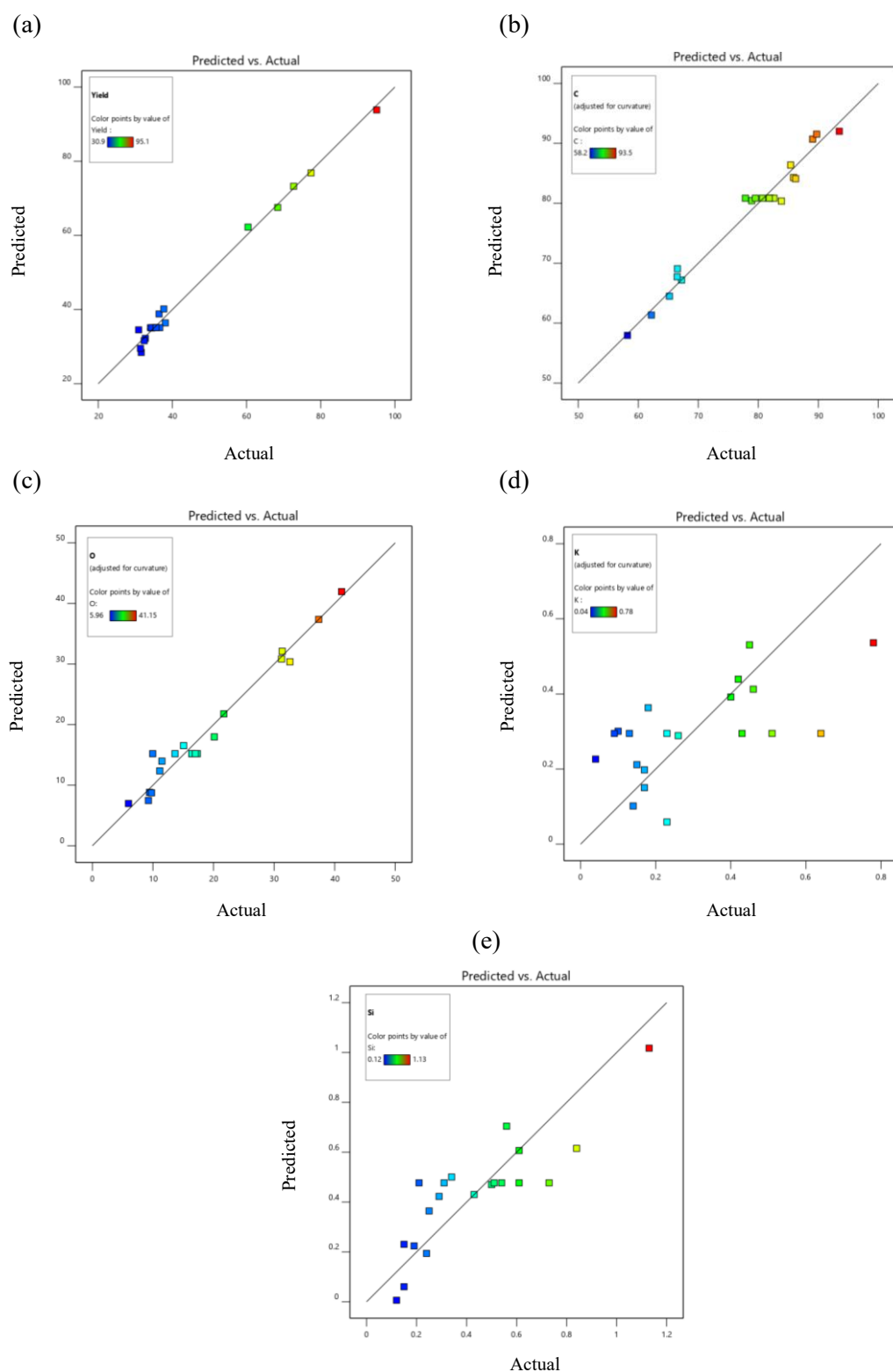


Figure 3.14 Predicted against actual of the PKS biochar RSM model. (a) Biochar yield response, (b) C content response, (c) O content response, (d) K content response, (e) Si content response.

3.2.1.2 Biochar Yield

PKS biochar yield was calculated using Equation (3.1). The results obtained are provided in Table 3.2. The range of results obtained is from 30.9%–95.1%. As reported by past research, biochar yield is highly affected by temperature, heating rate, and residence time (Yadav et al., 2019; Zhang et al., 2020). Through observation, biochar at 200°C did not carbonise fully, as there seemed to be no significant change of colour observed. There was only a loss of mass due to the PKS moisture loss. At 300°C, PKS was not fully carbonised, as the observed colour of the resultant biochar was a dark shade of brown, irrespective of the heating rate and residence time. At temperatures 500°C and above, PKS has been fully carbonised, and the observed colour was black. The PKS biochar yield obtained in another study through slow pyrolysis at 500°C, with a heating rate of 10°C/min and a residence time of 60 minutes, was 32.3% on an air-dry basis and 34.0% on a dry ash-free basis (Lee et al., 2013), closely aligning with the yield range of 34.1–38.05% observed in this research at the same temperature. These minor differences would be due to the different heating rates and residence time. The PKS biochar yield might vary from other studies due to different collection areas from palm oil mills or the different thermochemical conversion method used. In a study that used microwave pyrolysis at 2.45 GHz with 700 W at 10, 20, and 30 min holding time, resulted in 43, 41, and 33% of PKS biochar yield (Lim et al., 2022). In another study through pyrolysis, the reported PKS biochar yield at 500°C at a rate of 10°C/min was 33% (Jafri et al., 2020). Other studies that conducted slow pyrolysis on other biomass, such as sawdust, exhibited a yield of 28% at 500°C with a 10°C/min rate and 60 min residence time (Gupta and Kua, 2019).

Biochar yield of rice husk at 500°C, 7°C/min for 55 min was found to be 40.7% (Yadav and Jagadevan, 2021). This indicates that even though the same thermochemical conversion was used, the biomass is still an important factor to be considered when acquiring an appropriate amount of yield according to the demands of the research. As the current study aspires to be adopted for use as SCM, therefore, during optimisation, the biochar yield response was selected to be maximum to accommodate batch pyrolysis. By comparing Figure 3.15 (a), (b), and (c), it can clearly be seen with each trendline on how each factor is affecting the biochar yield. Figure 3.15 (a) shows a clear negative gradient, indicating that the higher the temperature, the lower the yield. The trendline in Figure 3.15 (b) is slightly inclined, indicating that the correlation between

yield and residence time is negative. Figure 3.15 (c) trendline indicates no correlation between the heating rate and yield. By analysing the trends exhibited by each factor, it can be understood that when high biochar yield has been desired, a temperature around 400°C to 500°C would be favourable, with a high heating rate of 15°C/min and a residence time of 120 min. This coincides with the optimised run by the model, which is at 409°C.

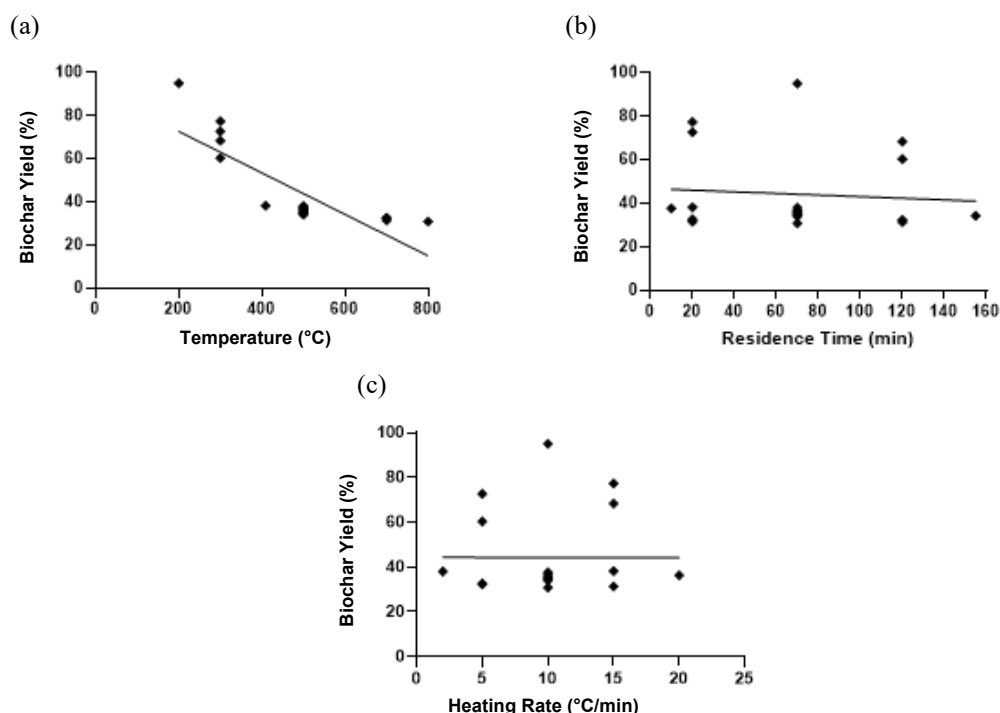


Figure 3.15 Conducted PKS pyrolysis runs (a) biochar yield against temperature, (b) biochar yield against residence time and (c) biochar yield against heating rate.

3.2.1.3 Elemental Analysis

Elemental composition of biochar, mainly C and O content and other elements such as K and Si were detected on the surface of PKS biochar. Other elements such as Al, Fe, N, Ca, Mg, and S were also detected on the biochar surface but in very low amounts. The range of results obtained for C, O, K, and Si content are 58.2–93.5%, 5.96–41.15%, 0.04–0.78%, and 0.12–1.13% respectively. Optimised run for C, O, K and Si resulted in 73.37%, 25.48%, 0.34% and 0.44%, respectively. Changes in elemental composition through different pyrolysis parameters can be reported from Table 3.2. Chemical stability of the biochar is a crucial property that relates to the ratio of oxygen to carbon, and the lower ratios determine the presence of a high stable carbon content in the biochar structure. This was reported to ensure the long-term durability properties of biochar cementitious composites (Gupta and Kua, 2019). It was stated that carbon-rich

biochar particles behave as micro-reinforcements in the cementitious matrix, which results in an increase in the fracture surface area, thus a more ductile failure (Ahmad et al., 2015). As the optimised PKS biochar in this study showed a high amount of C and ratio of O to C of 0.34, it is hypothesised to form a durable composite mix, when used as cement replacement. The addition of silica fume as cement replacement did previously prove that it has enhanced mechanical properties (Nochaiya et al., 2010). Therefore, the presence of Si in biochar is highly desirable. Si was found to be responsible for the pozzolanic reaction in cementitious materials (Muthukrishnan et al., 2019). The waste wood biochar used in the study by Gupta and Kua, (2020) exhibited similar ranges of K and Si content of 0.42 and 0.45%. A study that compared food waste biochar and silica fume as cement replacement reported that with replacement of 4% and 6%, the concrete composites showed a similar increase of compressive strength at days 7 and 28 comparatively to the control. Provided by the model as stated in Table 3.3, the K content is not significantly affected by the pyrolysis parameters. However, it can still be noted that in the optimised run the K salt is present and therefore is believed to accelerate cement hydration, as stated by (Restuccia and Ferro, 2016a). It was also reported this was due to the biochar acting as alkali activating, which consequently improved the mechanical behaviour of the biochar concrete composite. They have also reported that there has been an increase in the compressive strength and the fracture energy, which deemed the chosen biochar production parameters favourable for the use as SCM (Restuccia and Ferro, 2016a).

3.2.1.4 Biochar Thermal Stability

The thermostability of biochar depends on the temperature at which it was produced and on its original biomass. The higher the temperature used for production, the more stable the carbon skeleton with high heat resistance is formed (Suarez-Riera et al., 2020). One of the methods of assessing the stability of biochar has been known through quantification and qualification of stable C content by thermal, chemical, or thermochemical methods like thermal degradation or chemical oxidation (Leng et al., 2019; Mukherjee et al., 2021). Current research has opted for thermal degradation through TGA. The TGA results are divided into three stages: Stage 1 involves dehydration, which refers to the loss of moisture. Stage 2 pertains to the thermal stability, which is the breakdown of organic compounds. Stage 3 concerns combustion, which involves the decomposition of fixed carbon. Knowledge of the thermal

conductivity of biochar would help to understand its resistance, which in turn could improve the properties of concrete or mortar composites if the intended use is insulation. After conducting the RSM and optimisation, further TGA analysis was conducted on all pyrolysis runs and the optimised run. This was done to ensure that the finalised optimised run proves to be a potential with the other types of analysis. The data is provided in Figure 3.16. With Figure 3.16 (d), it can be clearly demonstrated that with the increase in pyrolysis temperature and the original biomass, the loss of weightage has decreased at stage 3, which indicates a positive correlation between the high thermal resistance with high pyrolysis temperature used for biochar production. Thermal resistance of biochar is exhibited by the high porosity, which would be visible with the FESEM analysis in Figure 3.17. Through comparison, it can be reported that there is a direct correlation between porosity and thermal conductivity. This is similar to the findings of (Tan et al., 2020; S. Yang et al., 2019) which have used different biochar from wood waste, bamboo, rice husk, and coconut shell. It was observed that the porosity of biochar was due to the release of volatiles during exposure of the biomass to elevated temperature during thermochemical conversion (Tan et al., 2020). To obtain energy-efficient buildings with high thermal resistance and insulation properties, mortar or concrete composites with the addition of biochar would be encouraged (Mensah et al., 2021). Gupta et al., (2019) studied the thermal resistance of wood waste biochar of 500°C concrete composites under elevated temperatures. The authors mentioned that exposing the composite to high temperatures showed a minimal loss in weight and strength compared to the control. Moreover, for their study, the addition of high thermal resistance biochar to cement mix led to low damage to the microstructure of concrete during high-temperature exposure, leading to 22–55% higher residual strength and water tightness compared to conventional mix.

Through Figure 3.16 (a), (b), and (c), which represent the TGA of the biochar samples for each run and have been separated according to the pyrolysis temperature. In Figure 3.16 (a) for the temperature 300°C, it can be seen that the dip at stage 2 occurred much earlier than in Figure 3.16 (b) for 500°C and (c) 700°C. This indicates that biochar at low temperature of 300 have a lower stability of compounds than in temperature higher. As for the dip in the breakdown of organic compounds in Figure 3.16 (b) for biochar produced at 500°C occurred at approximately 525°C. Moreover, for Figure 3.16 (c) occurred after 625°C.

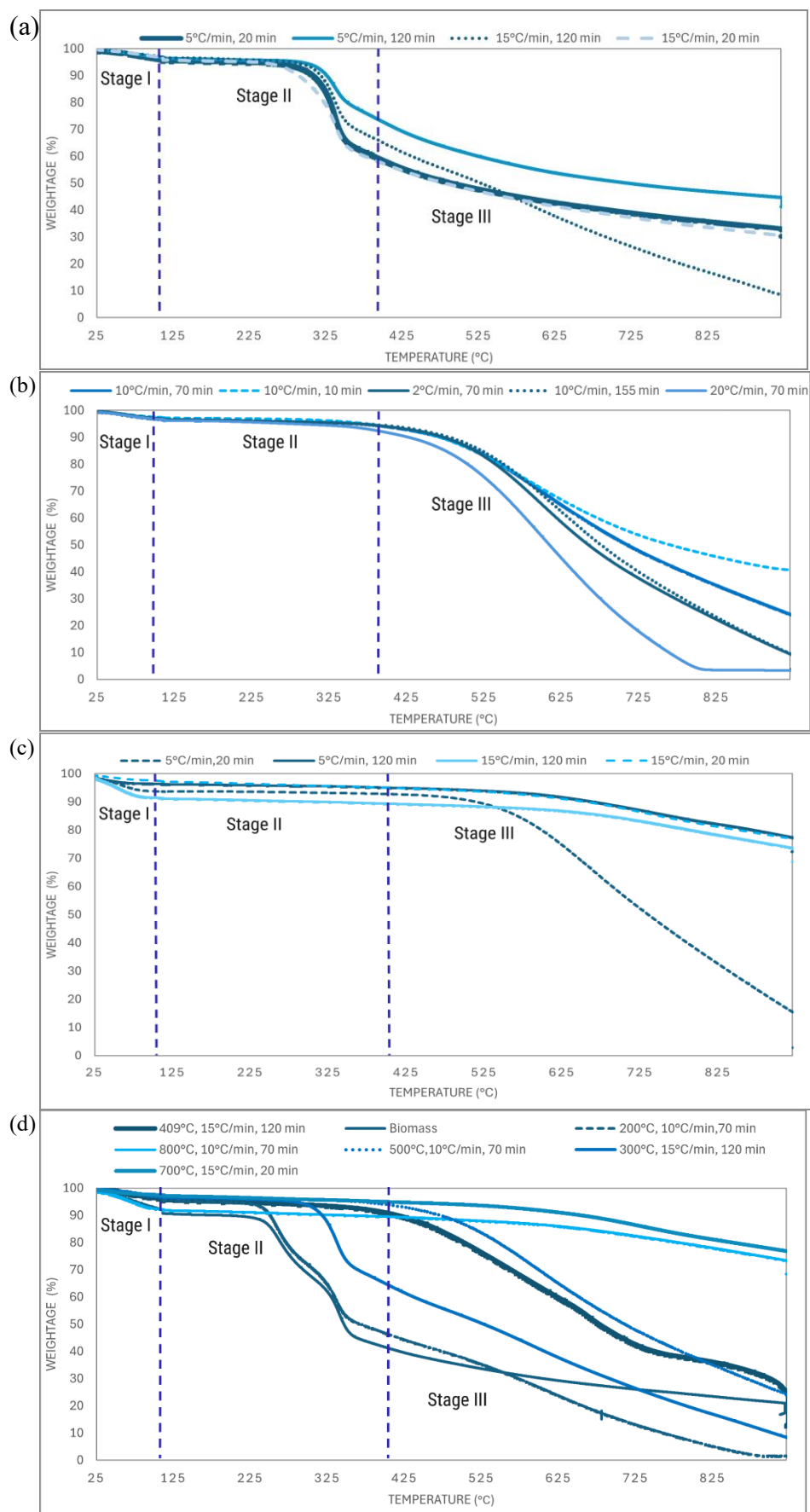


Figure 3.16 TGA analysis of PKS runs at (a) biochar at 300°C, (b) biochar at 500°C, (c) biochar at 700°C, (d) biochar at all temperatures with raw PKS biomass.

In Figure 3.16 (d), all the different temperature runs have been displayed with the optimised run, which is 409°C, and the biomass. The run conducted at 200°C and the raw biomass have both had the lowest weightage change at 920°C (stage 3) comparatively to the rest of the biochar samples. This indicates that both biomass is in its raw state and at 200°C is not thermally stable. Figure 3.16 (d) also shows that the runs conducted at 409°C and 500°C have similar trends; likewise, the runs conducted at 700°C and 800°C. These TGA results would be in agreement with the softwood biochar use as cement replacement by the study conducted by Dixit et al., (2019). The lower mass loss of the biochar before reaching 500°C during the TGA analysis also showed a lower mass loss when used as a cement replacement. This would indicate that the current optimised run at 409°C would potentially exhibit the same behaviour.

3.2.1.5 Biochar Morphology

Morphology of biochar is a crucial part of the analysis as it will affect the concrete mix and its water absorption abilities. Figure 3.17 shows a difference in the morphology of the PKS under different pyrolysis temperatures that have been run in this experiment. Optimised run of this experiment is 409°C, which shows a honeycomb-like structure similar to the runs conducted at 500°C and 700°C as shown in Figure 3.17. The ridges on the surface increase its roughness, which may improve the bonding between the biochar and cementitious matrix (Gupta et al., 2018b). This proves that the optimised run has the potential to be utilised as a cement replacement. It was also observed that there are differences on the roundness and uniformity of the pores at different temperatures. Only at 700°C it can be clearly seen that the uniformity of the pores is very clear in comparison with the others. Figure 3.18 presents the images with measured pore sizes to distinguish the effect of the pyrolysis temperature with the pore width. Figure 3.18 (a) shows the surface of the biomass as a staggered surface, and no hollow pores have been observed. During the thermal conversion, it can be observed through the following images in Figure 3.18 (b), (c), and (d) that the average pore sizes for 409°C, 500°C, and 700°C are 20.43 µm, 24.73 µm, and 15.11 µm respectively. It can be reported that with the increase in temperature there is a decrease in pore width but there is an increase in the uniformity of the pores. The optimised run at 409°C has a residence time of 120 min comparatively to the selected run in Figure 3.18 (c), which is 500°C for 70 min. It is believed that due to the difference in residence time, a slight increase in average pore size is observed.

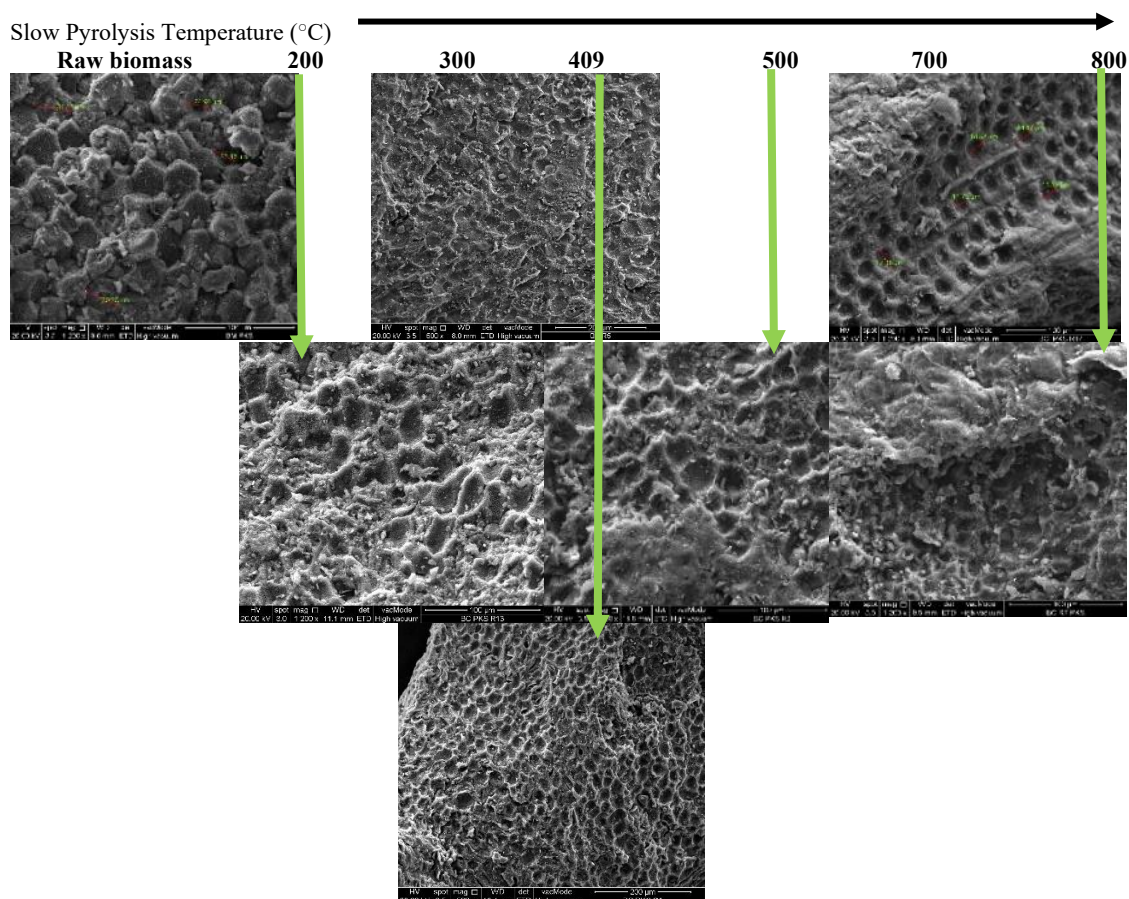


Figure 3.17 FESEM images of PKS under different temperatures.

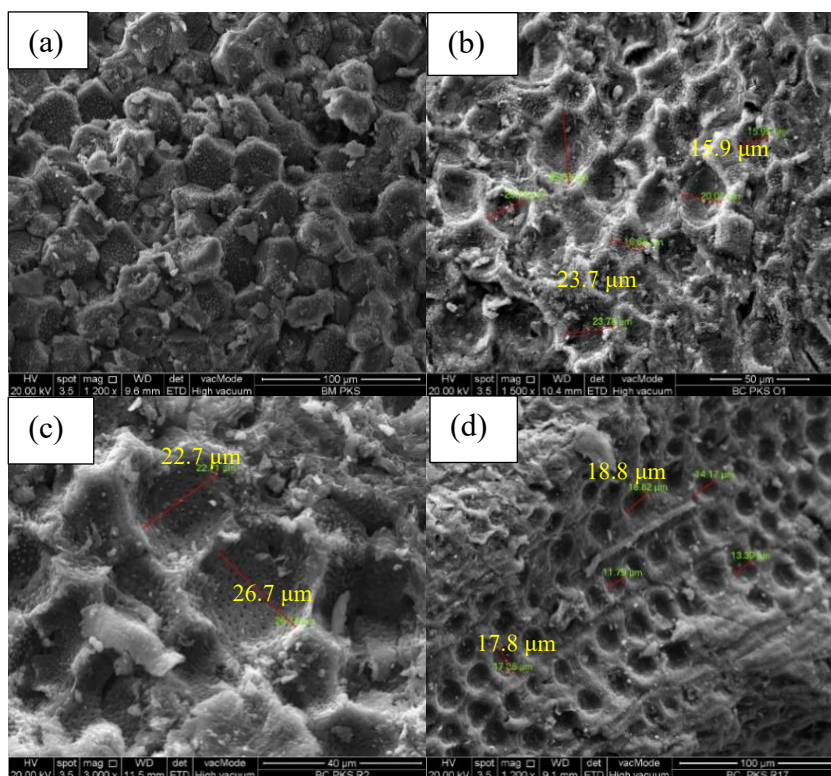


Figure 3.18 Labelled FESEM images. PKS biomass, (b) optimised biochar, (c) biochar at 500°C, (d) biochar at 700°C

3.2.2 Empty Fruit Bunch Biochar

3.2.2.1 Optimisation

Similar to the optimisation process carried out for PKS, it was also repeated for EFB in order to understand the changes in behaviour of the different biomass types under the same parameters, as the biomass differs significantly in PKS due to its granular nature and in EFB due to its fibrous nature. This is shown by the results provided in Table 3.5, where the optimised parameters for EFB were found to be at 455°C, 15°C/min, and 20 min. Like the optimised temperature for PKS biochar, both are lower than the typical temperature of 500°C mentioned in the literature. Additionally, using a lower production temperature would be advantageous as it aligns with the industrial need for reduced energy consumption (Harsono et al., 2013).

Table 3.5 RSM runs for empty fruit bunch biochar.

Run	Temperature (°C)	Heating Rate (°C/min)	Residence Time (min)	Biochar Yield (%)	C (%)	O (%)	K (%)	Si (%)
1	500	10	70	25.3	65.46	24.01	1.74	8.31
2	500	10	70	27.4	69.65	23.01	1.41	5.63
3	500	10	70	29.1	74.58	19.92	0.85	3.89
4	300	5	20	61.6	61.77	35.50	0.73	2.00
5	300	5	120	47.1	67.20	30.57	0.39	1.7
6	500	10	70	26.1	70.44	29.29	3.71	4.96
7	800	10	70	22.3	88.34	9.63	1.23	0.64
8	500	10	70	26.0	84.16	8.82	3.18	2.77
9	500	10	70	25.4	80.27	15.34	1.19	2.93
10	700	5	120	23.5	73.45	19.96	3.44	2.59
11	500	10	10	29.0	68.88	24.44	0.75	5.54
12	500	2	70	29.1	79.17	17.99	0.79	1.77
13	200	10	70	86.9	55.83	43.47	0.22	0.27
14	500	10	155	27.6	79.07	15.81	0.97	3.84
15	700	15	120	24.0	90.53	7.58	1.00	0.33
16	500	20	70	25.3	79.15	14.91	1.83	1.29
17	700	5	20	24.2	86.43	10.68	1.54	0.80
18	700	15	20	23.8	80.11	14.72	1.87	2.48
19	300	15	20	70.2	68.11	29.46	0.38	1.59
20	300	15	120	53.9	64.00	32.28	0.41	0.31
O ^a	455	15	20	37.0	71.98	23.40	0.61	3.68

O^a: Optimised temperature.

Figure 3.19 is a 3D representation of the individual responses, clearly showing the correlation between the factors and the responses. Analysis of variance (ANOVA) was conducted to determine the significance and nature of the interactions between the

factors and the responses, including the probability (p-value), Fisher's variation (F-value), and the correlation effect (R^2). Table 3.6 presents the ANOVA results for the models for EFB model. The coefficient of determination (R^2) is a measure of a model's goodness of fit. The R^2 for biochar yield, carbon, oxygen, and silicon content is close to 1, indicating that the model fits well between the experimental and predicted values, as shown in Figures 3.20 (a), (b), (c), and (d). However, the R^2 values for the K and Si content are lower than 0.8, indicating less agreement between the experimental and predicted values. The predicted R^2 values for the K, O, C, Si and biochar yield responses align with their respective adjusted R^2 values, with differences of less than 0.2. However, the Si response shows a negative predicted R^2 , suggesting that, for this response specifically, the overall mean may be a better predictor than the current mathematical model. The adequate precision (R^2) is a measure of the signal-to-noise ratio in the model. The adequate precision R^2 for all the responses is greater than 4, which indicates that the model is adequate. All the responses' models are significant, except for Si, as stated in Table 3.6 This may be due to a very low correlation between all the variables, as indicated in Equation (3.17). Equations (3.13)- (3.17) show the mathematical equations of the responses for the EFB model.

$$\text{Yield} = 26.446 - 18.736A + 0.601726B - 3.07666C - 1.9125AB + 3.7875AC - 0.1125BC + 12.641A^2 + 0.0513464B^2 + 1.73696C^2 \quad (3.13)$$

$$C = 73.9662 + 9.4564A + 0.756011B + 1.06244C + 0.9525AB - 0.485AC + 1.7325BC - 1.09303A^2 + 1.26383B^2 + 0.138166C^2 \quad (3.14)$$

$$O = 20.2105 - 10.0504A - 1.11573B - 0.991018C - 0.50125AB + 0.53125AC - 1.08375BC + 3.06107A^2 + -0.889664B^2 - 0.0963926C^2 \quad (3.15)$$

$$K = 1.90576 + 0.5964A + -0.0334922B + 0.131009C - 0.2225AB + 0.1675AC - 0.3BC - 0.407475A^2 - 0.081623B^2 - 0.345125C^2 \quad (3.16)$$

$$Si = 4.7741 + 0.0924A - 0.0446954B - 0.321039C + 0.1525AB + 0.1525AC - 0.615BC - 2.02087A^2 - 0.996638B^2 - 0.15342C^2 \quad (3.17)$$

Chapter 3 Optimisation of Palm Oil Waste Biochar Production

Table 3.6 ANOVA of the empty fruit bunch biochar yield, C, O, K and Si content.

Source	Sum of Squares	df	Mean Square	F-value	p-value		R ²	
Yield Model	6335.47	9	703.94	58.35	< 0.0001	significant	0.9813	
A	4387.97	1	4387.97	363.75	< 0.0001			
B	5.03	1	5.03	0.4171	0.5329		Adjusted R²	Std Dev
C	109.20	1	109.20	9.05	0.0131		0.9645	3.47
AB	29.26	1	29.26	2.43	0.1504			
AC	114.76	1	114.76	9.51	0.0116		Predicted R²	Mean
BC	0.1012	1	0.1012	0.0084	0.9288		0.8652	35.39
A²	1635.14	1	1635.14	135.55	< 0.0001			
B²	0.0498	1	0.0498	0.0041	0.9501		Adeq Precision R²	C.V%
C²	30.48	1	30.48	2.53	0.1430		25.553	9.81
Residual	120.63	10	12.06					
Lack of Fit	110.02	5	22.00	10.36	0.0113	significant		
Pure Error	10.61	5	2.12					
Cor Total	6456.10	19						
C Model	1228.02	9	136.45	3.01	0.0507	not significant	0.7301	
A	1117.79	1	1117.79	24.62	0.0006			
B	7.94	1	7.94	0.1749	0.6846		Adjusted R²	Std Dev
C	13.02	1	13.02	0.2868	0.6040		0.4871	6.74
AB	7.26	1	7.26	0.1599	0.6977			
AC	1.88	1	1.88	0.0414	0.8428		Predicted R²	Mean
BC	24.01	1	24.01	0.5289	0.4838		-0.4142	74.33
A²	12.23	1	12.23	0.2692	0.6151			
B²	30.15	1	30.15	0.6641	0.4341		Adeq Precision R²	C.V%
C²	0.1929	1	0.1929	0.0042	0.9493		6.3861	9.07
Residual	454.05	10	45.40					
Lack of Fit	206.70	5	41.34	0.8356	0.5757	not significant		
Pure Error	247.35	5	49.47					
Cor Total	1682.07	19						
O Model	1435.29	9	159.48	4.28	0.0165	significant	0.7941	
A	1262.63	1	1262.63	33.92	0.0002			
B	17.30	1	17.30	0.4648	0.5109		Adjusted R²	Std Dev
C	11.33	1	11.33	0.3044	0.5932		0.6087	6.10
AB	2.01	1	2.01	0.0540	0.8209			
AC	2.26	1	2.26	0.0607	0.8104		Predicted R²	Mean
BC	9.40	1	9.40	0.2524	0.6262		0.1887	21.37
A²	95.88	1	95.88	2.58	0.1396			

Chapter 3 Optimisation of Palm Oil Waste Biochar Production

Source	Sum of Squares	df	Mean Square	F-value	p-value		R ²	
B²	14.94	1	14.94	0.4014	0.5406		Adeq Precision R²	C.V%
C²	0.0939	1	0.0939	0.0025	0.9609		7.6724	28.55
Residual	372.22	10	37.22					
Lack of Fit	114.08	5	22.82	0.4420	0.8045	not significant		
Pure Error	258.13	5	51.63					
Cor Total	1807.51	19						
K Model	8.89	9	0.9880	0.9228	0.5433	not significant	0.4537	
A	4.45	1	4.45	4.15	0.0689			
B	0.0156	1	0.0156	0.0146	0.9063		Adjusted R²	Std Dev
C	0.1980	1	0.1980	0.1850	0.6763		-0.0379	1.03
AB	0.3961	1	0.3961	0.3699	0.5566		Predicted R²	Mean
AC	0.2245	1	0.2245	0.2097	0.6568		-1.2297	1.38
BC	0.7200	1	0.7200	0.6725	0.4313		Adeq Precision R²	C.V%
A²	1.70	1	1.70	1.59	0.2364		3.4168	74.90
B²	0.1258	1	0.1258	0.1175	0.7389			
C²	1.20	1	1.20	1.12	0.3140			
Residual	10.71	10	1.07					
Lack of Fit	4.00	5	0.7992	0.5955	0.7083	not significant		
Pure Error	6.71	5	1.34					
Cor Total	19.60	19						
Si Model	62.36	9	6.93	2.84	0.0594	not significant	0.7191	
A	0.1067	1	0.1067	0.0438	0.8384			
B	0.0278	1	0.0278	0.0114	0.9171		Adjusted R²	Std Dev
C	1.19	1	1.19	0.4882	0.5007		0.4664	1.56
AB	0.1861	1	0.1861	0.0764	0.7879			
AC	0.1861	1	0.1861	0.0764	0.7879		Predicted R²	Mean
BC	3.03	1	3.03	1.24	0.2911		0.3180	2.68
A²	41.79	1	41.79	17.16	0.0020			
B²	18.75	1	18.75	7.70	0.0196		Adeq Precision R²	C.V%
C²	0.2378	1	0.2378	0.0976	0.7611		4.3948	58.19
Residual	24.36	10	2.44					
Lack of Fit	2.89	5	0.5784	0.1347	0.9769	not significant		
Pure Error	21.46	5	4.29					
Cor Total	86.72	19						

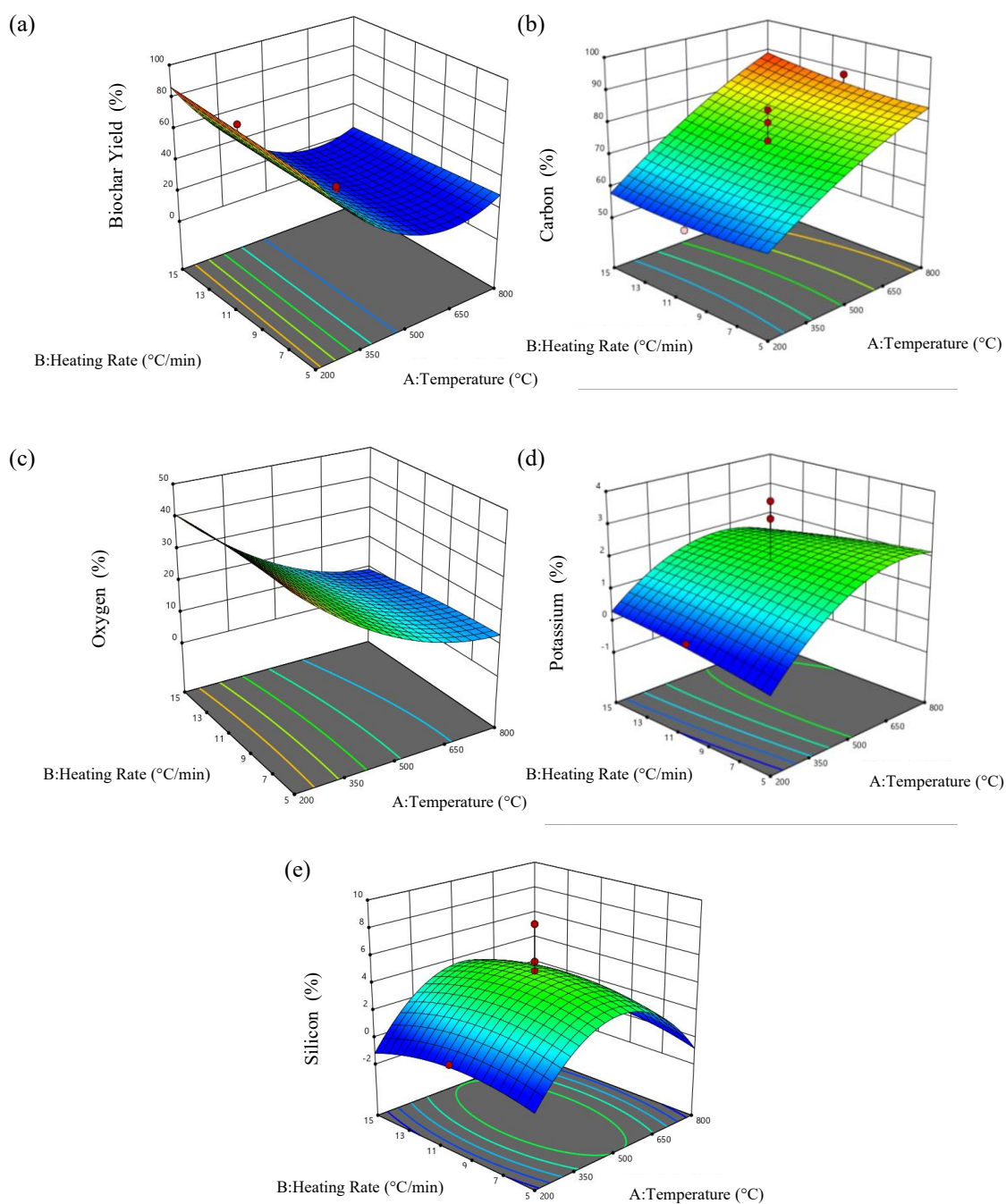


Figure 3.19 3D representation of responses by the RSM for EFB biochar. (a) Biochar yield, (b) C content, (d) K content, (e) Si content.

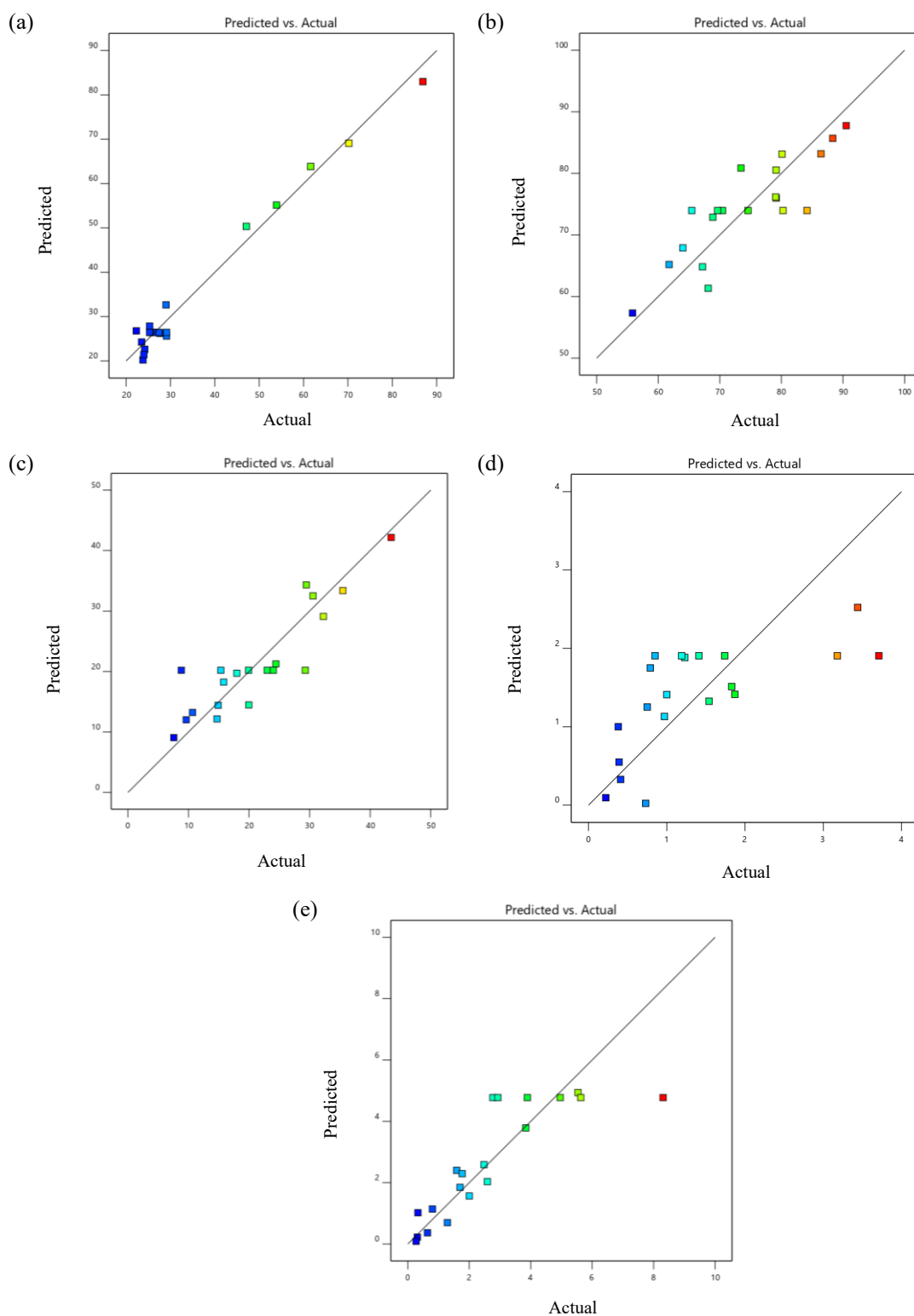


Figure 3.20 Predicted against actual of the EFB biochar RSM model. (a) Biochar yield, (b) C, (c) O, (d) K, and (e) Si content.

3.2.2.2 Biochar Yield

Biochar yield refers to the mass ratio of char to biomass. Further analyses were conducted for each varied pyrolysis factor to determine how biochar yield changed in response to each factor. Figure 3.21 shows the graphs produced for biochar yield across all pyrolysis runs, with each run having different factors of temperature, heating rate, and residence time. A linear best-fit line with a 95% confidence interval was drawn for each graph. From Figure 3.21 (a), (b), and (c), it is clear that (a) has the steepest slope, indicating that temperature had the greatest effect on yield compared to the other factors. This finding aligns with most studies (Ferreira et al., 2020; Md Said et al., 2022; Selvarajoo, 2021; Wang et al., 2020a; Yadav et al., 2019), even with the PKS biochar results. However, a study investigating the same pyrolysis factors as in the current research, using water hyacinth biochar for lead absorption, concluded that the heating rate has the greatest influence for this specific application (Zhou et al., 2020). This emphasises that especially for lead absorption, the change in heating rate of pyrolysis was more significant than the pyrolysis temperature.

The biochar yield in Figure 3.21 (a) shows that it gradually decreases with the increase in temperature, more so than in Figure 3.21 (b) along the heating rate. EFB did not carbonise at temperatures lower than 300°C, as demonstrated by a pyrolysis run carried out at 200°C. The mass loss at 200°C was solely due to moisture loss from the biomass, similar to the PKS run. Figure 3.21 (a) shows that the biochar yield at 300°C ranges from 70.2% to 47.1%, and at 500°C, from 25.3% to 29.1%. These ranges indicate that at lower temperatures, such as 300°C, heating rate and residence time have a significant impact on yield, whereas this is not the case at 500°C. A similar range in EFB biochar yield was observed in another study, where the yield at 300°C for pellets was 47% and for fibre, 50% (Md Said et al., 2022).

In a study that examined biochar from wood, the yield at 500°C and 700°C was found to be 30% and 25%, respectively (Wang et al., 2020a). This is higher than the yield in this research, which can be attributed to the fibrous and low density of the EFB used in this research. This highlights that the physical properties of biomass are crucial factors in biochar yield. It is worth noting that, based on the best-fit lines from Figure 3.21, residence time has a greater effect on yield than heating rate after temperature, which is consistent with findings from another study on rice husk biochar for use as fuel (Yadav et al., 2019). The resulting optimised pyrolysis temperature was 455°C, which

requires low energy consumption, making it advantageous for industrial adaptability. A biochar production plant in Selangor, Malaysia, stated that the equipment they use to produce char operates at low to medium temperatures, ranging from 250°C to 450°C (Nasmech Technology Sdn Bhd, n.d.).

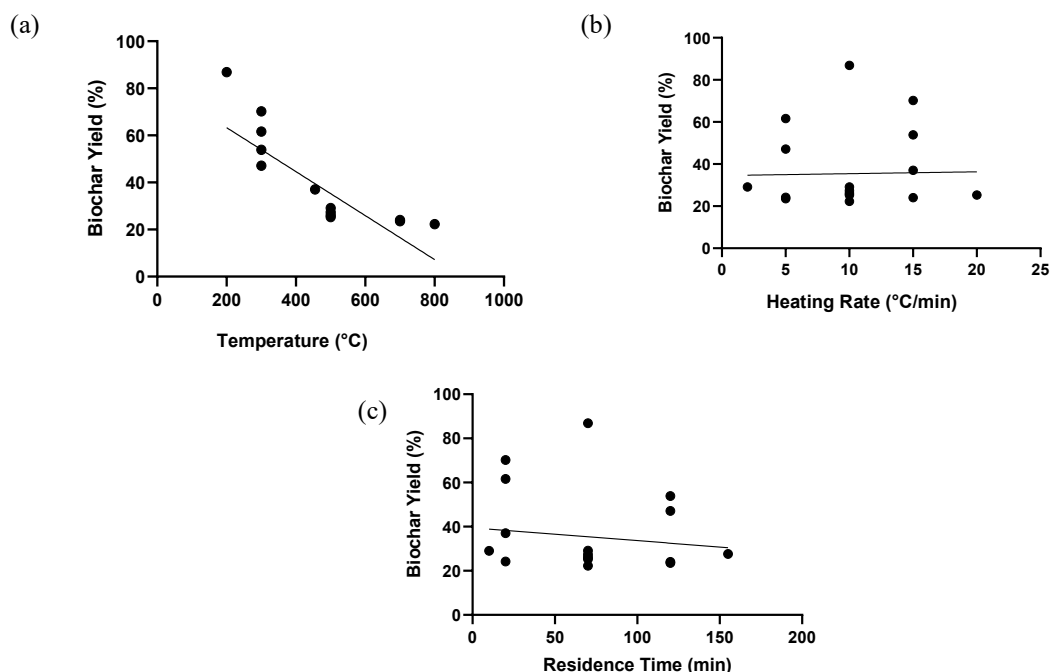


Figure 3.21 Conducted EFB pyrolysis runs. (a) Biochar yield against temperature, (b) biochar yield against heating rate and (c) biochar yield against residence time.

3.2.2.3 Elemental Analysis

Elemental composition of the surface was determined using EDX for the biochar samples, as shown in Table 3.4. Figure 3.19 illustrates the correlation between heating rate and temperature with selected elements such as C, O, K, and Si. From Figure 3.19 (b), it is evident that there is a direct correlation between temperature and carbon content, while in Figure 3.19 (c), the opposite is observed for oxygen content. This suggests that the higher the temperature required to produce biochar, the lower the oxygen-to-carbon ratio, resulting in high chemical stability of the biochar. It has been reported that when the oxygen-to-carbon ratio is less than 0.20, the biochar exhibits high stability and a half-life of up to 1,000 years (Bong et al., 2022; Spokas, 2010). The resulting O/C ratio of the optimised run for EFB is 0.33, which is very close to the optimised PKS ratio of 0.34. Since these values are close to 0.2, it can be assumed that a chemically stable biochar is produced, which would imply that mortars or concrete composites made with this biochar would be durable.

The range of results for C, O, K, and Si content is 55.83–88.34%, 9.63–43.47%, 0.22–3.71%, and 0.31–8.31%, respectively. Comparing EFB with PKS, the Si and K content detected in EFB is much higher than in PKS. Highest Si content detected for EFB was 8.31% at 500°C, 10°C/min, and 70 min. Similarly, the highest K content detected was 3.71% under the same parameters. For PKS, the highest Si content detected was 1.13%, and the highest K content was 0.78% under the same parameters of 500°C, 20°C/min, and 70 min. This is advantageous, as a study reported that K helps accelerate cement hydration, resulting in higher strength in mortar or concrete composites (Restuccia and Ferro, 2016a). The optimised pyrolysis run resulted in 71.98% C, 23.40% O, 0.61% K, and 3.68% Si. Since the addition of silica fume improves mechanical properties by assisting the pozzolanic reaction in the cement mixture (Nochaiya et al., 2010), there is growing interest in obtaining biochar with high Si content, as it is also more cost-effective than silica fume (Gupta and Kua, 2020). The optimised EFB run was found to have a higher Si content (3.68%) than PKS (0.44%). Additionally, higher traces of Mg and Ca were detected in most EFB biochar samples, while PKS biochar contained traces of Fe.

3.2.2.4 Biochar Thermal Stability

In Figure 3.22 (a)–(d), TGA was performed for all pyrolysis runs to understand the effect of temperature, heating rate, and residence time on the thermal stability of biochar. Figure 3.22 is divided into different temperatures: 300°C (a), 500°C (b), 700°C (c) and (d), which is a combination of different runs to analyse the differences between the temperatures collectively. The analysis has been broken down to three stages similarly to the Section 3.2.1.4. In Figure 3.22 (a), it can be observed that from temperature at 300°C to 350°C (stage 2), there is a drastic weight loss for all rounds of biochar produced at a pyrolysis temperature of 300°C. This is due to the low thermal stability of biochar produced at low temperatures, which correlates with its low chemical stability. In Figures 3.22 (b) and (c), the pyrolysis temperatures of 500°C and 700°C exhibit a similar pattern to each other, with the exception of the run in Figure 3.22 (b) that was conducted with a heating rate of 10°C/min and a residence time of 10 minutes. This suggests that both parameters contribute to the thermal stability of the resulting biochar.

Further investigation into which parameter has a greater correlation with thermal stability shows that in Figures 3.22 (a), (b), and (c), the runs with the lowest weight loss

from 25°C to 900°C (stage 3) are those with a higher residence time: (a) 20 minutes, (b) 155 minutes, and (c) 120 minutes, respectively. Figure 3.22 (d) shows the optimised run at 455°C alongside other pyrolysis temperatures and biomass for direct comparison. Biochar produced at 800°C has the highest thermal stability, while the lowest is observed at 200°C. It is noted that the biomass and the 200°C run show the same pattern, which is due to the fact that the biomass does not carbonise at low pyrolysis temperatures below 300°C, regardless of heating rate and residence time. Most studied pyrolysis temperature for cement replacement mentioned in the literature is 500°C. Therefore, to make a comparison using the same heating rate and residence time as the optimised run, an additional run at 500°C was carried out. This run and the optimised run show minimal weight loss up to 325°C. From 325°C to 625°C, the optimised run exhibited a greater decrease than the biochar produced at 500°C, which showed a gradual, uniform decrease and continued to lose up to 25% of its weight at 900°C. However, the optimised run showed a 50% weight loss at 900°C. An overall comparison between these two runs suggests that both potentially have similar heat resistance when used as a cement replacement. . Another study that investigated similar fibrous nature of biomass which was date palm leaf exhibited similar patterns for thermal stability for temperature of 300 to 600°C (Ben Salem et al., 2021).

A study in which paper mill sludge and rice husk biochar were produced at 500°C, and poultry litter biochar at 450°C, showed a similar trend: a smaller weight decrease at higher production temperatures (Akhtar and Sarmah, 2018a). However, it is noteworthy that this study found that regardless of temperature, different types of biomass used exhibited similar trends but different weight decreases. Similarly, in this study, PKS and EFB showed different weight decreases under the same production parameters. However, they showed similar trends for each biochar type at the set temperature of 300°C, 500°C and 700°C. In Figures 3.16 (d) and Figure 3.22 (d), PKS shows a 22% decrease in weight for biochar produced at 700°C, 15°C/min, and 20 min, which is lower than the 32% decrease observed for EFB. This is due to the lower density and fibrous structure of EFB. As Figure 3.22 (d) illustrates, that the higher the temperature, the greater the weight loss, indicating higher thermal resistance, which directly correlates with the porosity of the biochar and aligns with the results from other studies (Tan et al., 2020; S. Yang et al., 2019).

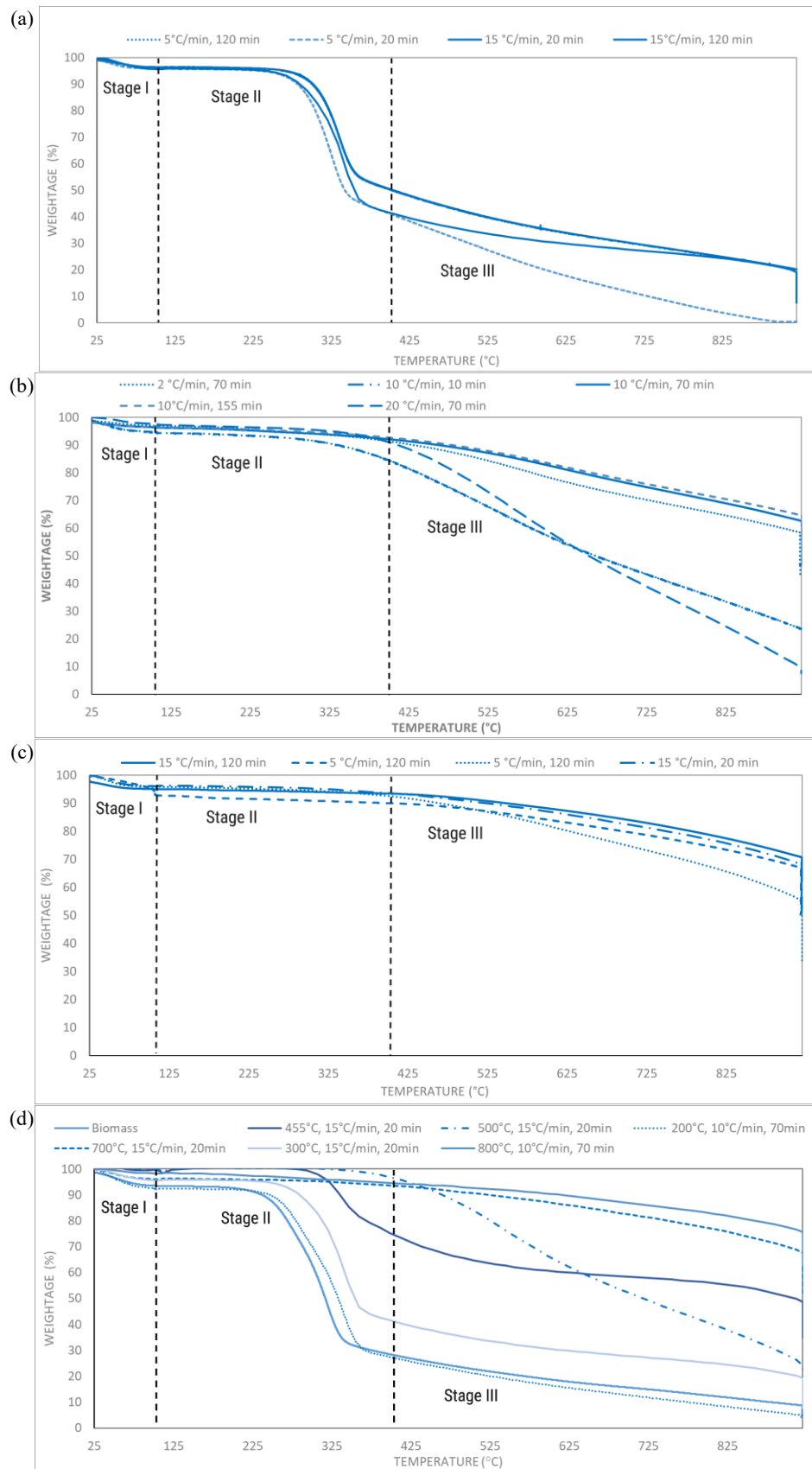


Figure 3.22 TGA analysis EFB pyrolysis runs at (a) biochar at 300°C, (b) biochar at 500°C, (c) biochar at 700°C, (d) biochar at all temperatures with raw EFB biomass.

3.2.2.5 Biochar Morphology

Morphology of biochar when used as a cement replacement has been widely highlighted as crucial for its application. Figure 3.23 shows the scanning electron micrograph of different biochar temperatures of EFB: (a) 300°C, (b) 455°C, (c) 500°C, and (d) 700°C. The cross-sectional area for the EFB can be seen with different shapes and varying uniformity of pores. A similar cross-sectional area has been observed in other studies conducted on EFB, which reports that the pores confirm the decomposition of the original compounds such as lignocellulosic matter of the biomass (Ferreira et al., 2020; Promraksa and Rakmak, 2020a).

Figure 3.23 (c) shows that biochar produced at 500°C has a higher uniformity and shape of pores compared to other temperatures. More evident pores can be seen in Figures 3.23 (b), (c), and (d) than in (a), confirming the complete decomposition and release of more volatile matter from the biomass at temperatures higher than 300°C. Although observation indicates that the material has turned into biochar at 300°C, these SEM images highlight the importance of further investigation of the resultant biochar at high magnification. Another study with EFB showed a similar pore morphology to that of EFB biochar (Salleh et al., 2012), as seen in Figure 3.23 (b). The authors reported that macropores ranging from 5 µm to 20 µm would be responsible for absorption and retention of water. Figure 3.23 (b) of the optimised EFB biochar produced at 455°C shows pores between 3 µm and 6 µm. These properties have been reported to be beneficial when mixed with cement for mortar composites, with pores ranging from 10 µm to 30 µm to retain water during initial hardening (Gupta et al., 2018b; Maljaee et al., 2021b). Similar morphology observation were also seen by the fibrous structure of date palm leaf biochar at 400°C and 500°C (Ben Salem et al., 2021).

Studies that have analysed biochar prior to mixing with cement have reported that due to the high porosity of biochar (honeycomb-like structure), a lower density of biochar mortar composites has been observed, alongside a slight increase in air content and a reduction in workability as it retains water. PKS and EFB have completely different skeletal structures: fibrous and angular. However, both have been subjected to the same thermochemical conversion parameters, allowing for a comparison of morphology based on pore uniformity for each temperature. An increase in porosity of biochar properties would potentially benefit biochar mortar or concrete properties by increasing insulation, decreasing density, and reducing free water. The increase in porosity has

been observed in both optimised biochar at 409°C PKS and at 455°C EFB, which has been mostly described as having a honeycomb-like structure. In terms of pore sizes, it has been observed that for PKS biochar, the average size was 20.43 μm ; however, for EFB biochar, the average size is 4.90 μm .

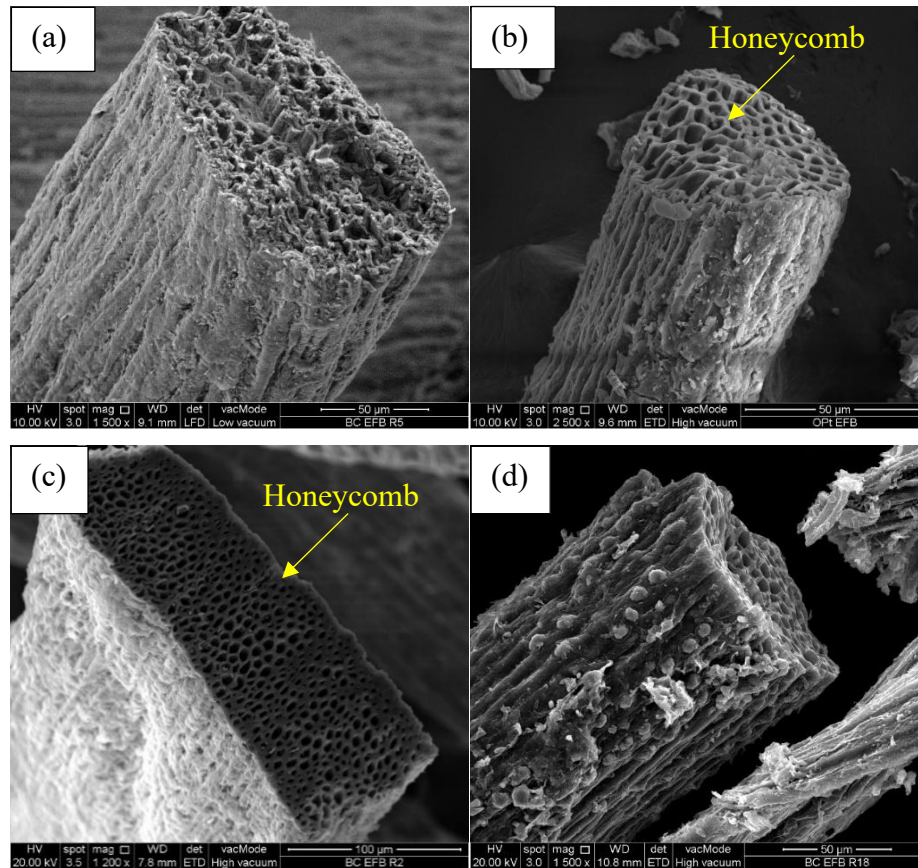


Figure 3.23 FESEM images of empty fruit bunch biochar produced at (a) 300°C, (b) 455°C, (c) 500°C and (d) 700°C.

3.2.3 Optimal Biochar Characterisation

Following the optimisation process of biochar production from both biomasses, further characterisation is crucial to understand and predict its behaviour prior to its use as a cement replacement. Table 3.7 provides the properties of four different types of biochar that was produced and their respective characteristics. As stated in the previous sections on biochar morphology, both PKS and EFB biochar show a honeycomb pattern for the pores. However, the sizes of the pores are not all uniform. The pores play a crucial role in the physical attributes of biochar, like its density, surface area, and adsorption capabilities. Even though the biochar yield, as stated previously, is directly correlated to the temperature, this is not the case with the density results, which highlights the importance of the material's volume and nature. An uncommon observation from the

literature is found with the density difference between the two EFB biochar produced. The low density of 0.59 g/cm³ observed for EFB biochar at 455°C is probably significantly influenced by its well-developed porous structure. In particular, the pore size, which plays a crucial role in adsorption and desorption processes, was measured at 144.7 Å and 141.6 Å. This emphasises that the structural characteristics such as porosity of biochar contribute to its low density.

Table 3.7 Biochar properties and characteristics.

Biomass	Palm Kernel Shell		Empty Fruit Bunch	
Pyrolysis Temperature (°C)	409	500	455	500
Heating Rate °C/min	15	15	15	15
Residence Time (min)	120	120	20	20
Water Absorption (%)	3.825	3.865	4.220	4.210
Density (g/cm³)	1.03	1.13	0.59	1.04
BET				
BET Surface Area (m ² /g)	2.19	35.1	0.815	1.62
Single Point adsorption total pore volume of pores (cm ³ /g)	0.00461	0.0235	0.00295	0.00400
Single Point desorption total pore volume of pores (cm ³ /g)	0.00318	0.0240	0.00289	0.00377
Adsorption average pore width (Å)	84.1	26.8	145.0	98.3
Desorption average pore width (Å)	58.0	27.4	142.0	92.7
Proximate Analysis				
Moisture Content (%)	4.60	1.43	1.66	1.1
Volatile Matter (%)	77.0	21.92	63.6	44.7
Ash Content (%)	3.68	15.19	9.71	12.8
Fixed Carbon (%)	14.7	61.47	25.0	41.4

A higher surface area is always correlated with the temperature at which the biochar is produced (Lahijani et al., 2018). A study reported that PKS has shown a higher surface area in 2 hours at 400°C than wood sawdust at 500°C for 3 hours at 2 m²/g (Shaaban et al., 2014). This emphasises that despite the higher temperature, the difference in feedstock selection is very important. The water absorption capacity for both PKS and EFB is consistent with the literature and shows that biochar with higher pyrolysis temperatures leads to greater water absorption. Water absorption properties are closely related to the total volume of pores for both adsorption and absorption, as this explains the ability of biochar to hold and store water and gas through its pores, regardless of their size and uniformity. Proximate analysis is usually performed to characterise the mechanical and chemical stability of biochar. The content of fixed carbon and ash determines the structural stability of the biochar, while the volatile components are

related to the brittleness of the biochar. Table 3.7 show the calculated proximate analysis from the TGA results. Higher pyrolysis temperatures decrease volatiles in both EFB and PKS, which is consistent with several studies (Shaaban et al., 2014; Tag et al., 2016; Zhao et al., 2017). This is due to the fact that as the temperature increases, the dehydration and thermal degradation of the biomass increases, further cracking the volatiles and converting them into syngas or oil instead of biochar. A study comparing EFB, PKS and oil palm fibres to optimise the yield of pyrolysis products using RSM (Promraksa and Rakmak, 2020a). The authors reported very high surface areas for PKS and EFB of 500 389.02 and 36.11 m²/g, respectively.

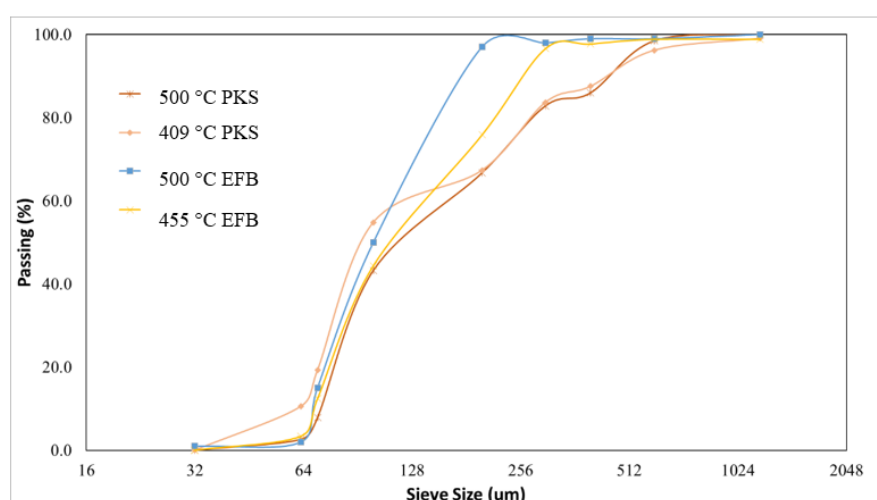


Figure 3.24 Particle Size Distribution of biochar.

Figure 3.24 shows the particle size distribution of the biochar samples and compares the differences and amount of fine particles for each biochar type. The figure shows the percentage of samples passed against the sieve size in micrometres, which is given on a logarithmic scale from 16 μm to 2048 μm. Five curves are plotted, corresponding to different materials: Biochar produced from PKS at 409°C and 500°C, and biochar produced from EFB at 455°C and 500°C. The distribution trends indicate a non-uniform particle size distribution. Since the grinding process was standardised for all samples, the differences in distribution are due to the nature of the material. The trends show that the PKS biochar has a less linear trend in size than the EFB biochar. This is due to the obvious difference in the nature of the materials, as PKS is granular while EFB is fibrous. It is important to determine the median size of the biochar in order to understand its behaviour when mixed with cement. The median lies at the intersection of each distribution that is 50% on the y-axis. The approximate median particle sizes

are 90 μm for 409°C PKS, 100 μm for 500°C EFB, 110 μm for 455°C EFB and 120 μm for 500°C PKS.

Figure 3.25 shows the FTIR spectroscopy analysis of four different types of produced biochar and their original biomass. The presence of functional groups was detected in the wavenumber range of 500 - 4000 cm^{-1} , a standard unit used in infrared spectroscopy. Each functional group has different percentage transmittance values representing the absorption of infrared light by the biochar and biomass samples. Using the table in Appendix B, the basic functional groups were identified. From the trends observed for each material, it is clear that both biomasses have a higher transmittance percentage of groups. This result is similar to other studies conducted when comparing different biomasses (date palm, coffee and PKS) with biochar at different temperatures (Ben Salem et al., 2021; Mukherjee et al., 2021; Promraksa and Rakmak, 2020). This difference is due to the degradation of hydroxyl groups in the biomass at temperatures above 400°C.

The large dips at about 1100 cm^{-1} and 3350 cm^{-1} are identified as oxygen groups ether (C-O) and alcohol (O-H) for the biomass materials. The presence of C-O and O-H is related to the cellulose content of the biomass, and the decrease in cellulose content in the biochar materials proves that they were broken down during pyrolysis. The loss of the presence of these groups O-H and C-H, which are not stable, leads to an increase in surface area and the formation of pores during pyrolysis (Mukherjee et al., 2021). alkenes (C=C) are detected at around 1500 cm^{-1} in both biomass and show minor presence in biochar, although they are more clearly recognisable in biochar produced at temperatures of 500°C. From the results of this study, it can be deduced that the definition of the peaks decreases with increasing temperature, as was also found in another study (Lahijani et al., 2018). Another study analysing PKS biochar and biomass showed similarly intense C=C and O-H peaks (Promraksa and Rakmak, 2020). The expansion between 3000 and 3500 cm^{-1} is also identified as hydroxyl group O-H in both biomasses. The biochar samples show no evidence due to the dehydration reaction and loss of volatile compounds during pyrolysis (Mukherjee et al., 2021).

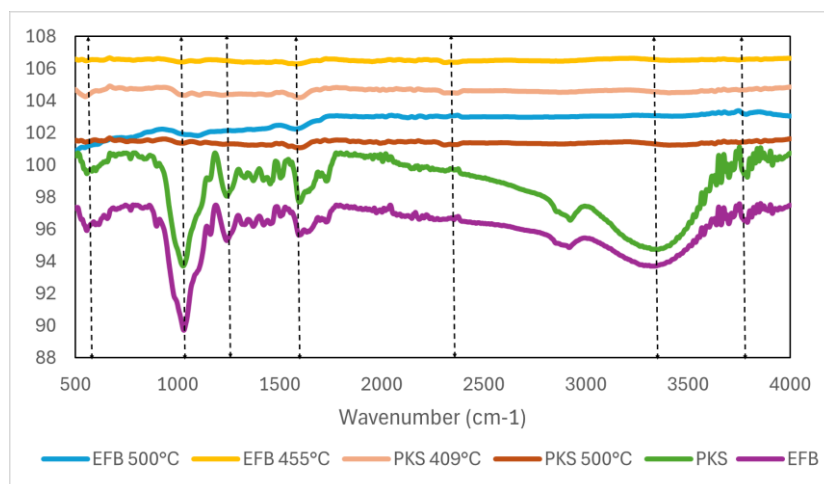


Figure 3.25 FTIR analysis of biomass and biochar.

Figure 3.26 shows the different crystalline phases of all types of biochar and their original biomass. The crystalline phases of the material were detected in a range of 10 to 90 2θ $^\circ$, which measures the angle between the two X-ray beams (incident and diffracted). Each detection of a crystalline phase has a different intensity. It is common for biomass to have finer peaks than biochar. As biochar from the biomass of wood, coffee, olive pits and rice husks have shown similar findings (Maljaee et al., 2021b; Mukherjee et al., 2021). These results are similar to the results of the FTIR analysis. The increase at about 20° to 30° 2θ is identified as cellulose in both PKS and EFB; however, the peak is more pronounced in PKS, indicating a higher cellulose content. The weaker increase at around 20° to 30° 2θ for the biochar samples shows the degradation of cellulose during formation. The increase specifically at 23° 2θ is identified as the presence of amorphous silica (Asadi Zeidabadi et al., 2018), which is present in all samples. The broad hump at 43° in the biochar represents graphitic and amorphous cellulose indicating the destruction of lignocellulose in the carbon matrix (Mukherjee et al., 2021).

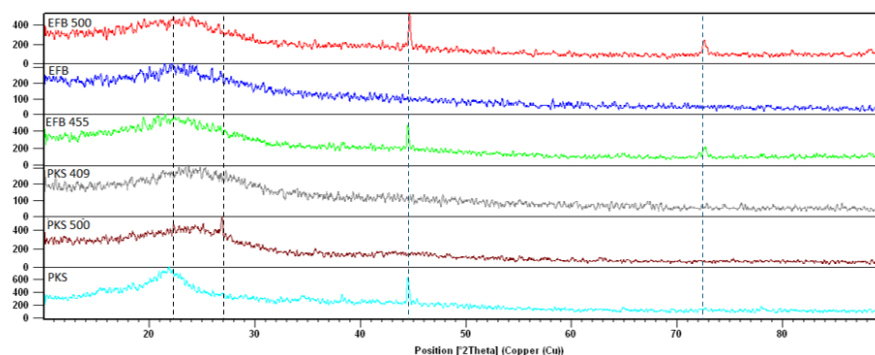


Figure 3.26 XRD analysis of biochar.

3.3 Summary of Findings

This chapter dealt with the first objective, namely the optimisation and production of biochar from PKS and EFB to be used as supplementary cementitious material. The optimisation process was carried out with RSM. The same pyrolysis parameters were set for both biomass to highlight the different behavioural changes that occur in the with the different nature of the material, as PKS is granular and EFB is fibrous. The factors that were varied to produce biochar were the pyrolysis temperature, heating rate and residence time. The optimisation process was carried out by maximising the responses, including the biochar yield, carbon, silicon and potassium content of the biochar and minimising the oxygen content. The final optimal parameters were 409°C, 15°C/min, 120 min for PKS and 455°C, 15°C/min, 20 min for EFB. Using the RSM model and mathematical equations, the significance of each pyrolysis parameter was determined, with temperature being the most important, followed by residence time and heating rate. The order of importance of these processes was also confirmed by thermally analysing the biochar at each individual run. After the optimisation process, biochar at 500°C was produced from both biomass. Biochar at 500°C was chosen as majority of the literature has used it and deemed it's the most suitable temperature for supplementary cementitious material. The four different biochar 409°C PKS, 500°C PKS, 455°C EFB and 500°C EFB were all mass-produced and used as cement replacement in the following chapter.

Chapter 4 Palm Oil Waste Biochar as a Cement Replacement

This chapter consists of utilising four types of palm oil waste biochar as a cement replacement for both mortar and concrete composites. Each mix of composites are then analysed and compared to the control samples. The content of this chapter covers the second and third objectives of this research. Which include evaluating different percentages of cement replacement with biochar mortar composites and then evaluating biochar concrete composites with the optimal percentage of cement replacement. Identifying suitable applications is essential when designing a building material composite that includes supplementary cementitious materials. This process involves evaluating the combination of properties of these materials to determine their suitability for various applications. By thoroughly analysing their characteristics, the most suitable applications can be effectively aligned to ensure optimal performance and functionality in building material. Multiple applications for mortar are possible, like masonry work, plastering, exterior work, tile installation, soundproofing and fireproofing. Additionally, for concrete, most applications would be for low structural elements such as pavement, driveways and drainage.

4.1 Methodology

4.1.1 Mortar Mix Preparation

Mortar mix ratio used in this research is 1:0.51:2 cement: water: sand (600 kg/m^3 , 309 kg/m^3 and 1200 kg/m^3). The amount of biochar used depends on the mass percentage replacement of cement from 1-8%. Fine aggregate used is quarry sand, and cement is type II with the properties given in Table 4.1. Ground biochar, sand and cement were evenly dry mixed in a metal plate. Following that, the mix was transferred to a wider plate for easier mixing with two metal scrappers when the water is added. After 24 hours of casting, the samples were demoulded and labelled as shown in Figure 4.1. The samples were then water-cured for 7 and 28 days for further testing.

Table 4.1 YTL Cement Type II properties.

Type of Cement: Castle	MS EN 197-1:2014 Cement II B-L 32.5 N	Results
Sulphate Content	Not more than 3.5	2.0
Chloride Content	Not more than 0.1	0.01
Setting Time: Initial	Not less than 75	135
Soundness	Not more than 10	1
Compressive Strength (Mortar Prism): 7 days	Not less than 16	25.0
:28 days	$32.5 < x < 52.5$	36.0

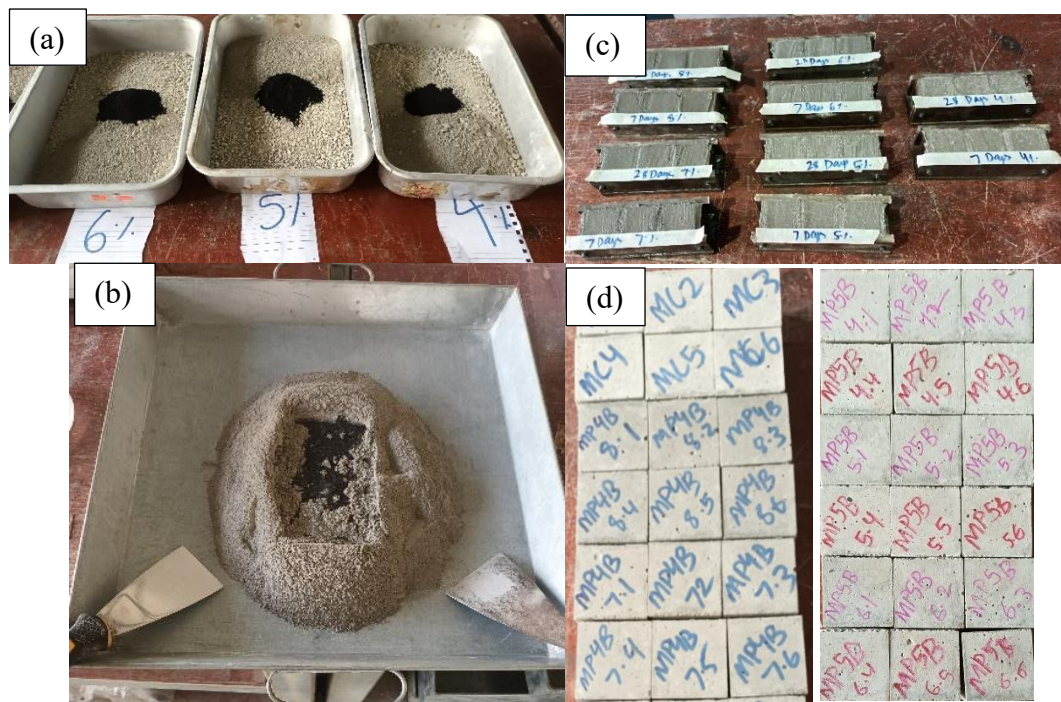


Figure 4.1 Preparation of mortar mix (a) materials, (b) mixing process, (c) casting (d) demoulding and labelling of samples.

4.1.2 Concrete Mix Preparation

Concrete mix ratio used in this research is 1:0.56:1.33:2.44 cement: water: sand: coarse aggregate (450 kg/m^3 , 250 kg/m^3 , 600 kg/m^3 and 1100 kg/m^3). The trial and error of different mixes tested have been mentioned in [Appendix C](#). The amount of biochar used was based on the evaluation conducted on mortar composites, which has been concluded to be 4%. The detailed discussion is mentioned in Section 4.2.1. Cement type II was used for concrete. Similarly, to the mortar mix preparation biochar was ground into powder and then added to the cement, fine and coarse aggregate. After 24 hours of casting, the samples were demoulded and labelled. The material preparation, mixing process, and casting are shown in Figure 4.2. To distribute the biochar evenly half of

the biochar quantity was first dry mixed with the fine aggregate. Followed by adding the cement and the other half of the biochar. Half of the coarse aggregate was added with half of the water quantity and allowed to mix evenly, followed by adding the rest of the material. The mixing machinery was stopped twice during mixing process to scrape the dry sides of the mixer and pushed to the middle for steady mixing. When an even mix was observed, the slump test was performed, and then the sample was casted into the moulds. The samples were then water-cured for 7 and 28 days for further testing.

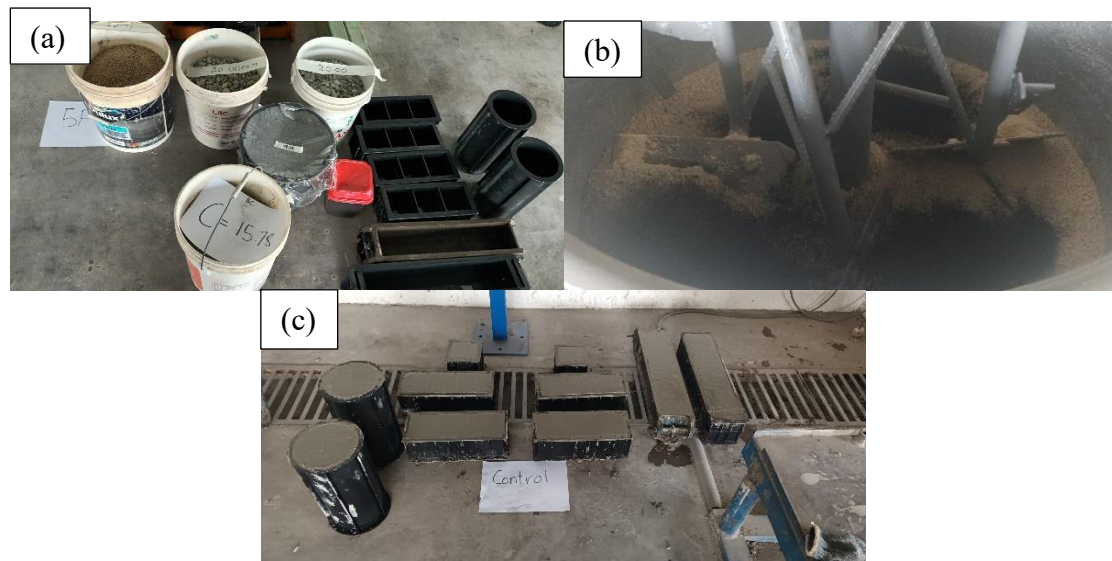


Figure 4.2 Concrete mix preparation (a) materials, (b) concrete mixing process and (c) casted samples.

4.1.3 Physicochemical Properties

A series of physical and chemical analyses were performed on the concrete and mortar composites at optimised percentage of cement. The methodologies for FESEM-EDX (microscopic viewing), FTIR (variation of surface functional groups), XRD (variety of crystalline phases) and TGA (thermal insulation properties) after 28 days of water curing have been stated in Chapter 3, Section 3.1.4. Prior to the analysis, the samples have been crushed to powder form by a mortar and pestle, as shown in Figure 4.3.



Figure 4.3 Mortar and pestle to crush the biochar concrete and mortar samples.

4.1.4 Compressive Strength

Mortar samples were casted using the moulds of 50 mm × 50 mm × 50 mm. Mortar composites with biochar percentages of 1-8%, were casted in three replicates and for each percentage the average result has been taken as the final compressive strength. The casting procedures has been done following standard BS EN 1015-11 2019 (BS EN 1015-11, 2019). A total of 6 samples were scheduled to be tested for 7 and 28 days for each percentage of biochar. Similarly for concrete, 6 samples were made with moulds of 100 mm × 100 mm × 100 mm and tested accordingly referring to BS EN 12390-3 2019 (BS EN 12390-3, 2019).

4.1.5 Flexural Strength

Moulds of 40 mm × 40 mm × 160 mm were used to cast mortar samples, as shown in Figure 4.4. The samples were cured for 28 days and then tested in accordance to BS EN 1015-11 2019 (BS EN 1015-11, 2019). For each mix (1-8% of biochar), three samples were casted, and the average result has been taken. Similarly, moulds of 100 mm × 100 mm × 500 mm were used for casting concrete samples and tested after 28 days referring to BS EN 12390-5 (BS EN 12390-3, 2019). Equation (4.1) was used to calculate the flexural strength. F represents the maximum flexural load; length (l), width (b), and thickness (d) are the dimensions of the mould used.

$$f = 1.5 \frac{F \times l}{b \times d^2} \quad (4.1)$$



Figure 4.4 Biochar mortar composites casted for 40 × 40 × 160 mm.

4.1.6 Capillary Water Absorption

The composites' capillary water absorption was measured after 28 days of water curing as in accordance to ASTM C1585 (ASTM C1585, 2020; Belaadi et al., 2023; Kushwah

et al., 2024; Tan et al., 2020). Three samples of 50 mm × 50 mm × 50 mm for mortar and 100 mm × 100 mm × 100 mm for concrete were casted. The samples were oven dried at 105°C for 48 hours and measured (M_{dry}). The samples were then kept in water and were periodically removed to measure their water retention at different time intervals. The samples were weighed at the following time intervals: 5 minutes, 30 minutes, 1 hour, 24 hours, 48 hours, and 72 hours. (M_{sat}) is the saturated mass measured at each interval. Equation (4.2) was used to calculate the water absorption percentage at every interval.

$$Water\ Absorption\ (\%) = 100 \times \frac{(M_{sat} - M_{dry})}{(M_{dry})} \quad (4.2)$$

4.1.7 Porosity

Similar to the water absorption test, three samples of 50 mm × 50 mm × 50 mm for mortar and 100 mm × 100 mm × 100 mm for concrete were casted and water cured for 28 days. A hydrostatic balance was used to measure the mass of the samples immersed in water (M_{water}). Samples were measured saturated surface dry in air ($M_{sat/air}$). The samples were then oven dried at 105°C until constant mass (M_{dry}). The following equation (4.3) was used to calculate the porosity of the samples (Belaadi et al., 2023; Kushwah et al., 2024).

$$Porosity\ (\%) = 100 \times \frac{(M_{sat/air} - M_{dry})}{(M_{sat/air} - M_{water})} \quad (4.3)$$

4.2 Results and Discussion

4.2.1 Optimisation of Cement Replacement

4.2.1.1 Effect of Cement Replacement with Compressive Strength

Compressive strength of biochar mortar composites for 7 and 28 days of water curing with a cement replacement of 1-8% is shown in Figure 4.5. The four types of biochar were used which include the two optimised temperatures derived from the first objective, namely 409°C PKS and 455°C EFB, and the other two biochar prepared from PKS and EFB at 500°C. The results also include the control sample without the addition of biochar. It is also important to note that the ratio of water and sand to cement were constant for all samples to better understand the behaviour of biochar when mixed with cement, and no superplasticizer was used. The legend for both figures can be found at the top of the diagram, as all figures (Figure 4.5 – 4.9) in this chapter have same colour code for each biochar type. The current objective is to identify the type and amount of biochar that can be used to attain a compressive strength of 25 MPa while still being in close relation to the control sample. This is to ensure that when evaluating other mechanical properties, the optimal mix with the most favourable type of biochar has the highest compressive strength with maximum amount of biochar.

Highest improvement in compressive strength was observed with 1% cement replacement using 455°C EFB, showing an increase of 10.56% (19.43 MPa) after 7 days and 25.76% (27.79 MPa) after 28 days. The lowest compressive strength after 7 days was achieved by 4% replacement of 409°C with a decrease of 27.68% (14.25 MPa) and after 28 days with 8% replacement of 455°C with a decrease of 31.14% (17.56 MPa). All biochar mortar samples for the 7 and 28 day curing showed a similar trend of decrease from 1 to 8%. Recognizing the trends for PKS, a higher compressive strength occurred at 500°C compared to 409°C, which is consistent with other studies (Akhtar and Sarmah, 2017; Gupta and Kua, 2018b; Wang et al., 2020b). The studies reported that the higher the temperature, the greater the increase in strength, as shown in Figure 2.4. However, EFB showed a higher trend at 455°C than at 500°C. This could be due the temperature difference is less than 50°C. For the mortar composite samples, the overall lowest compressive strength was found at 8% replacement for both 7 and 28 days curing and the highest compressive strength at 1% replacement for both curing durations. This proves the hypothesis and agrees with the literature that biochar can

only increase and improve properties at lower replacement percentages and that it is not necessary to experiment with higher replacement percentages, as for this research higher than 8% (Gupta et al., 2018b; Khushnood et al., 2016; Maljaee et al., 2021b; Sirico et al., 2020a).

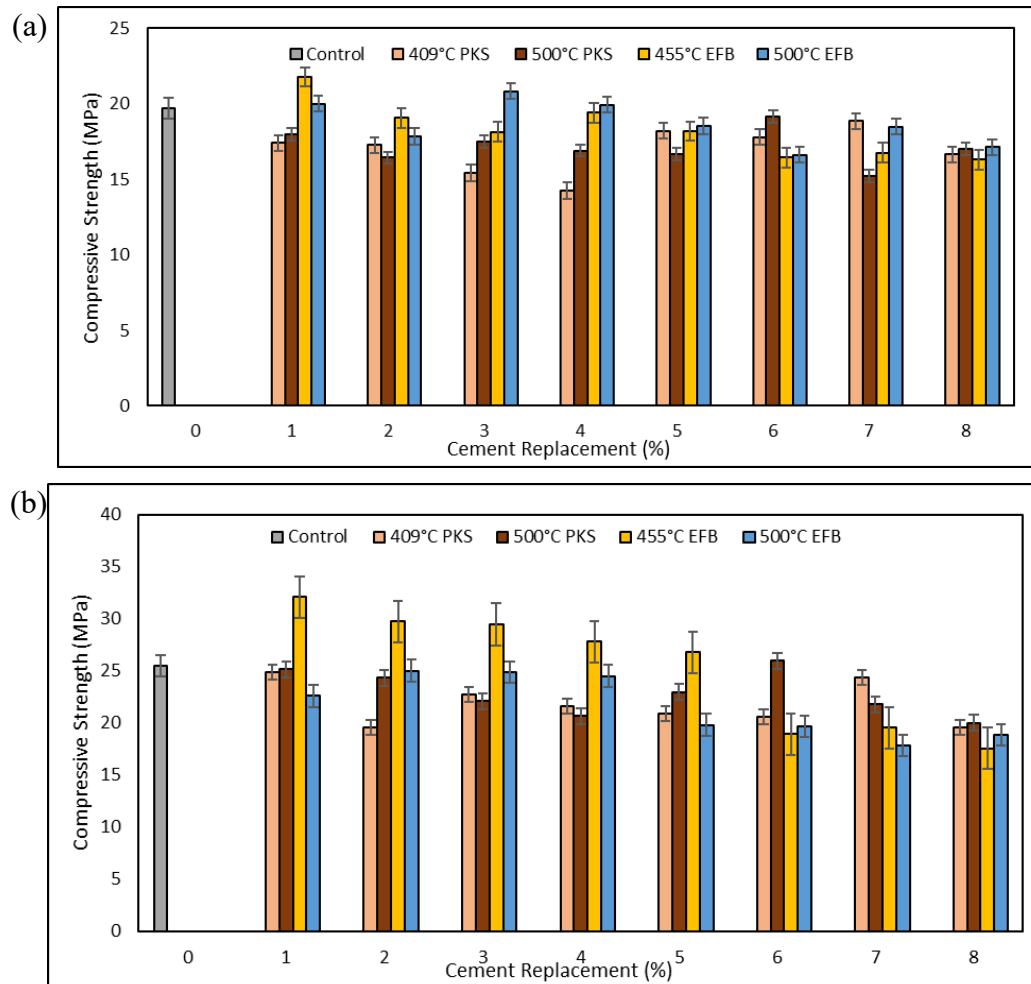


Figure 4.5 Compressive Strength of biochar mortar composites (a) 7 days curing and (b) 28 days curing.

Current research reveals that the results with the biomass EFB and PKS biochar are consistent with numerous other studies showing a higher increase in compressive strength with 1-2% replacement of different types of biochar; wood waste (Gupta and Kua, 2018a), food waste (Gupta et al., 2018b), corn stover (Praneeth et al., 2020a), palm rachis (Boumaaza et al., 2023). All mixtures in this study showed non-linear variations in the increase and decrease of 7 and 28 day strength. Except for the 455°C EFB biochar, which showed a linear decrease from 1% replacement to 8% replacement. It is known that the decrease in compressive strength with increasing amounts of biochar is due to the presence of microcracks caused by the high proportion of porous structure in the

biochar. This allowed more voids to form in the interfacial transition zone (Haris Javed et al., 2022; Praneeth et al., 2021; Wang et al., 2019). Of all the mixes 409°C PKS exhibited the lowest overall strength, while 455°C EFB showed the highest followed by 500°C PKS and 500°C EFB.

The evaluation of the mortar composites after 7 days of curing showed that the mix with the highest amount of biochar content that achieved a higher compressive strength than the control was 4% at 500°C EFB, which corresponds to an increase of 1.26% (19.95 MPa) compared to the control. After 28 days of curing, the mix with 4% and 5% 455°C EFB showed an increase of 8.9% (27.79 MPa) and 4.98% (26.77 MPa) respectively. This is only 1% difference to the cement replacement which emphasises that a small amount of biochar leads to a significant increase in strength, which is almost twice as high. The effect of biochar on compressive strength can be described as an internal micro filler effect that improves cement hydration due to the small particle size and porous structure (Souradeep Gupta et al., 2022b). This mechanism states that as the amount of porous biochar increases, the water retention capacity increases, which reduces the amount of water required for cement hydration and thus results in lower strength. In the analysis in Chapter 3 (Section 3.2.3), 455°C was found to an average particle size of 110 μm . Particle size distribution in Figure 3.24 shows that the EFB (455°C and 500°C) biochar has a higher number of finer particles than the PKS (500°C) biochar, which is reflected in the higher compressive strength of the EFB biochar. Except for 409°C PKS that had the lowest average size of 90 μm , this could mean that the cement hydration products formed were low and did not make up for the gaps in mortar mix that lead a high porosity nature of the mix as can be seen from Figure 4.6 (b) showing the porosity.

The highest increase in compressive strength observed in this research, was 25.67%, and aligns with similar findings reported in other studies. Gupta and Kua, (2018a) reported a compressive strength increase of 26% when using 2% biochar from wood waste produced at 500°C as an additive. This required additional pretreatment steps to produce the mortar samples and evidently biochar that was produced at a higher temperature than the EFB biochar used in this research, which was produced at 455°C. Another study exhibited 29.7% increase in compressive strength with 5% olive tree biochar (Kalderis et al., 2024). This high increase is due to the fact that the biochar is used as an additive and not as a cement replacement which would result in a less

sustainable option. The more sustainable material is used, the more the recycling of waste is promoted, the use of landfill is avoided and the demand for cement production is reduced. On the other hand, Qin et al., (2021a) reported a 30% increase using eucalyptus biochar produced at 500°C but with 6.5% cement replacement. Another study, which contradicts the high increase in compressive strength results, by 5% cement replacement with switchgrass biochar showed an increase by 10% only (Choi et al., 2012). This was due to the fact that the authors in the study increased the water-cement ratio content with the biochar content. As factors such as the water-cement ratio would have a crucial role in the use of biochar due to the porosity of biochar and increasing the water-cement ratio would lead to more formation of voids in the composite. The water-cement ratio was kept constant in this study. The mentioned results also highlight that even with same percentage replacements of biochar, the original biomass is highly dependent. As most studies have used wood biochar (mentioned in Table 2.4 and Figure 2.1) it is important to further investigate with other types of biomass.

In the early compressive strength in Figure 4.5 (a), the increase in strength of biochar was not as high as in the 28-day curing in Figure 4.5 (b). This could be due to the delay in the internal curing effect of the biochar, where it absorbs the water in the early stages and releases it later to further increase the cement hydration. This delay could be related to the BET surface area of the biochar. As in this research, all surface areas were low compared to the other studies that showed higher increase in early strength more than 28-day strength (Gupta and Kashani, 2021; Gupta and Kua, 2018a; Maljaee et al., 2021a; Manjunath et al., 2024). The pozzolanic process is the increase in cement hydration due to the reaction of calcium hydroxide in cement with pozzolanic substances such as silica and alumina elements. From Table 3.5, 455°C EFB (3.68%) has a much higher silica content than 409°C PKS (0.44%) in Table 3.3. Due to the pozzolanic effect, the high silica content in the EFB biochar promoted the hydration products of the cement, resulting in higher compressive strength (Haris Javed et al., 2022). Pozzolanic activity was also emphasised by materials other than biochar, such as fly ash from sugarcane bagasse, which contained 24% amorphous silica (Alvarenga and Corderairo, 2024). In the study, 20% fly ash was used and the strength was increased by 9%, with an average size of 10 µm. It is important to note that other factors such as the water-cement ratio and superplasticiser were not kept constant. Another that

study used similar ranges of temperature of biochar production (400°C and 500°C) (Manjunath et al., 2024). The authors used areca nut husk biochar produced from both and replaced cement by 2%. For 400°C biochar the compressive strength increased at 7 and 28 days by 16% and 21% and for 500°C biochar, the increase was 27% and 34% for 7 and 28 days. The difference is largely due to the fine particle size of the biochar in comparison to this research, as the average size of the areca nut shell biochar at 500°C is 783 nm and in this research 100 µm for 500°C EFB and 120 µm for 500°C PKS. The particle size of the biochar would contribute to the formation of gaps in the composite by increasing the porosity and decreasing the compressive strength. To gain a better insight into the effect of palm oil waste biochar on compressive strength, some comparisons with other studies have been summarised in Table 4.2.

Table 4.2 Compressive strength after 28 days curing of mortar composites with different supplementary cementitious material.

Material	Amount (%)	Added/ Replaced	Effect	References
Biochar 455°C EFB	1	Replaced	Inc ^a 25.67%	This Research
Biochar 500°C PKS	6	Replaced	Inc 1.8%	This Research
Biochar 455°C EFB	4	Replaced	Inc 8.9%	This Research
Biochar 500°C Wood Waste	1	Replaced	Inc 20%	(Tan et al., 2020)
Biochar Switchgrass	5	Replaced	Inc 10%	(Choi et al., 2012)
Biochar 500°C Wood Saw Dust	2	Added	Inc 26%	(Gupta and Kua, 2018a)
Biochar 500°C Palm Rachis	1	Replaced	Inc 13%	(Boumaaza et al., 2023)
Sugarcane Bagasse Fly Ash	20	Replaced	Inc 9%	(Alvarenga and Cordeiro, 2024)

^aInc: Increased

4.2.1.2 Relation of Compressive Strength with Other Mechanical Properties

Figures 4.6 shows the 28-day compressive strength of the biochar mortar composites with respect to density, porosity, water absorption and flexural strength. 1-8% biochar was used as cement replacement with the same water and sand to cement ratio. For each graph, a different mechanical property is represented with line graphs following the secondary y-axis. These combination charts were created to illustrate the different trends in each biochar and the correlation between compressive strength and each other property. Since biochar had the greatest effect on compressive strength compared to all the other mechanical properties, it was used as a basis for comparison to evaluate and optimise the cement replacement to be used.

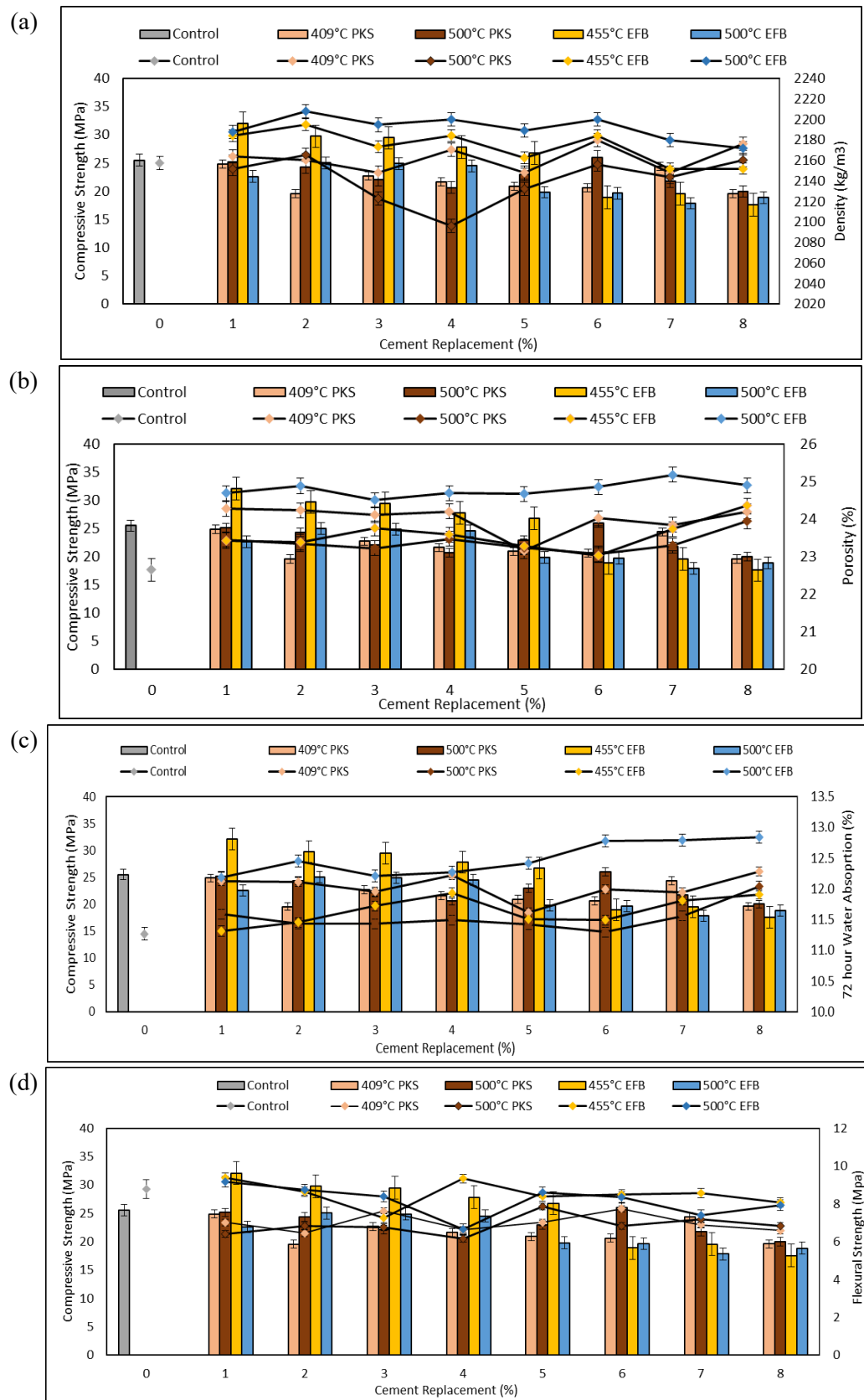


Figure 4.6 Mechanical properties with 28 days compressive strength of biochar mortar composites (a) density, (b) porosity, (c) 72 hr water absorption and (d) 28-day flexural strength.

With each type of biochar used in the mortar composites, the hardened density was both increased and decreased. The results of the hardened density of the biochar mortar composites ranged from 2208 kg/m³ to 2165 kg/m³ and the density of the control sample was 2157 kg/m³, as shown in Figure 4.6 (a). The highest density was achieved at 2% cement replacement with 500°C EFB which is 2.4% increase from the control and the lowest at 2% 500°C PKS with a 2.8% decrease. On the other hand, the porosity and water absorption rate increased for all biochar mortar composites compared to the control sample, indicating that the porous nature of the biochar significantly affected the mortar mix regardless of its production temperature, surface area and particle size.

The porosity results ranged from 25.18% to 23.03% for the mortar composites and 22.65% for the control sample, as shown in Figure 4.6 (b). The maximum porosity was found at 7% cement replacement with 500°C EFB with an increase of 11.2% and the minimum at 6% 500°C PKS. Both were higher than the control by 1.5%. The results of water absorption after 72 hours ranged from 12.84% to 11.30% for the composites and 11.27% for the control sample, as shown in Figure 4.6 (c). The detail results of the water absorption rate test of samples from 5 mins to 72 hours are given in [Appendix E](#). The maximum water absorption was found at 8% cement replacement with 500°C EFB with an increase of 13.9% and the minimum at 6% 500°C PKS that was still higher than the control by 0.3%. It is important to note that both lowest porosity and water absorption mix was shown at 6% 500°C PKS proving a close relation of these two properties. Unlike compressive strength, flexural strength did not show a similar increase. Flexural strength results ranged from 9.39 MPa to 7.62 MPa for all the composites and 8.79 MPa for the control, as shown in Figure 4.6 (d). The maximum flexural strength is achieved by 1% cement replacement with 455°C EFB with an increase of 6.9% and the minimum by 4% with 500°C PKS with a decrease of 29.9%.

Figure 4.6 (a) entails that there is no direct relation between the compressive strength and amount of biochar with the density of the mortar composite. However, there is a relation between the biochar type and density of the mortar composite. From Figure 4.6 (a) it can be clearly reported that the trend followed by 500°C PKS was the lowest and the highest by 500°C EFB followed by 455°C EFB and 409°C PKS. The density trends between the two different biomass are similar to the compressive strength as EFB biochar showed higher strength and density than PKS biochar. This property of the mortar composite can be linked to the BET surface area of the actual biochar as stated

in Table 3.6. The results show that the PKS surface area is much higher than that of EFB, and the highest surface area exhibited by 500°C PKS as 35 m²/g. This means that the increased surface area of the biochar drastically decreased the mass of the mortar composite. With regard to the second objective, optimising the maximum amount of biochar to achieve similar functions to the control. The density of the mix with 4% 455 EFB increased slightly by 1.3%. The slight increase in density is due to an increase in the compactness of the cement matrix with biochar, as the compressive strength was also increased.

Both porosity and water absorption properties in Figure 4.6 (b) and (c) have similar trends of each biochar as 500°C EFB show the highest results followed by 409°C PKS, 455°C EFB, 500°C PKS and the lowest was the control. Proving that the porous biochar nature significantly affects these properties regardless of the biomass type. In comparison with the amount of biochar added at 8% the resultant water absorption is much higher than the porosity. Meaning that the porosity of the sample caused with the increased amount of biochar allowed a higher amount of water diffusion within the mix at 72 hours. The results conveyed that even though the pore volume and water absorption of 455°C EFB biochar is higher than 500°C EFB biochar. The mortar composites with 500°C EFB showed higher water absorption and porosity. This could be due to the mean particle size of 500°C EFB (100 µm) lower than 455°C EFB (110 µm). Smaller particle size and high surface area of biochar would factor in the water absorption of mortar composites as reported by another study (Gupta et al., 2021b). Another study experimented with biochar from palm rachis with different pyrolysis temperatures and cement replacement from 1 to 5% (Boumaaza et al., 2023). They reported similar findings where higher portion of biochar increased both porosity and water absorption and the highest were composites with biochar produced at 500°C. Additionally, the study highlighted negative relation between porosity of a mix and the compressive strength exhibited by mixes. As the highest compressive strength by 1% of 455°C EFB had a porosity increase from the control by only 3.4%. Moreover the highest porosity exhibited by at 7% of 500°C EFB had compressive strength decrease from the control by 30.0%.

As mentioned in the literature most studies have experimented on biochar addition rather than cement replacement. Therefore, a study that added 2% of olive tree biochar to mortar showed a decrease of 27.8% of porosity and 27.3% decrease in capillary

absorption after 28 days (Kalderis et al., 2024). These findings differ from the current study as the biochar added as a filler and reduced the gap in the cement and aggregate matrix in the interfacial transition zone by making the mix more compact as it promoted cement hydrates formation. This also allowed an increase in the flexural strength with 5% addition of the same biochar by 13.3% (Kalderis et al., 2024). Whilst optimising to obtain a higher quality mortar composite it is more adequate if both permeability and water absorption are significantly higher than that of the control to avoid water ingress. Concluding the mix with 4% 455°C EFB has a porosity increase of 4.2% and water absorption of 5.9%. Although both properties are still higher than those of the 1% 455°C EFB mix, this is in line with the objective of identifying the most suitable mix. The aim is to match acceptable material properties with the highest biochar content. Therefore, the mix with 4% biochar is proposed as the optimal solution.

The flexural strength of the mortar composites after 28 days curing is shown in Figure 4.6 (d). The trends clearly show that mortar composites with 455 °C EFB exhibited the highest flexural strength, followed by 500 °C EFB, 409 °C PKS, with 500 °C PKS showing the lowest strength. For both type of biomass the optimised temperature showed a better flexural strength than 500°C opposing most of the literature as shown in Figure 2.5. This highlights the importance of choosing the type of biomass when utilising biochar as a supplementary cementitious material (Khushnood et al., 2016; Suarez-Riera et al., 2020). To prove this theory, a study using wood waste biochar at 500°C as an addition by 1% increased the flexural strength by 4.6% (Gupta et al., 2018). With an advantage of utilising biochar as cement replacement instead of using it as an additive this research with 1% 500°C EFB increased the flexural strength by 4.2% (9.16 MPa). A study that compared biochar as cement replacement and additive reported that when 2% of biochar was used as a cement replacement, the flexural strength decreased slightly by 2% (Suarez-Riera et al., 2020). However, when used as a filler and premixed with a water superplasticiser solution, an increase of more than 15% was observed. Comparing the use of 1% of 455°C EFB that tripled the increased the strength by 6.8% (9.39 MPa). A similar 6% increase was found by another study with 2% 500°C wood waste biochar addition to the mortar mix (Gupta and Kua, 2018a). Additionally, the study had pretreated the biochar prior to adding to the mortar by pre-soaking in water. This proves that the optimised biochar produced in this study is more beneficial, as no

pre-treatment was used, and the biochar was used as a replacement rather than an additive, still allowing for an increase in flexural strength.

As shown in Figure 4.6 (d) there are only three mixes that exhibited higher flexural strength than the control which are 1% 455°C EFB (9.39 MPa), 1% 500°C EFB (9.16 MPa) and 4% 455°C (9.33 MPa). This is consistent with the decision to use 4% 455°C EFB in order to achieve appropriate mechanical properties through a higher use of biochar. The reason PKS biochar showed a less flexural strength compared to EFB biochar could be due to the fibrous nature of EFB and angular structure of PKS. Which was previously highlighted that the shape of the biochar affects the mechanical properties (Maljaee et al., 2021a). The fibrous nature of the EFB in lined with cement and sand matrix and did not affect the tensile plane as much as PKS. Similar to the compressive strength, a decrease in flexural strength was observed with increasing amounts of biochar used, which is consistent with the literature on the general behaviour of biochar (Gupta et al., 2018b; Khushnood et al., 2016; Maljaee et al., 2021b; Sirico et al., 2020a).

It is important to differentiate the mortar and concrete composites as each would offer a different application. For this reason, each biochar is first tested as a cement replacement from 1 to 8% in mortar composites. Studies that have experimented on cement replacements higher than 8% biochar produced from a higher temperature than 500°C proved to show lower compressive strength (Qin et al., 2021a; Tan et al., 2020). This was done by optimising all mechanical properties with the aim of obtaining the mix with the highest percentage of biochar as a cement replacement which fulfils the second objective of this research. According to the above discussion and considering a higher strength and other properties than the control the optimised mix would contain 4% 455°C EFB. Thus, the second objective, optimising the amount of biochar of 4% was achieved. Experiments with 4% of biochar with concrete composites are discussed in the next section.

4.2.2 Biochar Concrete Composites

4.2.2.1 Impact of Biochar Type with Compressive Strength

Figures 4.7 to 4.9 show the mechanical properties of biochar concrete composites with 4% of biochar from 409°C PKS, 500°C PKS, 455°C EFB and 500°C of EFB with the control sample. The figures have been colour coded similarly to the mortar composite

graphs. Figure 4.7 shows the slump results of the concrete composite including the control sample. The control sample has the lowest slump of 38 mm, and the highest was exhibited by 500°C PKS (73 mm) followed by 455°C EFB (65 mm), 409°C PKS (58 mm) and 500°C EFB (48 mm). These results contradict a few studies that suggest biochar has a negative correlation with workability due to its porous nature (Sirico et al., 2020a; Yang and Wang, 2021). The workability of the composites are influenced size of the biochar particles, the surface area and the water retention capacity. The water retention property of biochar is mainly due to the adsorption and desorption pore width and pore volume. The 500°C PKS biochar had the highest mean particle size (120 μm) and had the smallest pore volume and pore width (Table 3.6 from Chapter 3 Section 3.2.3). Similarly, another study also exhibited increased slump with biochar from olive stone, forest wood, and rice husk (Maljaee et al., 2021b). This suggests that the biochar particles have delayed absorbing water from the mix, allowing more water to remain available during mixing. The rest of the biochar types showed similar behaviour and led to an increase in workability. Therefore, all the biochar types used in this study delayed the water absorption for the internal curing effect to take place. This is evidenced by the fact that both the mortar and the concrete showed a decrease in compressive strength after 7 days of curing, as shown in Figure 4.5 (a) and Figure 4.8 (a).

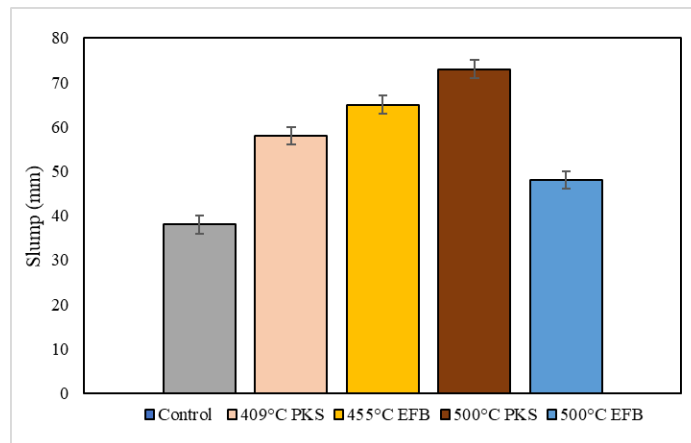


Figure 4.7 Slump of biochar concrete composites with 4% of each biochar type.

Some studies have attributed the increase in early strength of composites to the initial absorption of water from the mix (Gupta and Kashani, 2021; Gupta and Kua, 2018a; Manjunath et al., 2024). The composite with 500°C EFB showed the smallest increase in workability, likely due to its small pore width (0.004 cm^3/g) and large pore diameter

(98.3 Å), in contrast to the 500°C PKS biochar, which had a larger pore width (0.0235 cm³/g) and smaller pore diameter (26.8 Å). From the results it can be concluded that without the use of superplasticiser or an increase in the water to cement ratio compared to the control, the current biochar increased workability. Images of the slump test results have been also provided in [Appendix D](#). Figure 4.8 shows the compressive strength of different biochar concrete composites and the control sample after 7 days and 28 days of water curing. The control sample exhibited higher compressive strength than all biochar composites at both curing intervals.

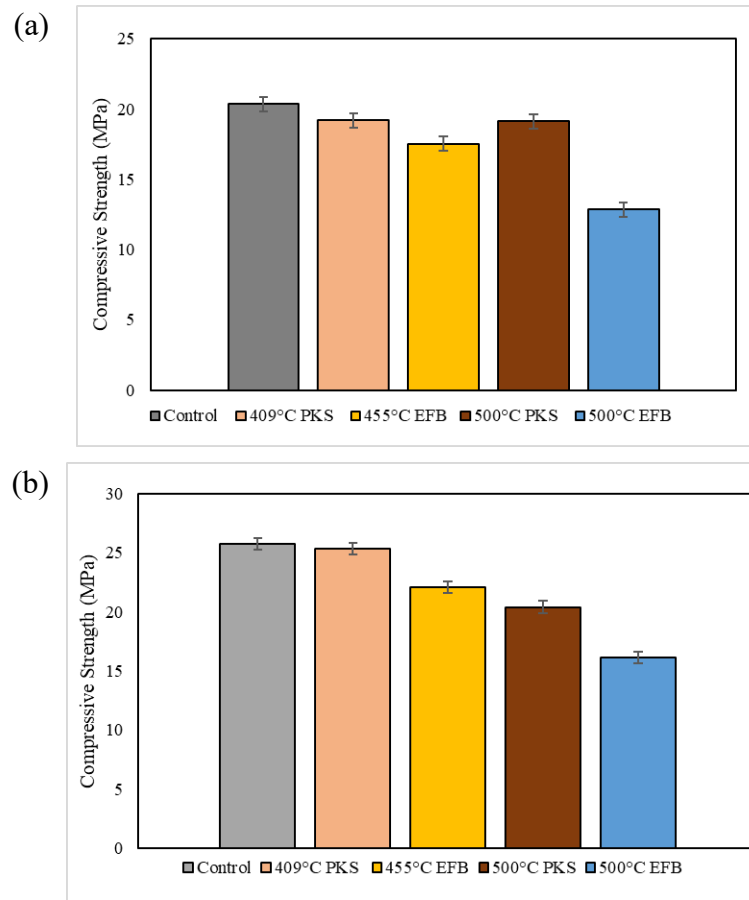


Figure 4.8 Compressive Strength of biochar concrete composites (a) 7 days curing and (b) 28 days curing.

In Figure 4.8 (a), the PKS biochar composites exhibit a higher strength than the EFB composites for both temperatures. The percentage decrease in strength for both PKS biochar is almost the same, with a decrease of 6.0% (19.13 MPa) for the 500°C PKS and a decrease of 5.7% (19.19 MPa) for the 409°C PKS compared to the control. The decrease in strength of the EFB biochar is 13.9% (17.52 MPa) for the 455°C EFB and 36.9% (12.84 MPa) for the 500°C EFB. From the results, it can be reported that for each biomass, the optimised biochar 409°C PKS and 455°C EFB has higher strength as

shown in Figure 4.8 (b) for the 28-day compressive strength than the commonly used temperature by the literature 500°C. The 409°C PKS showed a slight decrease of 1.5% (25.35 MPa), while the 500°C PKS showed a decrease of 20.7% (20.41 MPa) compared to the control. The EFB biochar showed a decrease of 14.2% (22.08 MPa) at 455°C and 37.4% (16.11 MPa) at 500°C. It is noteworthy that for both 7-day and 28-day strength, the 409°C PKS had the highest strength, while the 500°C EFB had the lowest. This proves that the use of lower temperatures to produce palm oil waste biochar as a cement replacement is appropriate for this concrete composite mix. In another study, a similar decrease to the 455°C EFB was observed when rice husk biochar produced at 500°C was used to replace cement by 0.1% which showed a 10% decrease in compressive strength of concrete composites (Akhtar and Sarmah, 2018a). This proves that the strength was drastically affected despite the use of 0.1% biochar. This means that even when using 0.1% biochar, micro filler effect occurred and increased the strength. In one study, a high increase in compressive strength of 30% was found, and the amount of biochar used as a cement replacement was 6.5% (Qin et al., 2021a). The authors emphasised that this was due to the micro filler effect caused by the high surface area of the biochar (250 m²/g). While the highest surface area in this research was by 500°C PKS (35 m²/g). This micro filler effect of biochar is the mechanism by which fine biochar particles in the mixture enable the formation of nucleation sites for cement hydrates on the biochar surface. However, with a surface area of 37.5 m²/g was exhibited by 5% rice husk biochar produced at 700°C, the compressive strength increased by 36% (Asadi Zeidabadi et al., 2018). This is due to the fact that the biochar was used as an additive and not replacement. The biochar was also subjected to a pre-treatment processes (by keeping biochar into potassium, calcium and magnesium solutions) before being added to the concrete composite which would increase the pozzolanic activity.

Large quantities of cement (more than 10%) can only be replaced by other supplementary cementitious materials that are either uniformly textured or have a high silica content that increases cement hydration through pozzolanic activity. Like a study that replaced cement by 11% with silica fume increased the strength by 9.2% (46.3 MPa) (Tak et al., 2023). The silica fume was reported to be in uniform size of 1 µm and a silica content of 90.26%. In contrast to the biochar used in this research, which exhibited a wide range of particle sizes and whose highest silica content at 455°C EFB

was 3.68%. Similarly, another study replaced cement by 15% with rice husk ash and increased the compressive strength by 7.8% (Bixapathi and Saravanan, 2022). Focusing at the compressive strength in these results, it can be concluded that the 409°C PKS biochar concrete composite is the most suitable replacement for the targeted strength of 25 MPa. To gain a better insight into the effect of palm oil waste biochar on the compressive strength of biochar concrete composites, some comparisons with other studies have been summarised in Table 4.3. In the table, the aspect of adding or replacing percentage of the total amount of cement is emphasised, as it would be more sustainable to reduce the amount of cement in the mixture if it were replaced.

Table 4.3 Compressive strength after 28 days curing of concrete composites with different supplementary cementitious material.

Material	Amount (%)	Added/ Replaced	Effect	References
Biochar 409°C PKS	4	Replaced	Dec ^a 1.5%	This Research
Biochar 455°C EFB	4	Replaced	Dec 14.2%	This Research
Biochar 500°C Rice Husk	0.1	Replaced	Dec 10%	(Akhtar and Sarmah, 2018a)
Biochar 700°C Rice Husk	5	Added	Inc ^b 36%	(Asadi Zeidabadi et al., 2018)
Biochar 500°C Eucalyptus plywood	6.5	Replaced	Inc 30%	(Qin et al., 2021a)
Silica fume	11	Replaced	Inc 9.2%	(Tak et al., 2023)
Rice Husk Ash	15	Replaced	Inc 7.8%	(Bixapathi and Saravanan, 2022)

^aDec: Decreased, ^bInc: Increased

4.2.2.2 Impact of Biochar Type with Other Mechanical Properties

Figure 4.9 shows the results of biochar-concrete composites after 28 days of water curing for (a) density, (b) porosity, (c) 72-hour water absorption and (d) flexural strength. Figure 4.9 (a) shows that the control sample has the highest density after 28 days of water curing, followed by a decrease of 1.3% for 500°C PKS, 1.4% for 409°C PKS, 1.9% for 455°C EFB and 4.4% for 500°C EFB. Similar to the compressive strength, PKS biochar showed a higher density than the EFB biochar. Figure 4.9 (b) shows that the percentage of porosity was highest for 500°C EFB with an increase of 4.9% compared to the control, followed by 2.2% for 409°C PKS and 1% for 455°C EFB, while 500°C PKS showed a slight decrease of 0.2%. Similarly, 500°C EFB showed the highest increase in water absorption rate calculated after 72 hours, as shown in Figure 4.9 (c), with an increase of 9.8%, followed by 0.8% for 455°C EFB, 0.7% for 409°C PKS and a decrease of 2% for 500°C PKS. Similar to the behaviour in the mortar

composites the trend in porosity and water absorption are similar for the concrete composites. Apart from the 500°C PKS concrete composite exhibited lower than the control. In Figure 4.9 (d), the control sample exhibited the highest flexural strength, followed by a decrease of 3.1% for 409°C PKS, 4.5% for 455°C EFB, 18.6% for 500°C PKS and 22.8% for 500°C EFB. The trend in decrease is similar to the compressive strength results after 28 days curing. In another study with a similar range of cement replacement, 3% wood waste biochar produced at 500°C reduced porosity by 4.2%, due to the low d₅₀ value of 9.13 µm (Tan et al., 2022). Finer biochar particle size can possibly produce a more compact composite, as the 3% also increased the density by 1% and the compressive strength by 8.4%. The same study also reported low significance of flexural strength similar to this research. However, with 1% replacement of the biochar the flexural strength increased by 3.6% (Tan et al., 2022). A different study replaced cement with 3.2% of wood waste biochar produced at 500°C increased the porosity and water absorption by 14% and 32% (Qin et al., 2021a). These high effects can be linked to the biochar surface area used which was 250 m²/g and it was much higher than biochar surface area of this research the 500°C EFB (1.6 m²/g) and PKS (35 m²/g) surface area.

It can be observed that the beneficial effects of the micro filler effect and internal curing were more pronounced in the mortar composites. This could be due to the presence of the coarse aggregates and the lower cement content in the concrete, which increases the gaps between the biochar and cement particles. This would then prevent the increase in cement hydrates as the biochar may not have been densely packed, as suggested by the low-density values of the concrete compositions. The clear difference in the behaviour of biochar in relation to the mechanical properties of mortar and concrete was noted. The discussion of the results for the mortar composites was only compared with other studies using mortar composites and similarly the discussion for the concrete composites was compared with studies using concrete composition. In summary, there is a lack of experimental research on biochar-concrete composites in the literature, although many studies on mortar composites have been conducted and have shown favourable results. To understand the full potential of the novel biochar, it is recommended that further experiments with concrete composites can be conducted. As this research has shown, the properties of mortar composites differ.

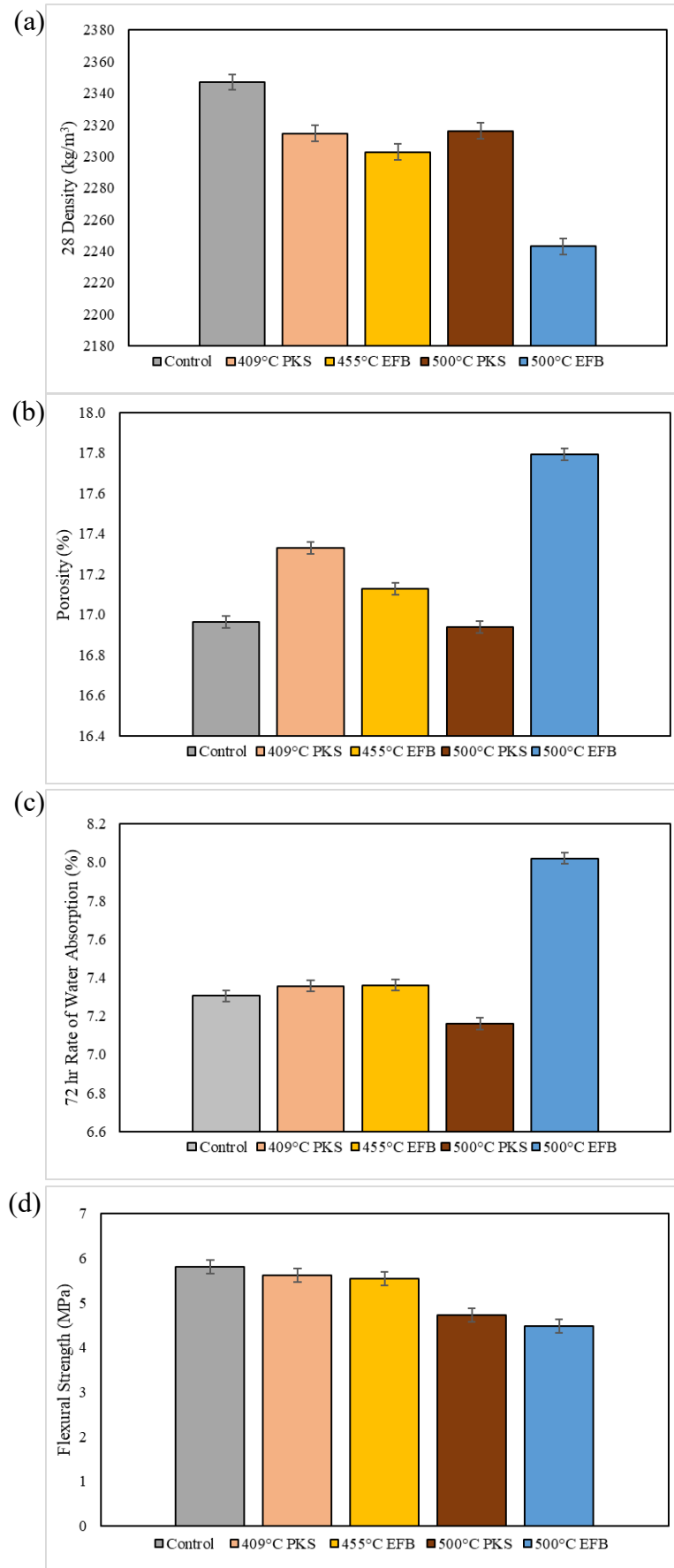


Figure 4.9 Mechanical properties of biochar concrete composites (a) density, (b) porosity, (c) 72 hr water absorption and (d) flexural strength.

4.2.3 Chemical Properties of Biochar Composites

Cement consists of four primary chemical compounds, namely tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite C_4AF (Neville A. M., 2011). When water is added to these compounds, cement hydrates are formed, which determine the mechanical properties of the building material. This process is known as cement hydration. The main products of cement hydration are calcium hydroxide (CH) and calcium silicate hydrates (CSH) as shown in Equation (4.4) and (4.5) (Neville A. M., 2011).



In order to fully understand the effect of biochar's role as a cement replacement it is important to investigate not only the mechanical but also the chemical characteristics. The following are chemical analysis that were done on the composites which include thermal analysis (TGA), crystalline structure (XRD), functional groups (FTIR) and microscopic observation (FESEM). They were performed on both mortar and concrete composites with 4% biochar after 28 days of curing.

4.2.3.1 Functional Groups

FTIR analysis in Figure 4.10 (a) and (b) indicate the presence of functional groups of the biochar mortar and concrete composites and the control sample after 28 days curing. The analysis specifies the wavelength (cm^{-1}) at which the chemical components are detected with their transmittance (%) that determines the intensity of the compounds detected. The aim of the FTIR analysis is to identify the presence of the chemical bonds involved with CSH and CH. Which are hydroxyl group (O-H), carbonyl group (C=O), alkenyl group (C=C), alkyl (C-C) and ether group (C-O). It is known that Si-O and C=O are usually detected around 781 to 980 cm^{-1} . Which signifies the presence of CSH (Akhtar and Sarmah, 2018b; Haris Javed et al., 2022; Manjunath et al., 2024). Similar fluctuations were found for concrete composites around 1011 cm^{-1} and mortar composites around 800 cm^{-1} . Any bonds detected between 3564 to 3900 cm^{-1} would indicate the presence of O-H from calcium hydroxide (Akhtar and Sarmah, 2018b). In this research both mortar and concrete showed the presence of O-H at approximately 3520 cm^{-1} . Dips detected in Figure 4.11 (a) for biochar mortar composites were at approximately 221, 1874 and 2576 cm^{-1} . With visible weak bonds detected at 1740,

2050 and 2988 cm^{-1} . The most prominent dips detected in Figure 4.11 (b) for biochar concrete composites were at approximately 1740, 2576 and 2988 cm^{-1} . Other visible weak bonds were detected at 300 and 2050 cm^{-1} . Similar dips with both composites were approximately at 1740, 2050 and 2988 cm^{-1} , which can be attributed the presence of the combination of calcite or portlandite (Akhtar and Sarmah, 2018b). The proximity of these bond detected are not exact as the literature suggest as other factors could play in terms of different cement and biochar type that would have affected the cement hydration.

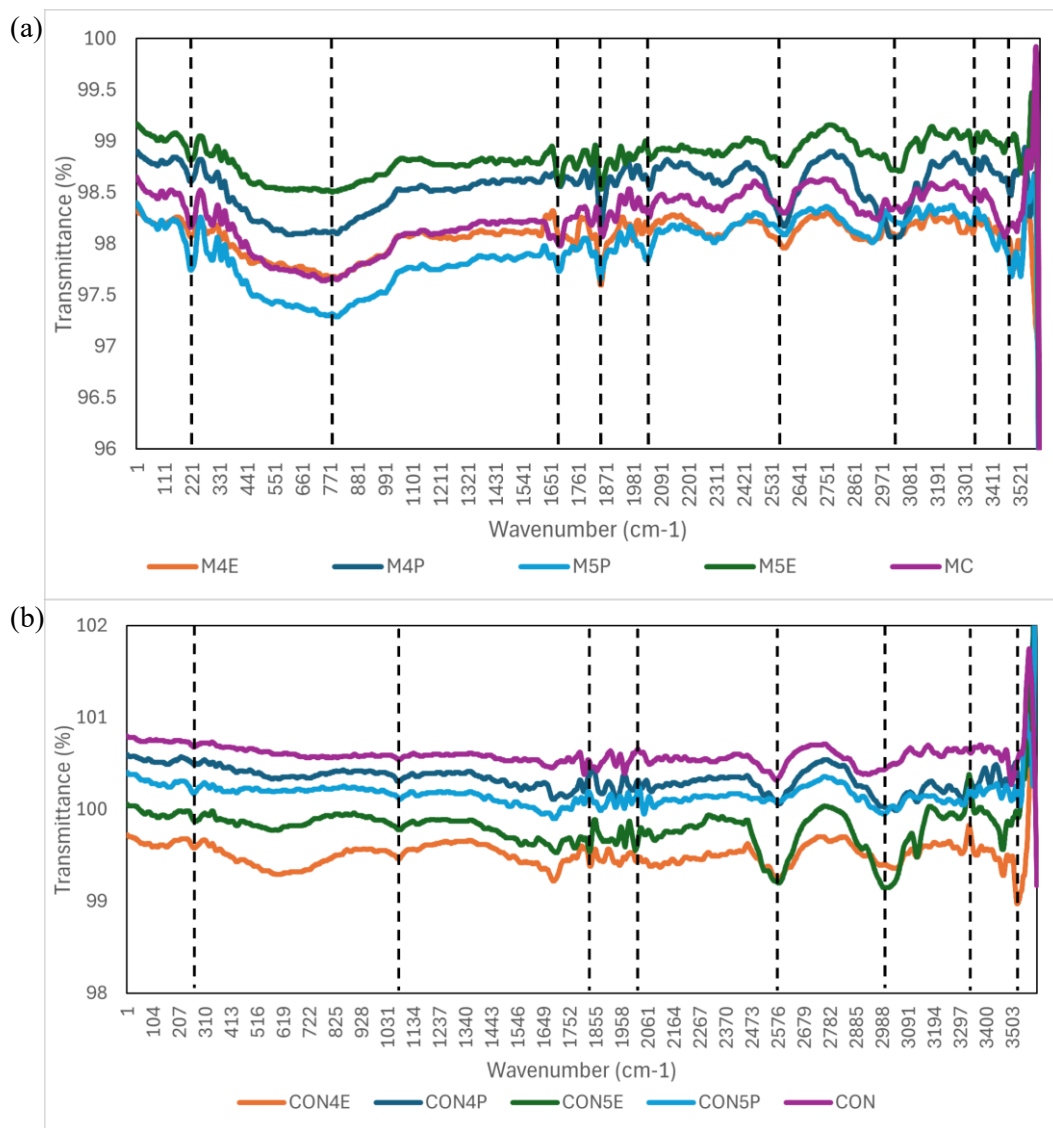


Figure 4.10 FTIR analysis of (a) biochar mortar composites and (b) biochar concrete composites.

A general conclusion from the mortar compositions is that regardless of the type of biochar used, the same peaks and bonds were detected with similar transmittance. With the exception of 409 PKSC, which has higher peaks at 1874, 2576 and 2988 cm^{-1} .

However, the mix with 500 EFB°C showed twice as higher peaks than other mixes for the concrete composites. These peaks are inconsistent with the low compressive strength exhibited by these two mixes. It is worth noting that it is a challenge to establish an accurate correlation between the chemical and mechanical properties of powdered concrete and mortar composites. Which then would then theoretically mean that the increase in mechanical properties was strongly influenced by the mechanical structure of the biochar and its placement in the interface transition zones.

4.2.3.2 Crystalline Structure

Understanding the crystalline phases in biochar composites helps provide a clearer picture of their crystalline nature of the minerals within the composites. Figure 4.11 (a) and (b) show XRD patterns, illustrating the crystalline phases present in biochar mortar and concrete composites, as well as in control samples after 28-day curing. The analysis illustrates peaks at separate diffraction angles ($2\theta^\circ$), which was used in identifying specific crystalline phases, while their intensities, were measured at an arbitrary unit reflecting the abundance of each phase detected. Key findings include the presence of calcium hydroxide (CH), calcium carbonate (CC) tricalcium silicate (C_3S), ettringite. C_3S a primary compound of cement and when hydration occurs form ettringite. CH is also a hydration byproduct, that plays an important role in the strength of mortar and concrete samples. CC is often found as the results of carbonation that could have occurred in the atmospheric air. The presence of CH was identified by the peaks at 18° , 50° , 68° $2\theta^\circ$ (Gupta et al., 2018b; Gupta and Kashani, 2021; Manjunath et al., 2024). CC was identified at 26° , 28° , 29° and 43° $2\theta^\circ$ (Gupta and Kashani, 2021; Kushwah et al., 2024). In addition, ettringite peaks were found at approximately 20° and 21° $2\theta^\circ$ (Gupta, 2021; Kushwah et al., 2024). C_3S peaks were found at approximately 39° and 59° (Kushwah et al., 2024). The CC peaks were the highest identified in all composites and the control samples regardless of the type of biochar.

Prominent peaks were observed in both mortar and concrete composites at 26° , 29° , 39° , 43° , 50° , 68° , and 20° 2θ , indicating a consistent presence of CC, CH, and C_3S across both sample types. The presence of these peaks demonstrate that the basic hydration processes were unaffected by the type of biochar used. Additional peaks unique to mortar composites Figure 4.11(a) were identified at 18° , 28° , and 59° $2\theta^\circ$, while those unique to concrete composites Figure 4.11(b) appeared at 42° , 57° , and 80° 2θ . These differences may be attributed to variations in the mix design, particle size

distribution presence of fine and coarse aggregates, and the interaction between biochar and the cement particles. Peaks corresponding to ettringite and C_3S were relatively similar in both control and biochar composites. This indicates that biochar did not significantly hinder the hydration of aluminate or silicate phases.

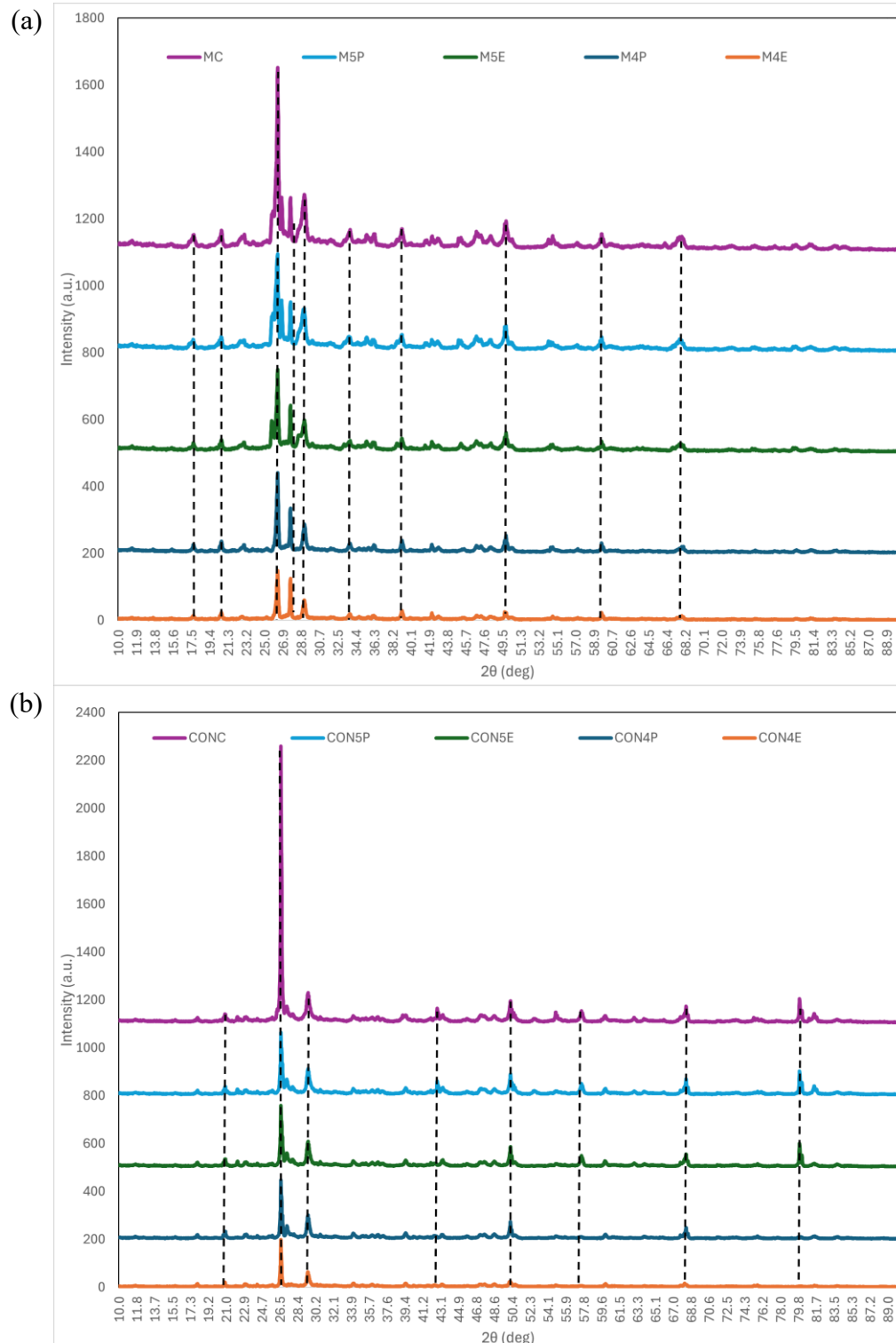


Figure 4.11 XRD analysis of (a) biochar mortar composites and (b) biochar concrete composites.

XRD analysis revealed that compared with the control paste, the, addition of biochar did not produce significantly higher hydration products. As the replacement ratio of biochar increased, the diffraction peak intensities of CH decreased slightly (Yang and Wang, 2021). In terms of comparative intensities between the samples, the control consistently showed the highest peaks for both mortar and concrete. This finding is consistent with previous analysis, such as the FTIR results. This could be due to the 4% of biochar particles may act as an inert filler with minimal chemical reactivity in the composite, leading to fewer hydration products compared to the control sample. This could also be due to the porosity of the biochar material that led to the cement hydrates which reduced their availability for detection in a crystalline form.

4.2.3.3 Thermal Analysis

Figure 4.12 (a) and (b) illustrates the thermal analysis conducted on crushed samples from mortar and concrete composites with the reference control mix after 28-day curing. The graphs show the percentage of the loss of weightage against the change. This analysis provides a clear breakdown and distribution of the hydration products' decomposition. This was done through the Bhatti's method to determine the quantity of cement hydrates in the following mixes (Dixit et al., 2019; Manjunath et al., 2024; Yang and Wang, 2021). This method states that the temperature ranges from 105-400°C is dehydration (dh), 400-500°C is de-hydroxylation (dx) and 500-900°C is referred to as decarbonation (dc). The dehydration section entails the drying of water from the calcium silicate hydrates (C-S-H). The de-hydroxylation is the thermal decomposition of calcium hydroxide (CH) and the decarbonation is the removal of CO₂ from crystallized calcite. The calculations that have been made according to loss of weight of the samples are given in Equations (4.6) to (4.8).

$$W_b = W_{dh} + W_{dx} + 0.41W_{dc} \quad (4.6)$$

$$DOH (\%) = \frac{W_b}{0.24} \quad (4.7)$$

$$CH_{dx} (\%) = 4.11 \times dx_{(400-500)} \quad (4.8)$$

The change in masses between these temperatures were added to measure the chemically bound water (W_b) as shown in Equation (4.6). It is calculated to determine the effect of biochar on the formation of hydration products. W_{dh} is the loss of mass between 105 to 400°C, W_{dx} is the loss of mass between 400 to 500°C and W_{dc} is the loss of mass between 500 to 900°C. The factor 0.41 is used to convert the loss of mass from

due to the CaCO_3 to the molecular weight of water in CH. The degree of hydration (DOH) is then calculated using Equation (4.7), 0.24 in the equation corresponds to the theoretical maximum water needed for complete hydration of cement. Further determination of the amount calcium hydroxide (CH_{dx}) is calculated using Equation (4.8), by multiplying the mass loss at the dihydroxylation stage to 4.11 the molecular weight ratio of CH to water.

An overview of the mortar composite results in Figure 4.12 (a) that the highest weightage loss is exhibited by the control followed by 500°C EFB, 500°C PKS, 409°C PKS and lowest by 455°C EFB. Figure 4.12 (b) shows the highest loss was exhibited by 455°C EFB, followed by the control, 409°C PKS, 500°C PKS and lowest by 500°C EFB. Indicating for mortar composites specifically 455°C EFB is most thermally stable and 500°C EFB for concrete composites. Concluding that EFB biochar offers a more thermally stable type of biochar to be used as a cement replacement. Figure 4.13 shows the amount of chemically bound water, percentage of calcium hydroxide and degree of hydration that have been derived from the TGA results.

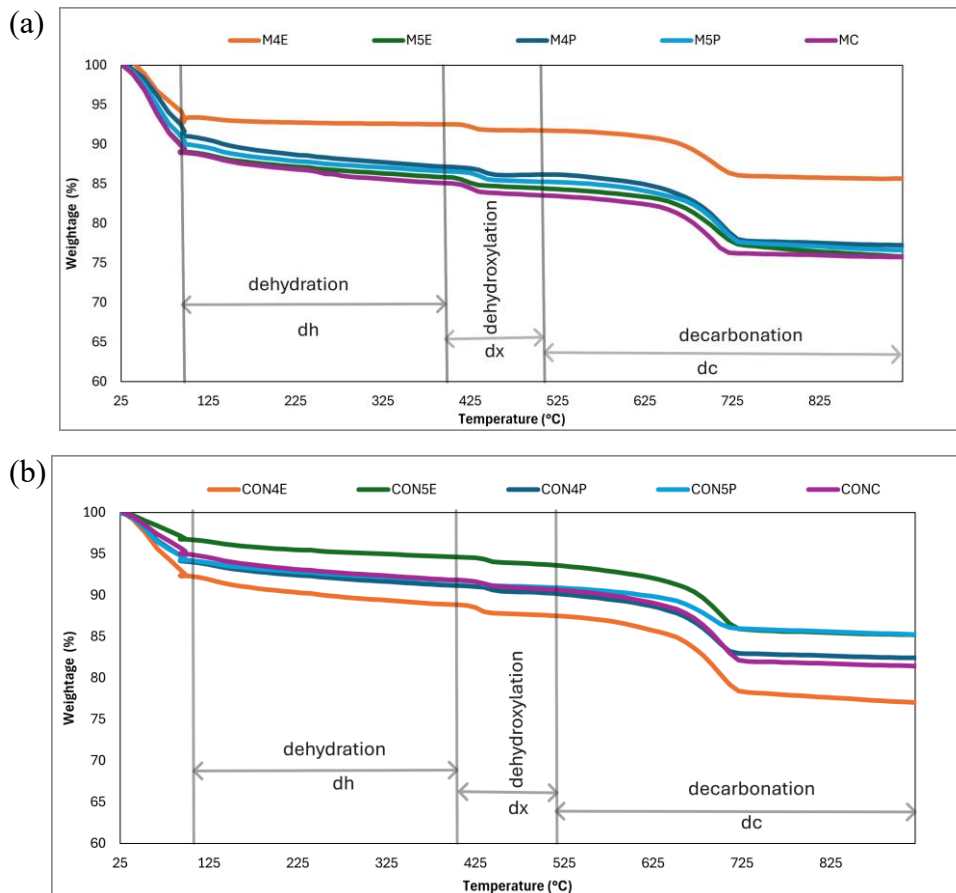


Figure 4.12 TGA analysis of (a) biochar mortar composites and (b) biochar concrete composites.

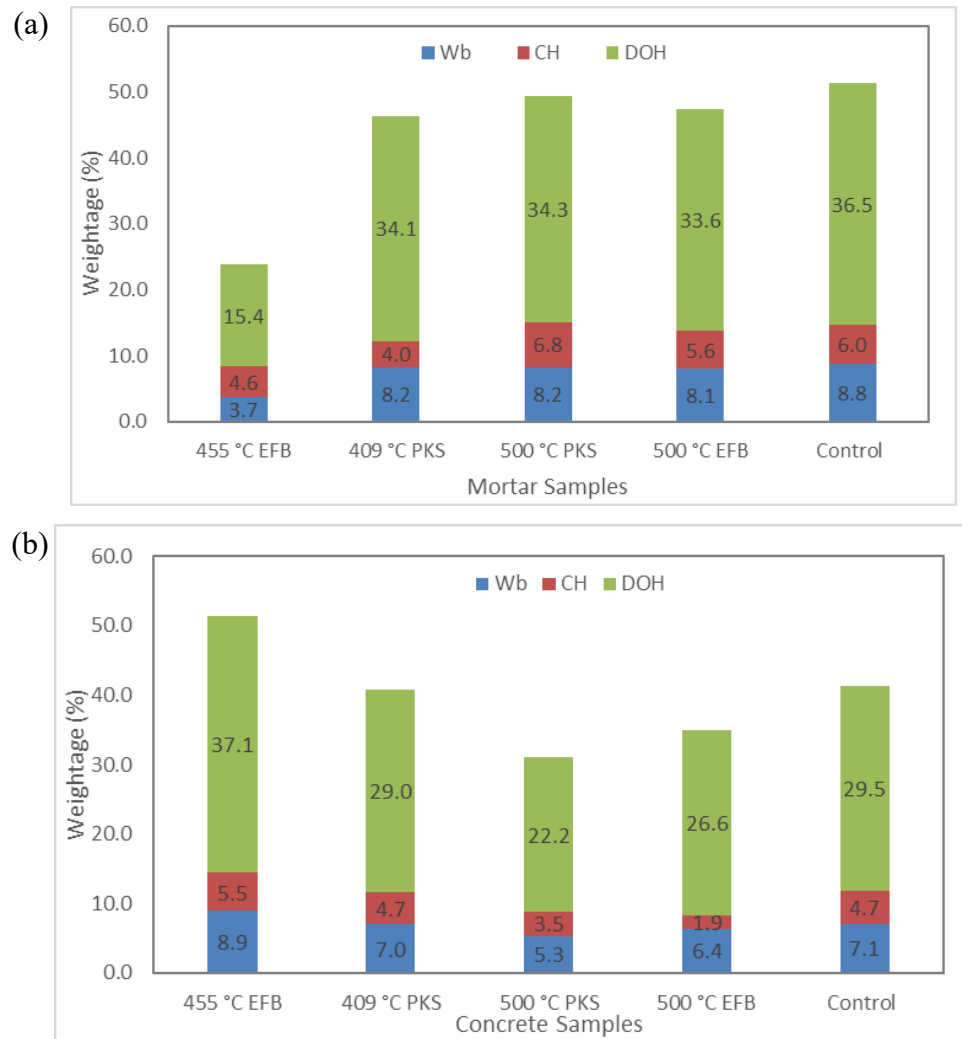


Figure 4.13 Degree of hydration of (a) mortar samples and (b) concrete samples.

The factors that highly effect the DOH would be the amount of biochar used, its surface area and the water to cement (w/c) ratio used in the mix. As some of the literature reports and increase (Gupta and Kua, 2018a; Rodier et al., 2019) and a decrease (Yang and Wang, 2021). In addition, the reactivity of biochar primarily depends on the type of biomass used (Mishra et al., 2023). Similarly, these factors would affect the chemically bound water and the CH percentage. Figure 4.13 (a) shows the highest DOH from the mortar composites was exhibited by 500°C PKS. For the concrete composites in Figure 4.13 (b) the highest was exhibited by 455°C EFB. This highlights that under different cement ratios the different behavioural and reactivity is shown by the biochar. 0.51 w/c was used by the mortar samples and 0.56 b w/c by the concrete. The CH and chemically bound water are in correlation with the DOH results.

A study that reported a difference in (rice husk) biochar percentage as a cement replacement has decreased the DOH and CH content of the samples (Yang and Wang,

2021). The authors reported that for the control, 2% and 5% the DOH were 90.8%, 88.7%, and 85.9% and for the CH were 0.213, 0.208, and 0.191 g/g respectively. The authors account this decrease in DOH and CH due to the decrease in amount of cement that has been replaced by the biochar therefore there were fewer cement particles in comparison that would hydrate and form CH. Another study that used biochar as an additive, they have found an increase of 67% of hydration with 5% of saw dust biochar (Gupta and Kua, 2018a). These authors also stated that the increase in hydration was due to pre-soaking the biochar with water. This retain water aided the cement hydration with the amount of water that was already added to the mix. A study that reported with 1% biochar the chemically bound water decreased compared to the control however with 1.5% biochar it increased higher than the control (Mishra et al., 2023). Which highlights that the higher the quantity of biochar means a high amount of porosity within the composite is formed. Even with minor additions as low as 0.5% the amount of retained water was altered. A similar study that used 2% sugarcane bagasse biochar as an additive also reported similar findings of increased cement hydration (Rodier et al., 2019). TGA and DOH results of this research show that palm oil waste biochar both EFB and PKS have had a significant effect on the mixes.

4.2.3.4 Microscopic Viewing

SEM imaging is commonly used in composites to identify the presence of cement hydrates, primarily calcium hydroxide (CH) and calcium silicate hydrate (C-S-H). The FESEM analysis was conducted for the control samples and mortar composites and concrete composites ash shown in Figure 4.14 (a)-(e). In Figure 4.14 the CH has been marked with a yellow circle, the CSH with red and biochar sample with green. Figure 4.14 (c) and (d) shows the mortar and concrete composite with 4% of 409°C PKS. In Figure 4.14 (e) and (f) show the mortar can concrete composite with 455°C EFB. The CSH was identified as needle shaped (Haris Javed et al., 2022; Manjunath et al., 2024). The concentration of CSH can be seen a lot more defined in the concrete composites in Figure 4.14 (a),(c) and (e). A concentration of CH can be viewed in the composite samples with 409°C PKS. Figure .14 (f) show the presence of biochar and the formation of cement hydrates around the particle. This is due to the negative charges on the biochar attract the positively charged clinker grains and form as nucleation sites for cement hydrates (Senadheera et al., 2023).

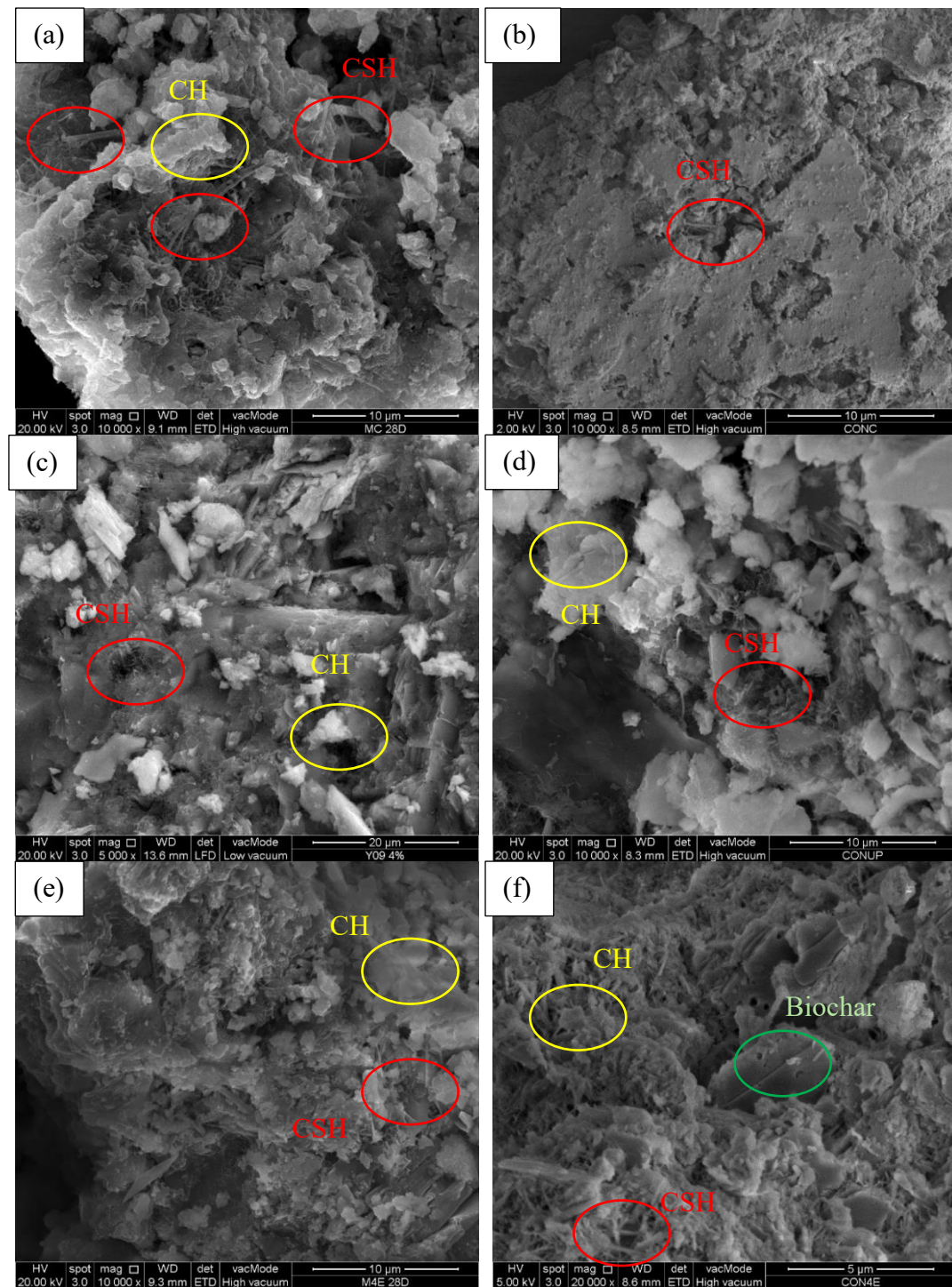


Figure 4.14 FESEM image of control samples (a) mortar and (b) concrete. 4% of 409°C PKS with (c) mortar composite and (d) concrete composite. 4% of 455°C EFB with (e) mortar composite and (f) concrete composite.

4.3 Summary of Findings

In this chapter, the effects of different types of biomass derived biochar, produced at different pyrolysis temperatures, were evaluated and compared with respect to properties of mortar and concrete composites. This was done under the second and third objectives of this research. The second objective was to compare the effects on the

mechanical properties of mortar with each type of biochar in a range of 1 to 8% cement replacement. The third objective was to evaluate the biochar concrete composites in terms of the optimum percentage resulting from the second objective. The results of this chapter are therefore as follows:

- **Biochar Mortar Composites:** Comparison and analysis of the mechanical properties of biochar mortar composites with 4% 455°C EFB showed adequate results for the target strength of 25 MPa. The 28-day compressive strength for this mix increased to 8.9%. In the search for the optimum percentage, the other properties such as density, porosity, water absorption and flexural strength were compared with the compressive strength. At 4% 455°C EFB, the density increased by 1.2%, porosity by 4.2%, water absorption by 5.8% and flexural strength by 6.1% compared with the control. This led to the conclusion that 4% cement should be replaced by biochar.
- **Biochar Concrete Composites:** The evaluation of 4% of each type of biochar was tested on concrete composites. The mixture at 409°C showed the highest strength of the biochar composites with a decrease of 1.5% from the control. The same mixture showed a decrease in density of 1.4%, an increase in porosity of 2.2%, an increase in water absorption of 0.7% and a 3.1% decrease in flexural strength.
- **Analyses** such as TGA, FTIR, XRD and microscopic images were carried out on 4% biochar mortar and concrete composites. The results show minor changes within the composites with either type of biochar. This suggests that the effect of biochar on mechanical properties is mainly due to its structural properties such as average particle size, surface area and porosity.

The results in this chapter show that the proposed optimal biochar produced under the first objective successfully improves mechanical properties when used as a cement replacement. This forms the basis for the investigations in the next chapter, where the potential of these composites to sequester carbon dioxide will be tested once the designed properties for 25 MPa are achieved.

Chapter 5 Carbon Sequestration of Biochar Composites

This chapter deals with the fourth objective of the carbon sequestration studies carried out on optimised biochar, mortar and concrete composites. Since these samples have undergone mechanical and chemical analyses, this chapter adopts a structured approach to evaluate their carbon sequestration potential and enhance their sustainability. A brief explanation of the novelty of this chapter follows, followed by the methodology and results and discussion. The tests performed include thermal analysis, presence of functional groups, crystalline structure and microscopic analysis of the biochar samples after the carbonation experiment. The same tests were also carried out on the biochar mortar and concrete composites, including mass and pH change tests after the carbonation experiment.

5.1 Carbon Sequestering Potential

Biochar is known to sequester carbon in numerous industries. Many characteristics, such as the carbon content of biochar, its porous nature and its adsorption capabilities, suggest that biochar is an effective carbon adsorbent. One of the objectives of this research is to understand the carbon sequestering capabilities of the optimised biochar, biochar mortar and concrete composites on a laboratory scale. The results were evaluated and the potential of carbon adsorbed through various analyses was discussed. The novelty of this research was to test and evaluate the carbon sequestration potential of biochar mortar and concrete composites after 28 days of water curing, specifically using palm oil waste biochar with 4% cement replacement. In this study, the focus was placed on carbon adsorption after the composite reached its target strength within 28 days, rather than using carbon curing methods as done in previous research. This approach aimed to develop a more effective sustainable mortar and concrete mix. Carbon sequestration is sought after the material has achieved all the targeted mechanical properties to improve its sustainability.

5.2 Methodology

The experimental setup for this study was adapted from Gupta et al., (2018d), with some modifications concerning the size, the gas inlet and the materials used for the structure. Figure 5.1 below shows the experimental setup in a box measuring 500 × 750 × 400 mm, which was designed and fabricated for the purposes of this study.

The initial design can be found in [Appendix F](#). On one side of the box there is a hinged door and on the other side an opening with a diameter of 12.7 mm for the gas flow. An industrial carbon dioxide cylinder with a concentration of 99.95% and a carbon dioxide detector (Gasman Personal Single Gas Monitor Crowcon) were used. Standard clay has been placed on the box at the door edges to prevent the gases from escaping. The setup is shown in Figure 5.1 (a). The test setup was first checked to ensure that no carbon dioxide gas escaped. A trial run was performed by sealing the box with clay after the gas was introduced and the flow had reached 13.15 ± 5 v%/v (volume per cent carbon dioxide per volume of total atmospheric gas) as measured by the detector. The gas flow was stopped, and the detector was monitored for 5 hours. During the entire period, there was only a decrease of 0.01 v%/v, which ensures that there is no leak in the experimental set-up. The experimental set up for the trial run is shown in Figure 5.1 (a).

10 g of each type of powdered biochar in equal amounts were placed in a petri dish and sealed in the box with the gas detector for 24 hours as shown in Figure 5.1 (b). The samples were analysed by TGA, XRD, FTIR and FESEM-EDX. The methodology for each analysis is described in Chapter 3 (Section 3.1.4). The same analysis was repeated for biochar mortar and concrete composites, including a control sample for comparison. A cube of $100 \times 100 \times 100$ mm was used for the concrete samples; $50 \times 50 \times 50$ mm for the mortar samples, as shown in Figure 5.1 (c) and (d). 24 hours after the samples have been kept in atmospheric air, they have been broken into half using an electrical 14" (355.6 mm) masonry saw (Figure 5.2). Another test has been conducted on the composites using phenolphthalein ($C_{20}H_{14}O_4$) solution as a pH indicator for carbonation intensity. Drops of the solution were placed on the inner surface to see the intensity of carbonation that has taken effect and seeped through the samples. The indicator solution would turn the samples into different shades of pink, indicating the intensity of the carbonation process. Comparison is then made according to the intensity of the pink colour; that would indicate if the sample has completely carbonated, moderately carbonated or non-carbonated. If it has turned dark pink, this indicates a less carbonated sample and a strongly alkaline sample. If, on the other hand, it has turned a light pink colour, this indicates a higher degree presence of carbon dioxide and a less alkaline sample.

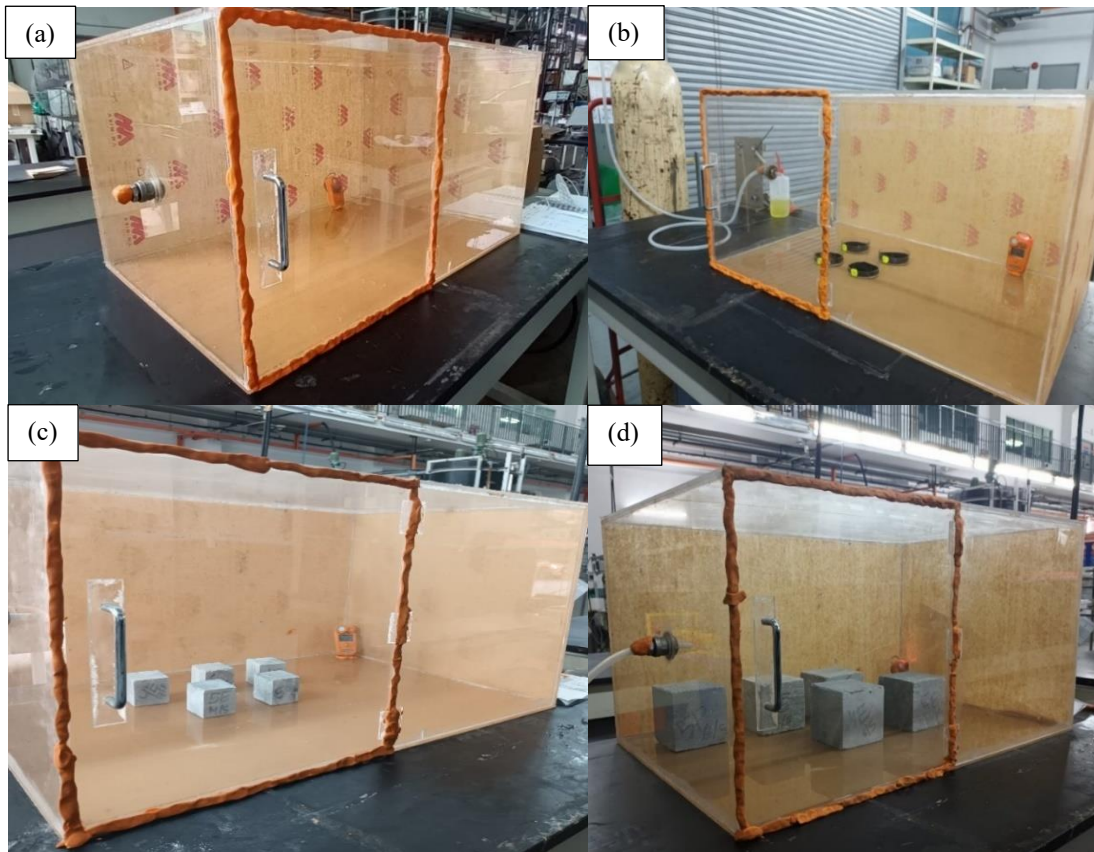


Figure 5.1 Experimental setup of the carbon sequestering studies. (a) Trial round of experimental setup. Set up for (b) biochar samples, (c) mortar samples, and (d) concrete samples.



Figure 5.2 Professional 14" masonry saw.

5.3 Results and Discussion

5.3.1 Palm Oil Waste Biochar

As already mentioned, several properties of biochar are strongly influenced by the type of biomass and the production parameters. This section deals with the change in the chemical composition of biochar when stored in a concentrated CO₂ environment for 24 hours. The storage of carbon in biochar-cement composites depends on the ability of the biochar to sequester carbon. Therefore, it is important to understand the potential of biochar before it is used as a cement replacement. The aim of this research was to obtain the most sustainable mortar and concrete composite from biochar. Carbon is the main component of biochar and its use as a cement replacement would not only attain sustainability in terms of carbon sequestration but also carbon storage. In this research, no pretreatment processes such as chemical or physical modification. Such as pore size and the presence of functional groups (Arif et al., 2020; Liu and Huang, 2018) of biochar were used to improve CO₂ adsorption. This decision was made to fully quantify the capabilities of raw biochar that can be used as a carbon sink and cement replacement. The following tests discuss the changes that have occurred in the biochar after the carbonisation test, demonstrating its potential for sequestration.

5.3.1.1 Thermal Analysis

To evaluate the effects of the thermal stability of biochar after the samples were exposed to concentrated CO₂, TGA analysis was performed on the samples 24 hours after exposure to atmospheric air, as shown in Figure 5.3. From the TGA, the proximities analysis was calculated using equations (3.3) to (3.6) and presented in Table 5.1. Figure 5.3 shows the four biochar samples. In the graph, 4E stands for 455°C EFB, 5E for 500°C EFB, 4P for 409°C PKS and 5P for 500°C PKS. The TGA results are divided into three stages. Stage 1 is dehydration, that is the loss of moisture. Stage 2 is thermal stability, the breakdown of the organic compound. Stage 3 is combustion, the decomposition of the solid carbon. In stage 3 in Figure 5.3, the PKS biochar shows a lower weightage decrease than the EFB biochar. The low weightage decrease signifies that the biochar has a higher solid carbon content and is more thermally stable. This is also due to the fact that the pyrolysis parameters for PKS were higher than for EFB, especially the residence time, which was 120 minutes. Stage 1 for all biochar samples show no significant difference and as calculated in Table 5.1, the moisture content is

between 2.3 and 4.4%. The fixed carbon content correlates directly with the weight loss in stage 3, with the highest value at 500°C PKS, followed by 409°C PKS, 500°C EFB and the lowest at 455°C EFB. The increase in thermal stability can also be attributed to the carbon content due to the CO₂ adsorption of the biochar. The studies on carbon sequestration of biochar report similar results (Liu and Huang, 2018).

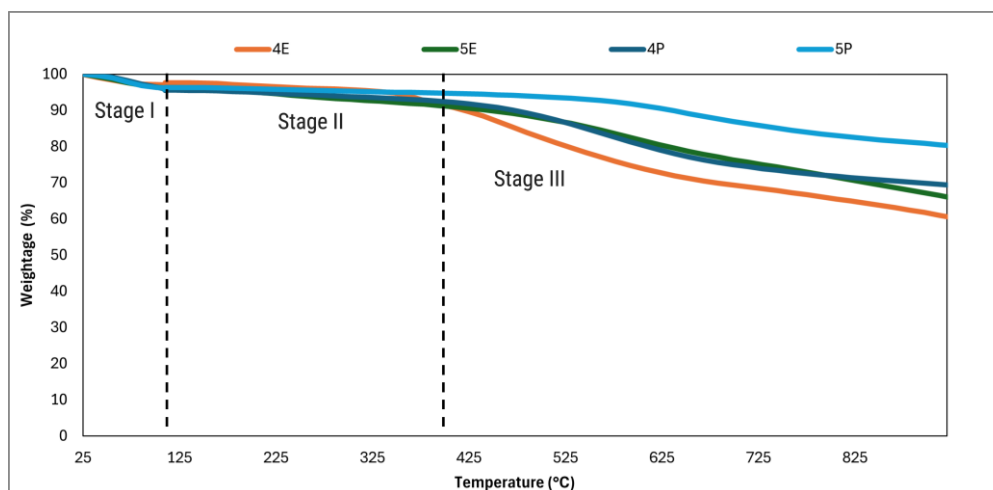


Figure 5.3 Thermal analysis of biochar samples post carbonation.

Proximate analysis shows the significant changes in the content of carbon, volatile matter and ash content. Table 3.1 shows the proximate results of the biochar before the carbonisation test. The fixed carbon content increased by 282.3% (56.2% of fixed carbon) at 409°C PKS, 49.2% (37.3% of fixed carbon) at 455°C EFB, 12.1% (68.9% of fixed carbon) at 500°C PKS and 22.2% (50.6% of fixed carbon) at 500°C EFB. These results are consistent with the hypothesis that after carbonisation of the biochar, the carbon content increases and the volatile matter content decreases. However, at 500°C PKS, the volatile matter content increased slightly by 0.36%. Another significant change observed is the decrease in ash content for all samples except at 409°C PKS, which increased by 79%. As previously mentioned, the fixed carbon and ash content influence the structural stability of the biochar, while the volatile components are associated with its brittleness. This indicates that biochar has increased in structural stability and its brittleness decreased. The decrease in ash content may also expose more additional pores on the biochar for adsorption (Klasson et al., 2015). Another study also compared the increase in fixed carbon content after CO₂ adsorption and reported different biochar from bamboo (8.6%), wood (6.1%) and coconut shells (5.7%), which correlates with the porosity of the biochar (Zhang et al., 2023). In this research, the 409°C PKS showed the highest combination of surface area (2.19 m²/g) and pore width

(adsorption 84.1 Å and desorption 58 Å) compared to the rest of the biochar. This allows a higher CO₂ content to be adsorbed and less to be desorbed. As a result, the ability to retain the CO₂ and react chemically with the biochar increases. Even with a high surface area of 389.02 m²/g, another study tested CO₂ adsorption in PKS biochar at 500°C over 11 hours. The authors have reported that chemical modifications were required to improve adsorption (Promraksa and Rakmak, 2020). However, this was not done in this investigation as it would affect the properties of mortar and concrete composites when the biochar is used as a cement replacement. Thus, the results of the thermal and proximate analysis of the biochar indicate that it was significantly altered by the adsorption of CO₂.

Table 5.1 Proximate analysis post carbonation of biochar samples.

Biochar	409°C PKS	500°C PKS	455°C EFB	500°C EFB
Label	4P	5P	4E	5E
Moisture Content (%)	4.4	3.6	2.3	3.6
Volatile Matter (%)	32.8	22.0	52.6	44.0
Ash Content (%)	6.6	5.4	7.7	1.7
Fixed Carbon (%)	56.2	68.9	37.3	50.6

5.3.1.2 Functional Groups

FTIR analysis has been conducted on the biochar after the carbonation experiment to detect shifts or the presence of newly formed functional groups due to exposure to concentrated CO₂, as shown in Figure 5.4 (a) and (b). Overall, it can be observed that more functional groups were detected in the biochar samples than in the samples prior to the carbonation experiment (Chapter 3 Section 3.2.3). However, as with the biochar samples before carbonation, the transmittance of functional groups remains low under 2%. The table of functional groups in [Appendix B](#) was again used to identify the peaks. In Figure 5.4, prominent peaks in certain vibrations are highlighted by dashed lines. The presence of carbonyl and oxygen groups were identified: C-O in the range 1100 to 1200 cm⁻¹, C=O 1640 to 1700 cm⁻¹ and O-H between 3100 and 3350 cm⁻¹. The O-H groups can also be related to the moisture content of the biochar. 409°C PKS shows a prominent peak for C=O, indicating higher CO₂ absorption, which is consistent with the proximate analysis. The presence of these groups may also mean that the biochar is still capable of adsorbing more CO₂ (Dissanayake et al., 2020). The lower transmittance of the functional groups in relation to CO₂ could be due to the fact that the biochar

actively retains the CO₂ particles due to its porous structure and does not adsorb completely to the biochar surface (Lahijani et al., 2018).

The peaks in the range 661–881 cm⁻¹ are associated with carbonate groups (CO₃²⁻), which indicates the formation of carbonates during the carbonation process. The vibrations in the 460, 771–881 cm⁻¹ range are assigned to unsaturated alkenes (C-H) and aromatic rings (Ben Salem et al., 2021). This is consistent with the hypothesis that new peaks would form when a high concentration of CO₂ is introduced into the biochar. In Figure 5.4, the vibrations extending from 2311–2421 cm⁻¹ are assigned to the nitrogen groups C=N, which are also found in sugarcane biochar, bamboo, wood and coconut shells (Creamer et al., 2014; Zhang et al., 2023). Nitrogen compounds have also been reported to contribute to carbon sequestration, so the presence of these compounds would indicate the potential for further carbon sequestration. Vibrations between 1871–2320 cm⁻¹ can be categorised as the formation of carbonyl groups in association with CO (Zhang et al., 2023). The presence of oxygen-containing groups on the surface has also been described as a property that increases the interaction and absorption of water molecules (Sevilla et al., 2011). These results show a significant presence of functional groups detected on the biochar after carbonisation, which are likely to be influenced by factors such as the initial composition of the biochar.

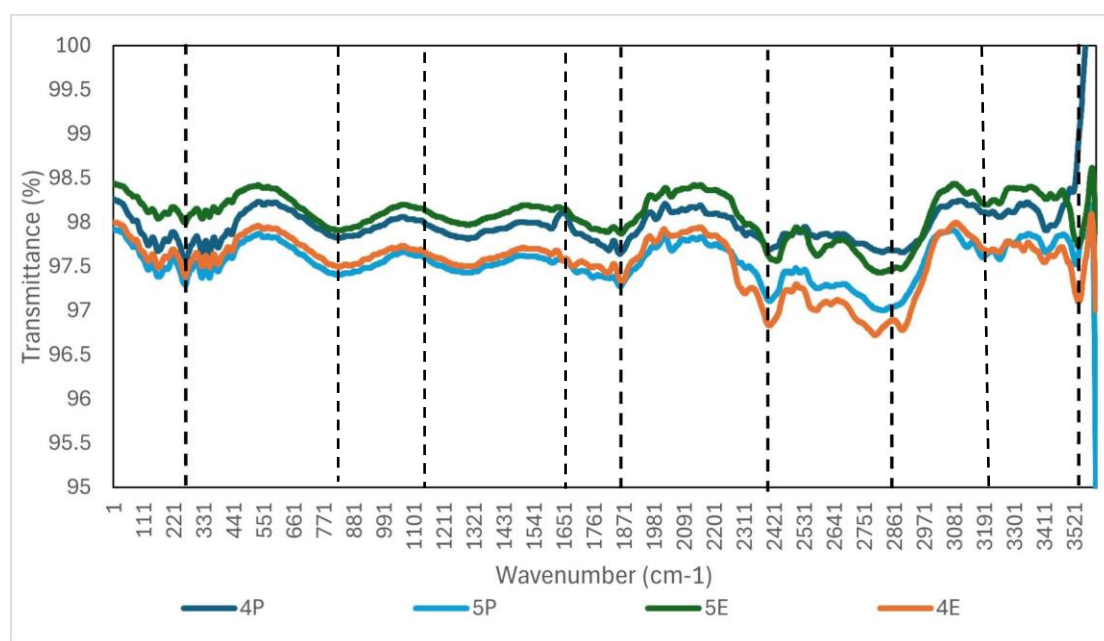


Figure 5.4 FTIR analysis of biochar samples after the carbonation test.

5.3.1.3 Crystalline Structure

Figure 5.5 shows the XRD analysis of the biochar samples to detect any changes in crystallinity or shifts in peaks due to exposure to concentrated CO₂ within 24 hours. Figure 5.5 shows the four biochar samples in the graph CO24E stands for 455°C EFB, CO25E for 500°C EFB, CO24P for 409°C PKS and CO25P 500°C PKS. After carbonisation, the XRD patterns showed changes in the crystalline phases of the biochar, including the appearance of new peaks at certain 2 θ positions such as 15°, 24° and 33.5°. The same peak, but with different intensity, was found at about 45°. The range between 15 and 30° was shifted with an intense peak at 24° in contrast to the previous highest peak at 23° (Chapter 3 Section 3.2.3). Which clearly defines a shift and a change in the crystalline structure of the biochar due to the carbonation process. This shift is observed in all four biochar types. This is consistent with the hypothesis that the crystalline structure of the biochar would change within 24 hours due to exposure to concentrated CO₂. The peak at 24° is related to the crystalline cellulose content of the biomass, which has not yet been degraded (Ben Salem et al., 2021; Mukherjee et al., 2021). The hemicellulose was detected at about 33.5°. The 45° is caused by calcium carbonate (CC) and the vibrations were more pronounced at 409°C PKS. These results are consistent with the changes detected by the TGA and FTIR results, which only show a change at 409°C PKS. Similarly, the FTIR results show no significant differences between the biochar types tested. An overall analysis of the crystallinity and stability of the biochar after carbonisation shows that it is mainly an amorphous material with cellulose and low carbonates.

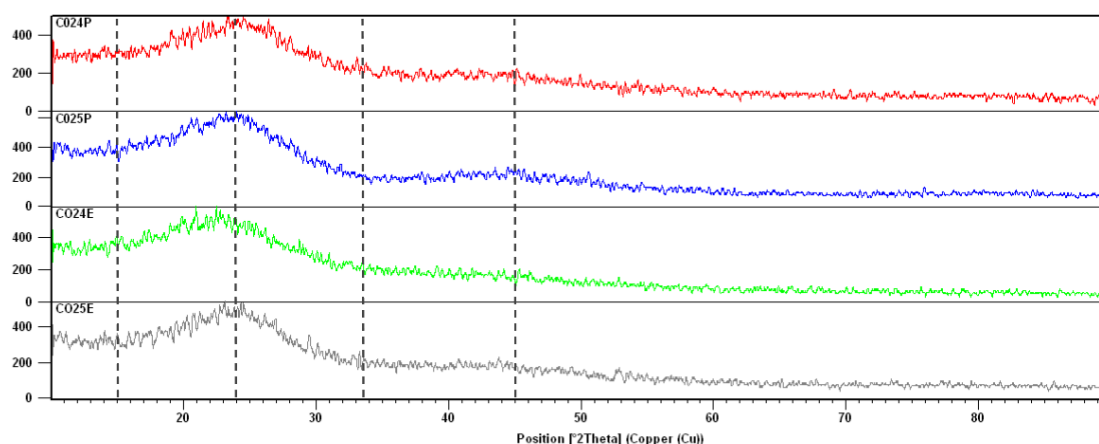


Figure 5.5 XRD analysis of biochar samples after the carbonation test.

5.3.1.4 Microscopic Viewing

Another aspect of the biochar that would determine the ability to adsorb CO₂ would be the distribution and size of the pores of the biochar in relation to the kinetic diameter of the CO₂ molecules (Winters et al., 2022). Figures 5.6 and 5.7 show the FESEM images of four types of biochar after the carbonisation test. Figure 5.6 shows the 409°C PKS, 500°C PKS, 455°C EFB and 500°C EFB after exposure to concentrated CO₂ for only 24 hours. A yellow arrow shows the different pores that were clogged by the white mould particles, which could mean that the biochar particles reached a saturation point within 24 hours. Another study that conducted the carbonisation test using date palm leaf biochar with similar pore structure and pattern as EFB reported that it reached an equilibrium state and stopped CO₂ adsorption after only 20 to 40 minutes (Ben Salem et al., 2021). To identify the mineral formation clogging the pores, EDX tests were performed at both 409°C PKS and 455°C EFB. The tests show that a high content of carbon and oxygen was detected in the particles, confirming the formation of carbonyl compounds through the carbonisation process.

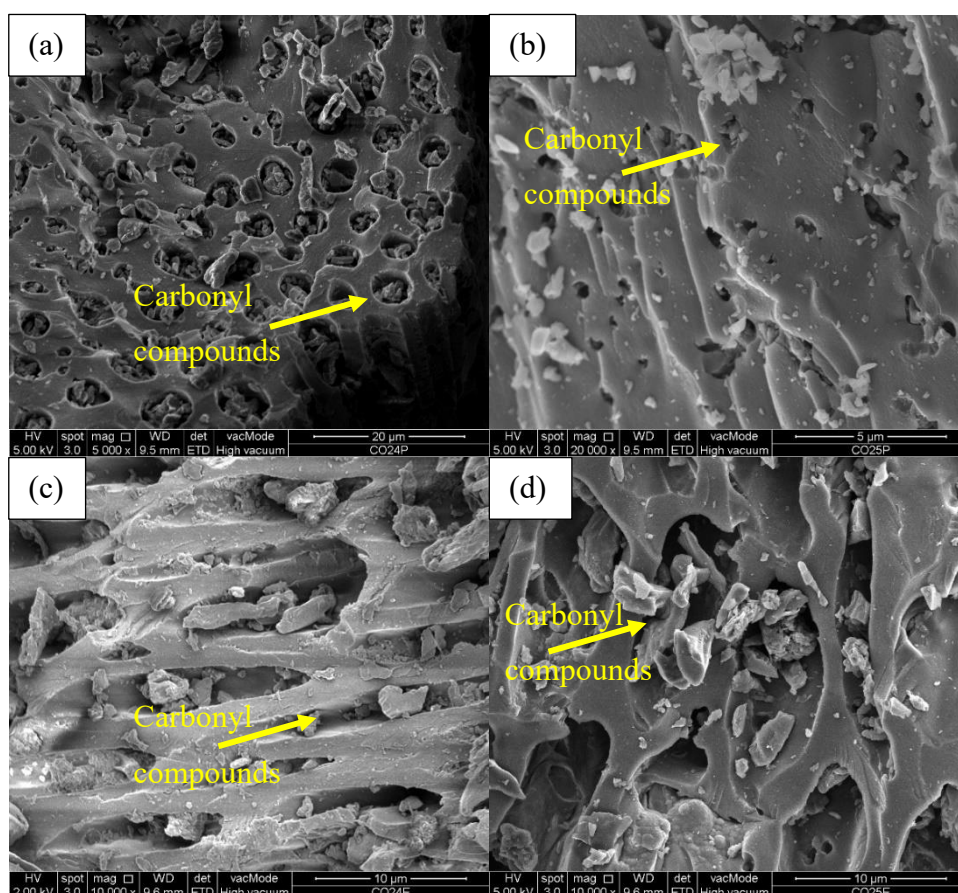


Figure 5.6 FESEM images of biochar samples post carbonation test. (a) 409°C PKS, (b) 500°C PKS, (c) 455°C EFB and (d) 500°C EFB.

The images in Figure 5.6 are consistent with the hypothesis that most of the trapped CO₂ was mainly due to physical adsorption due to the pores rather than chemical composition. This is consistent with the minor significant chemical changes detected by FTIR and XRD. This result was also reported by other studies (Ben Salem et al., 2021; Klasson et al., 2015; Sevilla et al., 2011; Shafawi et al., 2021; Zhang et al., 2023). The physical adsorption of CO₂ on biochar occurs via Van Der Waals interactions between gas molecules and the solid surface, which is influenced by the specific surface area, pore size and pore volume of the biochar. Therefore, it is important to evaluate the porosity of biochar and its pore sizes to understand its absorption and retention capacity.

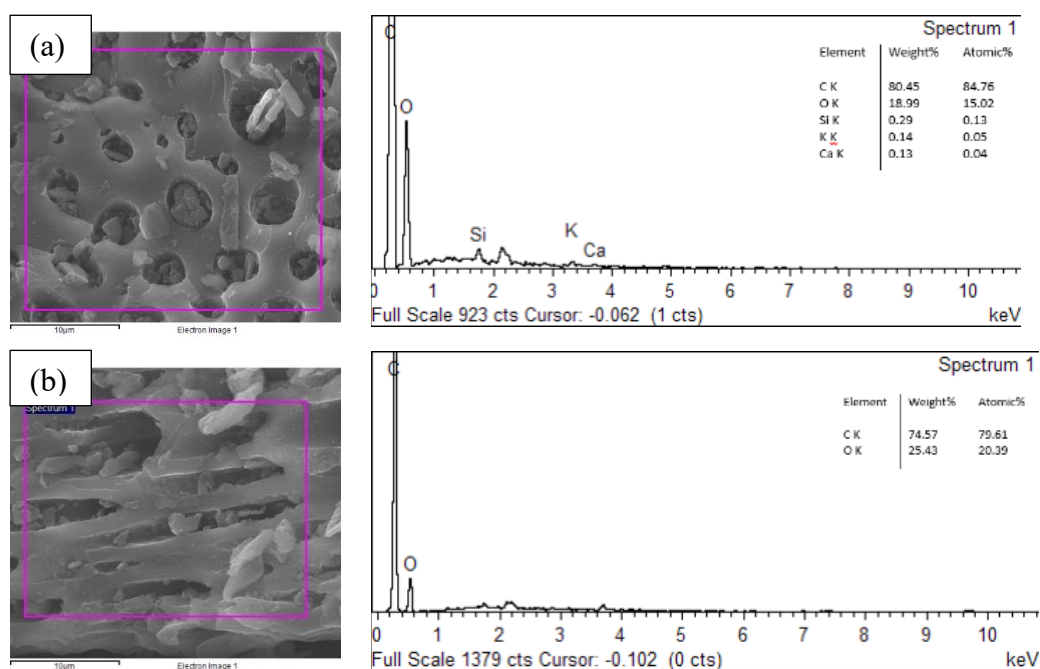


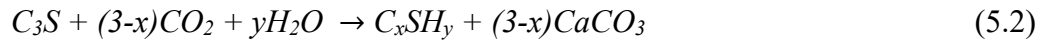
Figure 5.7 FESEM-EDX of biochar samples post carbonation test. (a) 409°C PKS and (b) 455°C EFB.

In a study in which biochar was treated with potassium and sodium hydroxides to increase the surface area for adsorption of CO₂, with biochar produced at temperatures 550-600°C (Gupta and Kua, 2017). They reported that when the kinetic diameter of the CO₂ molecule is 0.33 nm, CO₂ adsorption decreases at high pyrolysis temperatures, resulting in larger or smaller pores. The results of this study suggest that temperature has the greatest influence on the surface area and pore distribution (Chapter 3 Section 3.2.1.5 and 3.2.2.5). This is caused by the release of volatile substances from the biomass. 500°C PKS in Figure 5.6 (b) show the smallest pore size, which is less than 5 μm, as shown by the scale at the bottom of the image. One study found that CO₂

adsorption is influenced by the tubular pore structure of the biochar (Zhang et al., 2023). The characteristics of the tubular pore structure of biochar are defined by its size, shape, quantity and distribution. As previously confirmed by the different SEM images (Section 3.2.1.5 and 3.2.2.5), the PKS biochar exhibited a more tubular pore structure than the fibrous structure of EFB due to its granular shape.

5.3.2 Biochar Concrete and Mortar Composites

Carbonation is the chemical reaction of the formation of water and CaCO_3 when CO_2 reacts with Ca(OH)_2 shown in Equation (5.1) (Groves et al., 1990; Šavija and Luković, 2016a). It often occurs when the cementitious materials are carbon cured at the early stages and CO_2 reacts with cement hydrates. Other phases in the cement paste, including C-S-H, ettringite, and un-hydrated cement, undergo reactions with carbon dioxide (Šavija and Luković, 2016b). Un-hydrated C_3S react directly with CO_2 to form CSH and CaCO_3 Equation (5.2) (Song et al., 2023).



This research investigated if replacing cement with 4% of different types of biochar would aid the carbonation process after it has been water cured. As mentioned earlier the experiment was conducted within 24 hrs only to theorise that when used for any application and without carbon curing it would still sequester CO_2 . The mortar and concrete results have been combined and discussed for each test. The mass changes after the CO_2 test are first discussed followed by the phenolphthalein test, TGA, FTIR, XRD and the FESEM imaging.

5.3.2.1 Mass Change

The change in mass of the mortar and concrete samples before and after the carbon sequestration test was measured and is shown in Figure 5.8 (a) and (b). The mass of the samples was measured three times, and the following equations (5.3) and (5.4) were used to calculate and understand the behaviour of the samples under concentrated CO_2 exposure for 24 hours. P1 is the original mass, P2 is the mass after 24 hours of concentrated CO_2 , P3 is the carbonated samples after 24 hours of exposure to atmospheric air. In equation (5.3), the amount of CO_2 and moisture absorbed by the samples is determined by subtracting the mass of the samples immediately after 24

hours in the box with concentrated CO₂ (P₂) from the originally measured mass (P₁). This increase in moisture is due to the formation of water during the carbonisation process, as indicated in equation (5.1). Equation (5.2) gives the loss of moisture that has occurred during carbonisation, possibly including the original moisture content of the samples. It is calculated by subtracting the mass of the samples after 24 hours in air (P₃) from the mass of the samples immediately after the concentrated CO₂ exposure (P₂).

$$CO_2 + H_2O \text{ Absorbed} = P_2 - P_1 \quad (5.3)$$

$$H_2O \text{ loss to Atmosphere} = P_3 - P_2 \quad (5.4)$$

MC and CONC in Figure 5.8 (a) and (b) represent the control samples. M followed by 4P (409°C PKS), 4E (455°C EFB), 5P (500°C PKS), 5E (500°C EFB) represent the biochar mortar composites. Similarly for the biochar concrete composites CON, followed by 4P, 4E, 5E and 5P. Figure 5.8 (a) shows that the highest initial mass change contributing to the maximum CO₂ and moisture uptake (represented by blue bars) occurred for the mortar composite at 4% 455°C EFB (1.8 g), followed by 409°C PKS and (1.7 g), control (1.5 g), 500°C PKS (1.4 g) and the lowest at 500°C EFB (1.3 g). This initial mass increase is attributed to the diffusion process of concentrated CO₂ in the environment with the samples. The difference in sample size between mortar and concrete resulted in a greater mass increase for concrete compared to mortar, as shown in Figure 5.8. For the concrete composites in Figure 5.8 (b), it can be seen that the highest CO₂ and moisture absorbed is also by the concrete composite with 4% 455 EFB (5.3), followed by 409°C PKS and (4.3 g), 500°C PKS (4 g) and the lowest by 500°C EFB (1 g). However, the control concrete sample unexpectedly showed the highest increase of 6.3 g. The high moisture increase could also be due to the fact that the environment in the box was sealed, and all samples absorbed moisture at once. It has been reported that high humidity promotes the carbonation process, while pressure influences its progression (Šavija and Luković, 2016b). The moisture leakage of the mortar composites into the atmosphere (represented by the red bar) is related to the same trend in the porosity properties of the samples as described in Chapter 4 Section 4.2.1.2. The 500 EFB°C showed the highest moisture loss, the control samples the lowest. For the concrete composites, the highest porosity was also found at 500°C EFB (Section 4.2.2.2) and the lowest at 500°C PKS. However, the lowest moisture loss was observed in the concrete composites between 409°C and 500°C PKS.

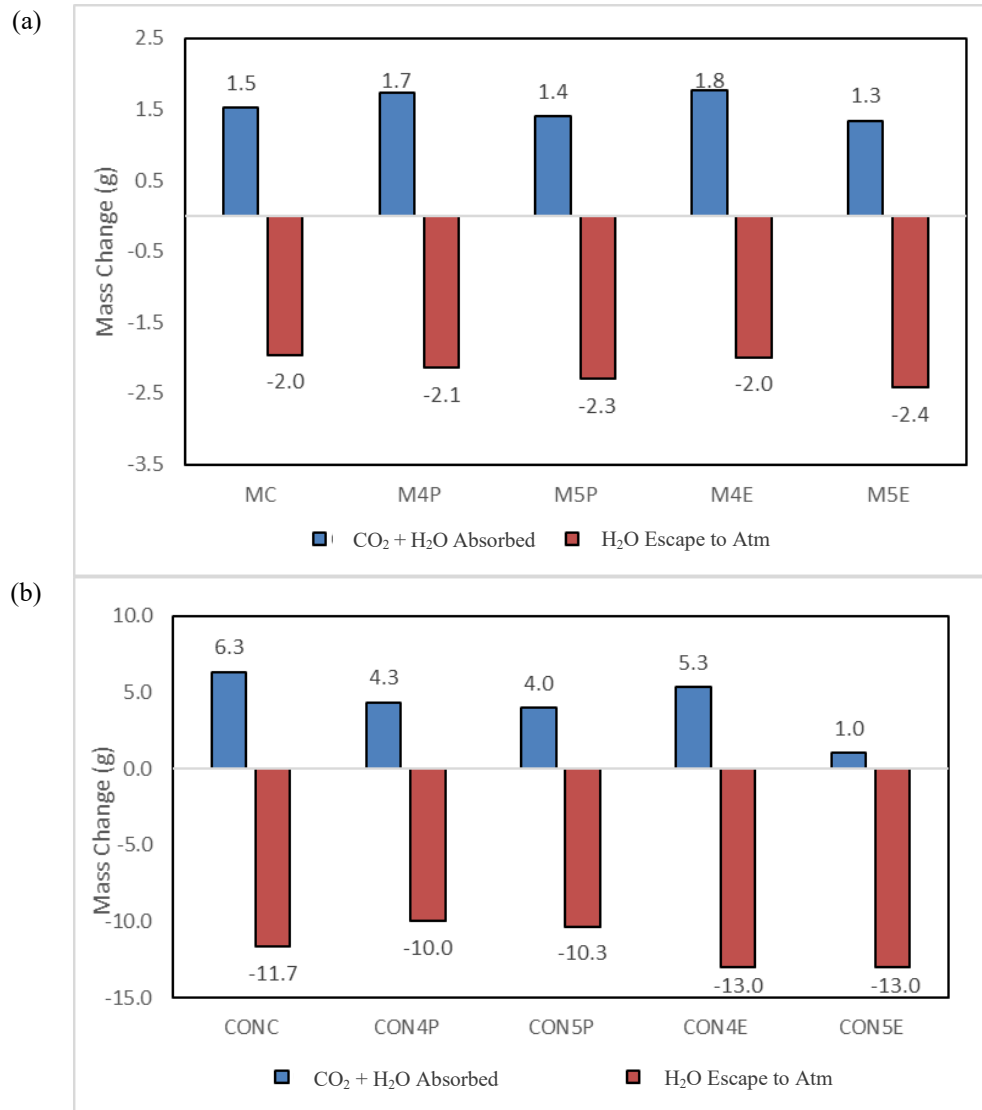


Figure 5.8 Mass change before and after the carbonation test of (a) mortar samples and (b) concrete samples.

One study reported that a significant mass change occurred after only 2 hours of exposure to concentrated CO₂ (Praneeth et al., 2022). The mass change of biochar mortar and concrete composites is sensitive to the time of CO₂ introduction. In other studies where CO₂ was used as part of the carbon curing process, more significant mass changes were observed, primarily due to the initial formation of cement hydrates (Chen et al., 2022b; Gupta, 2021; Gupta and Kua, 2019; Liu et al., 2023; Praneeth et al., 2020a; Wang et al., 2020a). In contrast, the samples in this study were already cured with water and the cement hydrates had already formed. Therefore, the additional mass changes shown in Figure 5.8 are likely due to the physical adsorption of CO₂. Further tests were conducted and discussed to determine whether the chemical composition of the samples had also changed. The biochar mortar and concrete composites, the sample with 455°C

EFB and 409°C PKS biochar proved to have the highest potential CO₂ sequester through physical adsorption compared to 500°C of PKS and EFB.

5.3.2.1 Phenolphthalein Test

A phenolphthalein test was carried out on all samples in order to visually represent the different intensity of carbonisation through different shades of pink (Figure 5.9). The different shades are an indication of the possible depth of carbonation in the samples and their pH value over a 24-hour period. Figure 5.9 shows the phenolphthalein test on the biochar composites from mortar and concrete as well as on the control samples. The dark pink spots observed are highlighted by the black outlined circles, indicating that no carbonation reactions took place. Both the control samples of mortar and concrete showed larger areas without carbonation compared to the other biochar composite samples, with even all corners shaded dark pink. Most studies have conducted the phenolphthalein tests after curing the carbon for 28 days, which makes it difficult to accurately compare the results as this research focuses on the potential of the composites to sequester carbon over 24 hours (Chen et al., 2022b; Gupta, 2021; Gupta and Kua, 2019; Liu et al., 2023; Praneeth et al., 2020a; Wang et al., 2020a). The same studies have reported that increasing the biochar content increased the rate of carbonation. A study of palm oil shell biochar (produced at 400°C) with an addition of 0.5% to the mortar showed a clear difference in colour, with a slight pink tint after 7 days, but no trace of pink after 28 days (Flórez et al., 2019). With a similar time span of 7 to 28 days, another test also showed visible changes in the form of a decrease in the depth of the dark pink colour when 5 biochar was replaced with biochar (Liu et al., 2023).

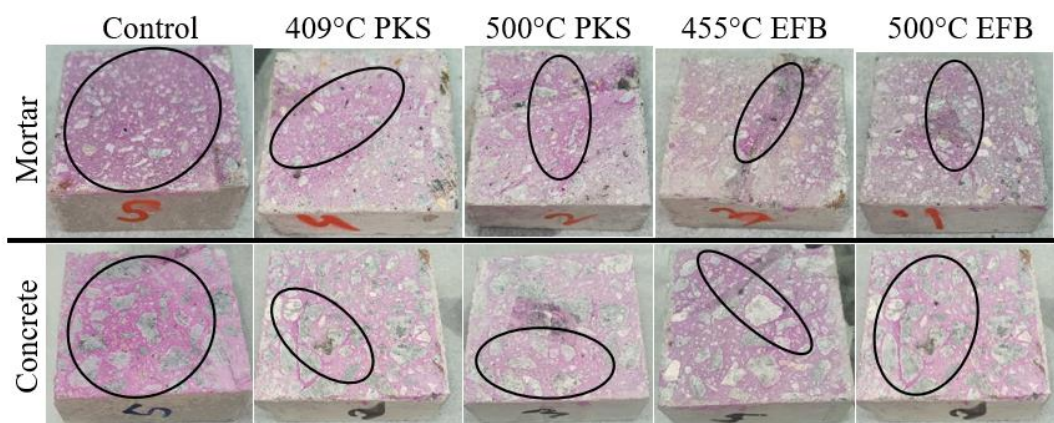


Figure 5.9 Phenolphthalein test on samples post carbonation test.

To relate the mass change and the phenolphthalein test, the occurrence of carbonisation can be indicated by physical adsorption. Although the control samples initially showed a high mass increase, carbonation was very low during the phenolphthalein test compared to the biochar composites. At the optimised pyrolysis temperatures, the mass gain for both materials was 409°C PKS and 455°C EFB, while the phenolphthalein test only showed a clearer difference between the mortar and concrete composites at 455°C EFB.

5.3.2.3 Thermal Analysis

Figure 5.10 shows the TGA of the mortar and concrete composites after the carbonation test. MCC and CONCC in Figure 5.10 (a) and (b) represent the control samples. M, followed by 4PC (409°C PKS), 4EC (455°C EFB), 5PC (500°C PKS), 5EC (500°C EFB) represent the biochar-mortar composites. The situation is similar for the biochar-concrete composites CON, followed by 4PC, 4EC, 5EC and 5PC. The Bhatti method was used to analyse the TGA data, as already described in Chapter 4 Section 4.2.3.3 (Dixit et al., 2019; Gupta, 2021; Manjunath et al., 2024; Mishra et al., 2023; Yang and Wang, 2021). As mentioned earlier, the dehydration phase involves the removal of water from calcium silicate hydrates (C-S-H). Dehydroxylation refers to the elimination of water from calcium hydroxide (CH), while decarbonation involves the release of CO₂ from crystallised calcite. This means that the greatest mass loss occurs in the decarbonisation phase, which means that CO₂ retention is highest. Figure 5.10 shows that the highest CO₂ retention for the mortar sample is the control (MCC) and for the concrete samples is the composite at 409°C PKS. The CO₂ lost at this temperature was obtained by diffusion and reacted chemically with CH. In another study, it was found that the materials retain CO₂ not only through the chemical reactions of carbonation, but also through diffusion (Senadheera et al., 2023). The results of the equations (4.6 to 4.8) are shown in Figure 5.11 for mortar and concrete samples after the carbonation experiment. Figure 5.11 (a) shows that for the mortar samples, the control has the highest DOH (31.8%) and the 455°C EFB has the lowest DOH (18.5%). Figure 5.11 (b) shows that the concrete composite with 500°C EFB had the highest DOH (30.3%) and the 500°C PKS the lowest (17%). The difference in the behaviour of biochar with mortar and concrete composites is, as already mentioned, due to the different water-cement ratio. As reported in another study (Barbhuiya et al., 2024), it is also a common challenge to ensure uniform distribution of biochar in a mixture.

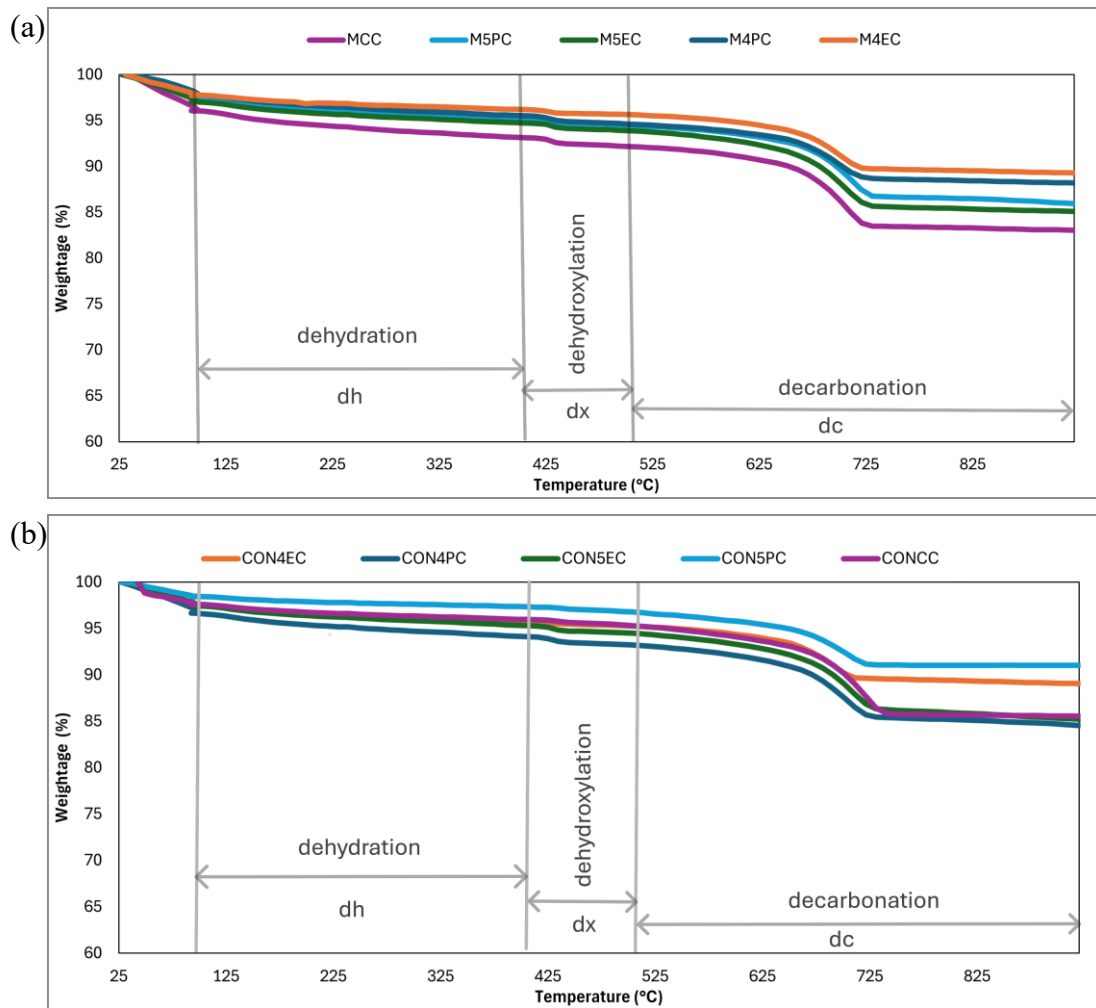


Figure 5.10 TGA post carbonation test of (a) mortar samples and (b) concrete samples.

One study suggests that when the amount of biochar was increased by 1%, the chemically bound water decreased less than in the control (Mishra et al., 2023). The authors then reported that when the biochar content was increased to 1.5%, the chemically bound water increased more than in the control, as water retention also increased with the increase in biochar content. However, in this research, 4% biochar was used to replace cement. The porosity, distribution and water retention properties of each type of biochar play an important role in influencing DOH. Of all the biochar composites, the 500°C EFB exhibited high DOH and chemically bound water. The CH content of these composites was low, proving that the reaction of adsorption of CO₂ and reaction with CH would produce a high amount of cement hydrates and water content, as indicated in Equation 5.1.

The highest CH content of the biochar composite was by 409°C PKS for both mortar and concrete composites. This particular composite also exhibited high DOH (23.4 and

28.6%) and chemically bound water (5.6 and 6.9%), indicating that carbonation has occurred and further carbonation is possible. This is consistent with the phenolphthalein and mass change tests. These changes can be attributed to the basic property of the 409°C PKS biochar, as it had the highest combination of pore volume and pore width for adsorption ($0.00461 \text{ cm}^3/\text{g}$ and $84.1 \text{ \AA}$) and desorption ($0.00318 \text{ cm}^3/\text{g}$ and $58.0 \text{ \AA}$). This allowed the biochar to absorb and bind CO_2 when the samples were exposed to the high concentration for 24 hours. Considering all factors from the thermal analysis tests, which include DOH, CH and chemically bound water, the optimal composites would be 409°C PKS and 500°C EFB.

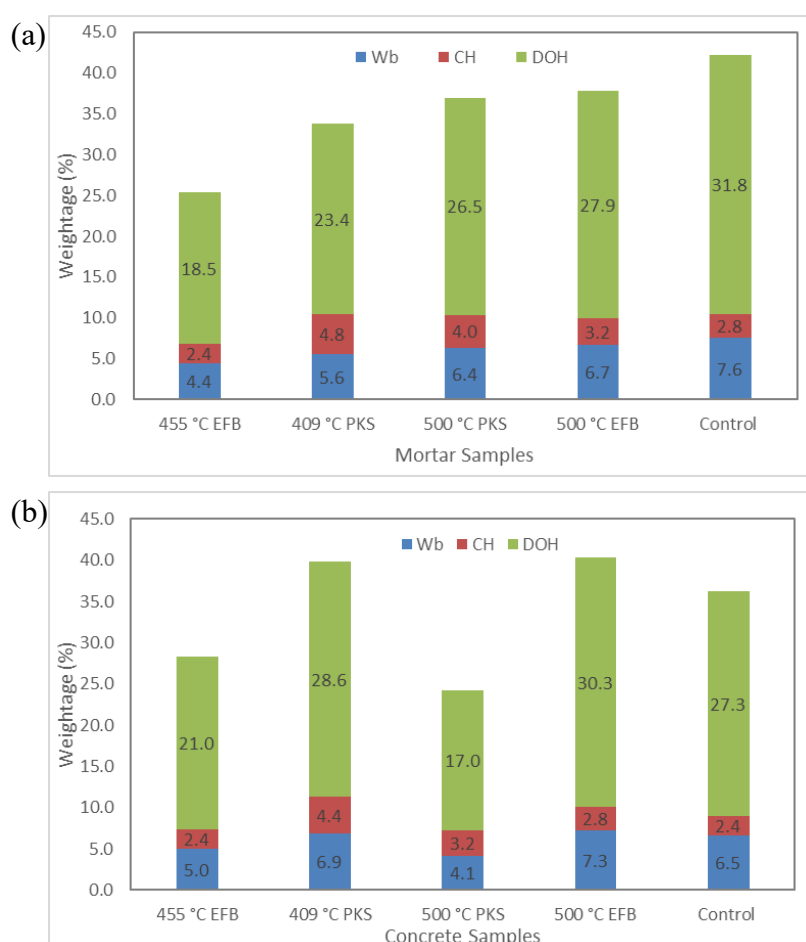


Figure 5.11 Degree of hydration of (a) mortar samples and (b) concrete samples.

5.3.2.4 Functional Groups

The FTIR analysis of the carbonated samples is shown in Figure 5.11 (a)-(b). The colour coding and labelling are similar to the TGA results. The test was performed to determine the detection or increase in carbonyl functional groups that would occur after the carbonisation experiment. It was also performed to determine shifts and the presence of new peaks in the composites. Figure 5.11 (a) of the biochar-mortar

composites shows that the composites with 409°C PKS and 500 PKS°C had a higher transmittance than the EFB composites and the lowest for the control sample. In particular, the carbonyl group (C=O) was detected in the range of 1410- 1510 cm^{-1} (Chang and Chen, 2006). The presence of these carbonyl groups proves that carbonation has taken place, which was more pronounced in the mortar composites with PKS biochar. The C-O group around 1061 and 1150 cm^{-1} was also detected in the concrete composites with biochar. The combination of C=O and Si-O was also detected to identify the intensity of CSH (Akhtar and Sarmah, 2018b; Haris Javed et al., 2022; Manjunath et al., 2024). More C=O was detected in mortar composites than in concrete composites between 1500 and 2000 cm^{-1} . This indicates a higher carbonation C_3S and the formation of CSH as indicated in equation (5.3).

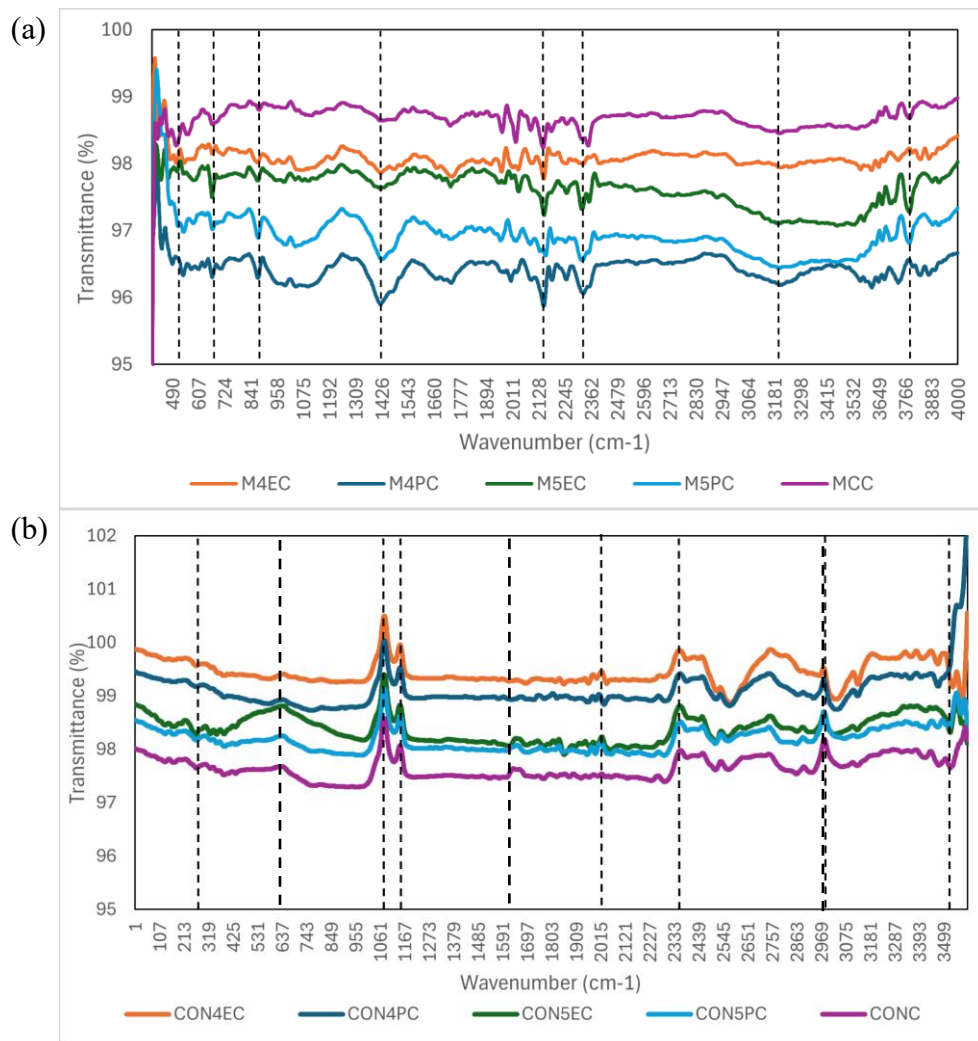


Figure 5.11 FTIR analysis post carbonation of (a) mortar composites and (b) and concrete composites.

Further evidence of carbonation can be provided by the loss of hydroxyl groups detected between 3000 and 3600 cm^{-1} . This hydroxyl group is linked to the CH (Akhtar and Sarmah, 2018b, 2018a; Haris Javed et al., 2022). A decrease in CH means a higher reaction with CO_2 forming CC, as indicated in equation (5.2). Of the mortar samples, the control sample shows the least vibration and EFB at 455°C, which is consistent with the low CH content of 2.8 and 2.4% calculated from the TGA results from Figure 5.11 (a). However, no noticeable changes were observed in the concrete composites when all composites were compared. An overall analysis of the FTIR results shows that the comparison between the control and the composites after the carbonation process is very small. This could be due to the fact that a considerable amount of CO_2 was absorbed by diffusion during carbonisation and not chemically adsorbed, as shown by the phenolphthalein, mass change and TGA results.

5.3.2.5 Crystalline Structure

The XRD analysis is carried out on mortar and composites after the carbonisation experiment, as shown in Figure 5.12. The colour coding and labelling are similar to the TGA and FTIR results. It was performed to investigate the difference in crystalline structure after the samples had been exposed to a concentrated CO_2 environment. This test was important to identify the intensities mainly between CH and CC. It was confirmed that carbonation occurs at low intensity of CH and higher presence of CC according to the equation (5.2). The peaks with respect to CH were low at 17°, ~47°, ~34°, 50° and 68° 2 θ for both mortar and concrete, confirming the degradation of CH (Chang and Chen, 2006; Gupta, 2021; Kushwah et al., 2024; Manjunath et al., 2024). It is noteworthy that the CH intensities in the control samples are higher than in the biochar composites for mortar and concrete. The presence of CC was detected at 26°, 27°, 28°, 36° and 40° 2 θ (Chang and Chen, 2006; Gupta, 2021; Praneeth et al., 2020a). C_3S was detected at 38° 2 θ for both composites. can still occur after 24 hours. In addition, further smaller C_3S peaks were observed at around 59° 2 θ in Figure 5.13 (b). This indicates that more carbonation through formation of CSH from C_3S according to equation (5.3). In both Figure 5.13 (a) and Figure 5.13 (b), an important observation is that the composites with 500°C PKS and 500°C EFB have a slightly higher intensity of peaks than the composites with 409°C PKS and 455°C EFB. This suggests that biochar with a higher carbon content may play a role in influencing the changes in the crystalline structure of the composite during carbonisation. However, the observed

differences in crystallinity are relatively small and consistent with the results of the FTIR analysis. The results show no significant changes in functional groups or crystalline phases in the material after exposure to CO₂ for only 24 hours. This suggests that while the carbon content of the biochar may have some influence on the initial phase of carbonisation, the short exposure duration limits the extent of chemical changes in the composite.

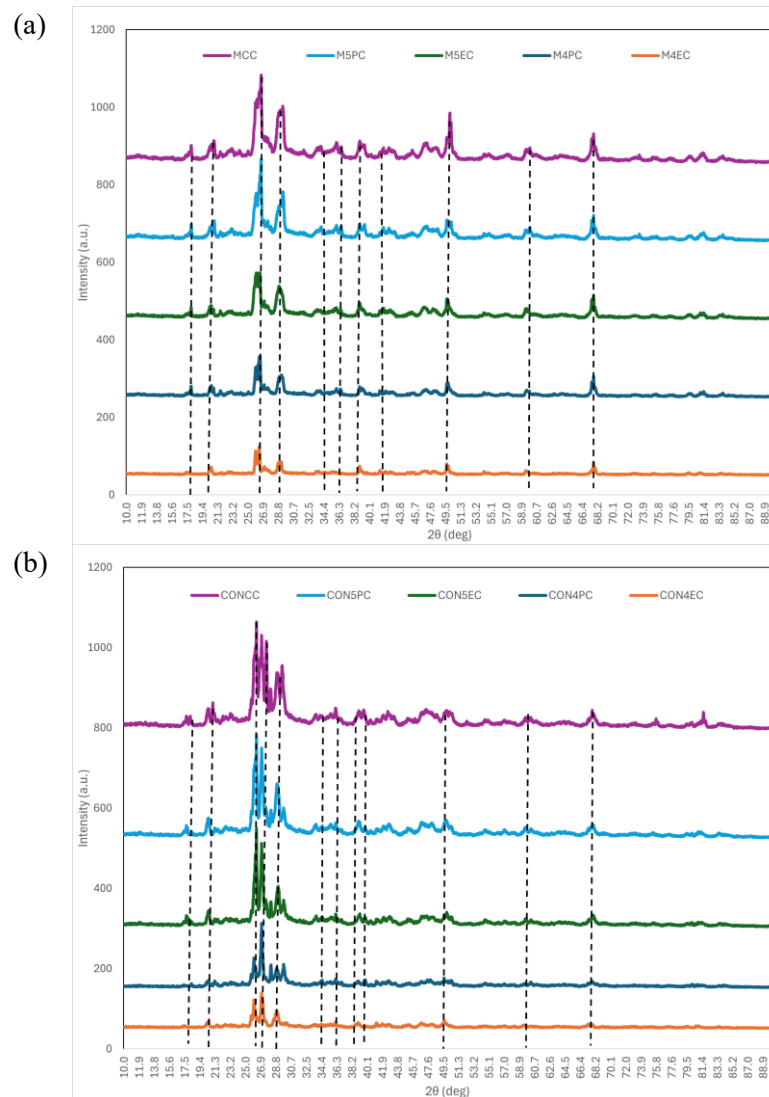


Figure 5.12 XRD analysis post carbonation of (a) mortar composites and (b) concrete composites.

5.3.2.6 Microscopic Viewing

Figure 5.13 (a)-(f) shows the FESEM images of the mortar and concrete samples after the carbonisation test. In the images, the CH is highlighted with a yellow circle, the CSH with a red circle and the biochar sample with a green circle. The images show that the cement hydrates CH and CSH can be seen in all samples. An important observation

in Figure 5.13 (c) is the formation of cement hydrates in and around the pores of the biochar, highlighted by the green arrows. The tubular structure of the 409°C PKS enabled the retention of water in the pores and thus the formation of cement hydrates. In this process, the biochar serves as a nucleus for the formation of cement hydrates when it absorbs water or CO₂ (Song et al., 2023). The carbonisation process involves the formation of CC and CSH from CH, as described in equations (5.1) and (5.2). The clear presence of CH in Figures 5.13 (a)- (f) indicates that the samples have the potential for further carbonation and have not yet reached their full saturation point after 24 hours.

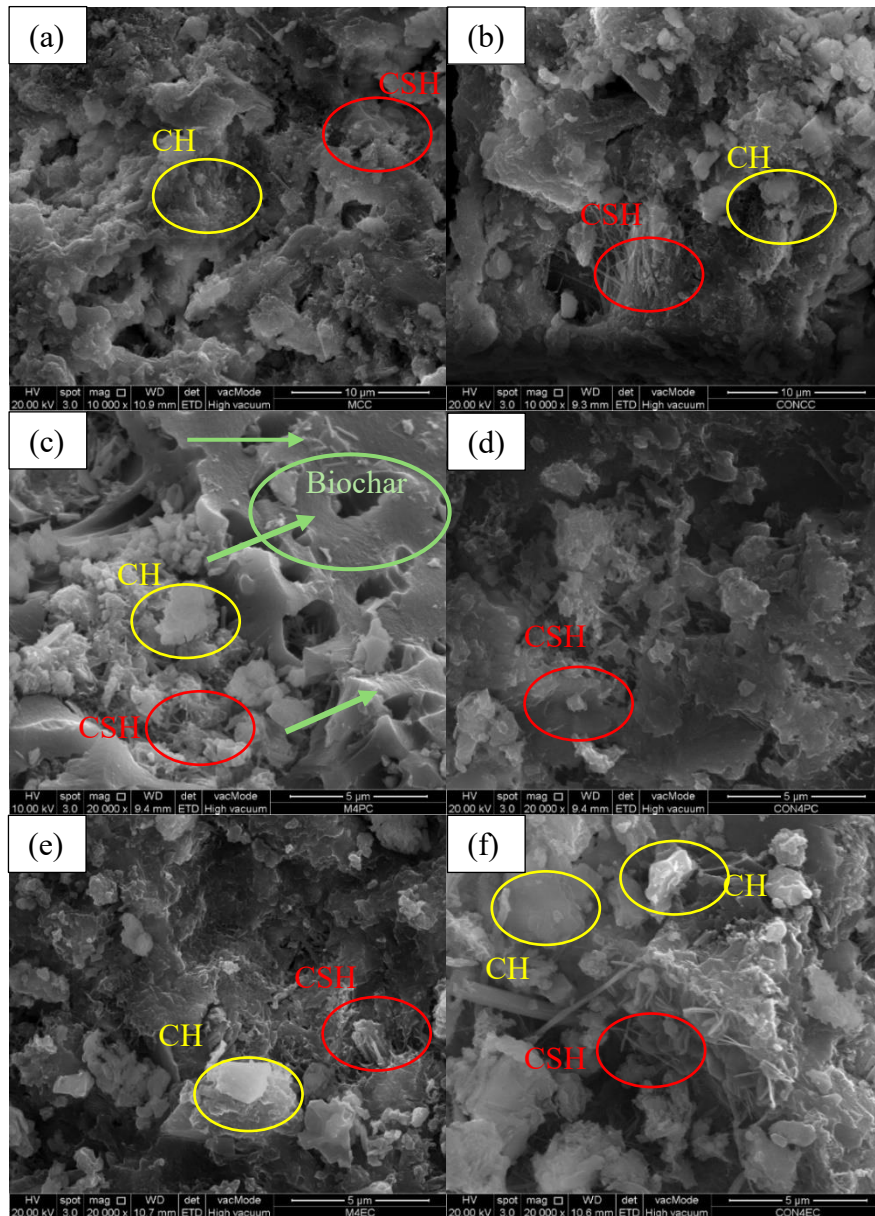


Figure 5.13 FESEM images of samples after the carbonation test, (a) mortar control, (b) concrete control, (c) 409°C PKS mortar, (d) 409°C PKS concrete, (e) 455°C EFB mortar and (f) 455°C EFB concrete.

5.4 Summary of Findings

The hypothesis underlying this objective suggests that mortar and concrete composites, after attaining their target compressive strength and other required design properties, can sequester CO₂ post-casting without the need for any pre-treatment or alternative curing techniques. This chapter can be broken down into two major conclusions of the carbonation process on biochar samples, biochar as cement replacement for mortar and concrete composites:

- **Biochar:** The TGA results revealed a notable change in the carbon content and thermal properties of the biochar, particularly at 409°C for PKS. FTIR and XRD analyses identified minor formations of new carbonyl compounds. Additionally, microscopic images indicated that the pores of the biochar were saturated with these newly formed carbonyl compounds, suggesting that the biochar reached its saturation point within the 24-hr duration of the study.
- **Biochar Mortar and Concrete Composites:** The mass change and phenolphthalein tests have shown significant changes between the samples and showed carbonation has taken place more prominently in composites with 409°C PKS and 455°C EFB. The analysis conducted in relation to the TGA showed an optimal presence of carbonation in composites with 409°C PKS and 500°C EFB. However, the crystalline and function groups change in the composites were not significant. This indicates that most of the sequestered CO₂ within 24 hours was due to physical adsorption.

The use of biochar as a cement replacement for mortar and concrete composites is itself a utilisation of carbon storage. Kurniawan et al., (2023) have demonstrated the dual role of the biochar material in carbon sequestration by investigating its ability to sequester carbon during biomass conversion and its subsequent adsorption capacity. In addition, the use of biochar as a partial replacement for cement serves as an environmentally friendly solution for waste disposal and as an approach to carbon sequestration, providing benefits for both the environment and industry (Song et al., 2023). These authors stated that 2.5 gigatonnes of CO₂ could be sequestered annually through the various applications in different sectors. Another study reported that the use of 1 biochar in concrete could possibly sequester 0.5 gigatonnes of CO₂ in a year, which is equivalent to about 20% of the annual CO₂ emissions of the cement-based industry

(Akinyemi and Adesina, 2020). The discussed results of this chapter have led to the conclusion that the biochar mortar and the concrete composites with the optimum biochar of 409°C PKS and 455°C EFB have the potential to sequester CO₂ in the long term. This then leads to the next chapter, in which the long-term environmental impact of the samples is discussed through a life cycle assessment study.

Chapter 6 Life Cycle Assessment of Biochar Composites

This chapter covers the final objective of this research: the life cycle assessment (LCA) of the biochar mortar and concrete composites. The aim of this research is to design sustainable building materials that can be environmentally beneficial compared to the conventional mix. This is done by assessing the environmental impact of each type of sample with 4% of cement replacement with biochar for both mortar and concrete applications. Scenarios were developed for each sample using the OpenLCA software and compared with conventional method. The LCA for concrete and mortar composites were assessed individually as each material could be utilised for different applications that include brick laying, sound proofing, low structural elements, pavement and drainage.

6.1 Methodology

LCA framework is outlined from ISO 14040 and 14044 standards (Guinée, 2001). It begins with identifying and defining the goal and scope of the study. This is followed by collecting the Life Cycle Inventory (LCI) data that involves the energy and the emissions of a given process. Next is the selection of the environmental impact assessment known as the Life Cycle Impact Assessment (LCIA). It evaluates the life cycle based on the defined functional unit of the material and converts the LCI data to a list of environmental impact methods. Finally, the interpretation of the results was conducted, and as part of the process being performed, changes are proposed to each stage of the LCA as indicated by the arrows in Figure 6.1. Current research consists of two comparative LCA studies conducted separately to identify the concrete or mortar mix with the least environmental burden.

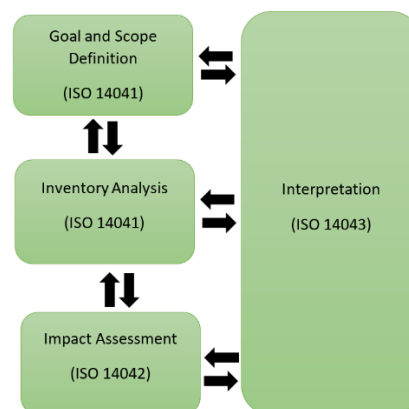


Figure 6.1 The different stages of the life cycle assessment process.

6.1.1 Goal and Scope

The first aspect of the LCA studies is to define the goal and scope, which are to evaluate and compare the environmental impact associated with the manufacturing of the different types of biochar mortar and concrete composites. Defining the LCA consists of determining and stating the purpose of the study, the system boundaries taken into consideration, the functional unit, the materials used, and finally the scenarios that have been set. The purpose of both LCA studies is to determine which type of biochar utilised in either composite concrete or mortar has the least environmental impact. The system boundaries of the study entail which stages of the life cycle are taken into consideration. For the concrete LCA, system boundary known as cradle to gate is considered, which implies the process from manufacturing the materials required for the concrete mix, the transport, the waste deposited in the landfill, and finally the concrete batching plant as circled by the dashed line in Figure 6.2 (a). For the mortar LCA, the system boundary gate to gate is considered, which implies the manufacturing of the materials required for each specific mortar mix and only the waste deposited to the landfill as circled by the dashed line in Figure 6.2 (b). Distances were not taken into account in the LCA of the mortar mix, as it focuses exclusively on the manufacturing materials, which can be sourced directly from the production site regardless of the location. In contrast, the LCA for concrete includes the transport distances from the production site to the concrete batching plant, therefore distances from the palm oil mill were also taken into account. The materials considered for both LCA studies are cement, fine aggregate, biochar, and biomass deposited as waste; additionally, coarse aggregate is used for the concrete LCA. The functional unit of the LCA study indicates the amount of the final product. They were considered when keying in the inventory data, such as energy and emissions required to produce each material. For both LCA studies, 1 m³ of final product concrete and mortar is chosen. All the fundamental materials for each mix are calculated in terms of mass (kg) that are required for 1 m³ for mortar and concrete.

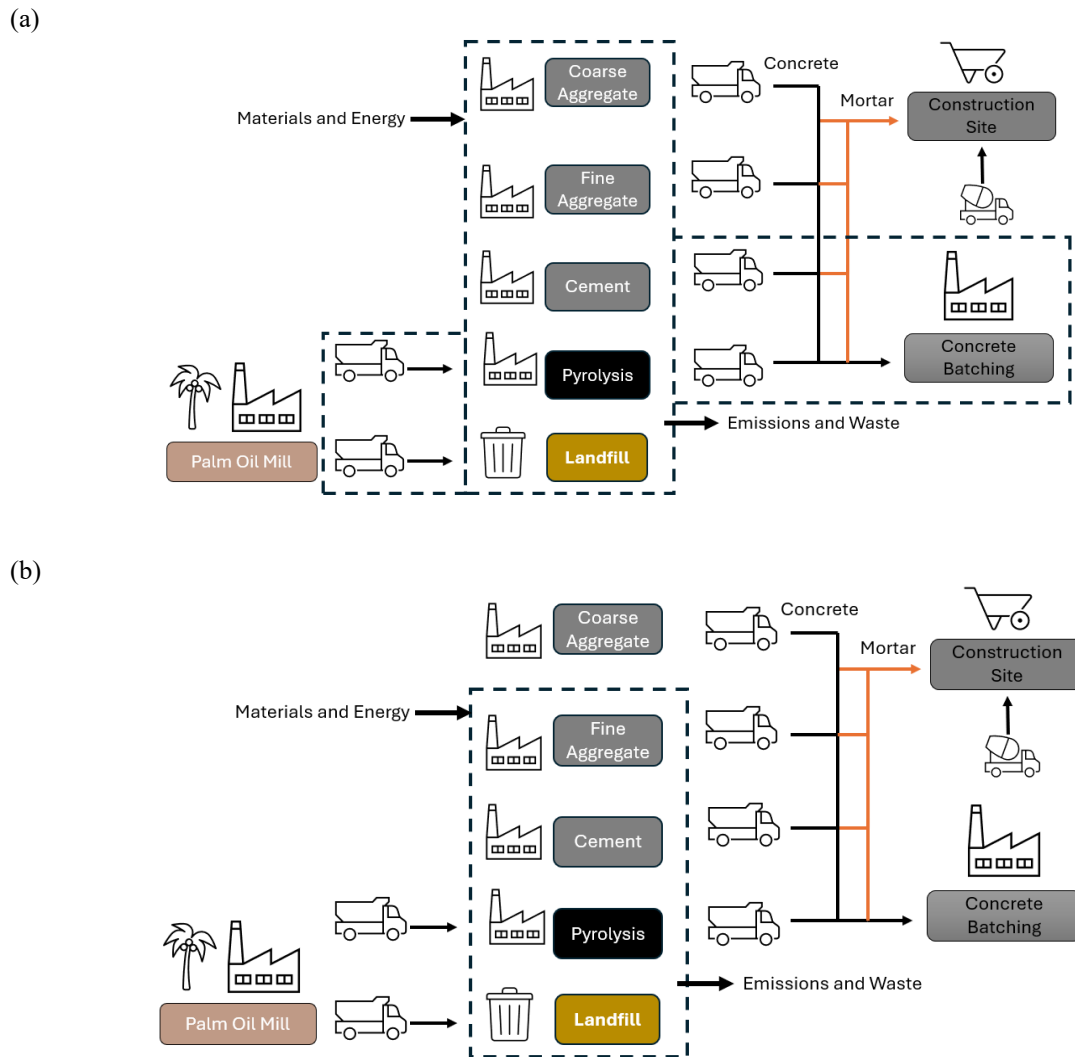


Figure 6.2 (a) Concrete LCA system boundary, (b) Mortar LCA system boundary.

5 scenarios have been set for the two LCA studies, as shown in Table 6.1. The type, and the amount of biochar used in each scenario is listed. The first scenario of both LCAs consists of the control mixes involving no biochar and consists only biomass quantity that would be deposited at the landfill site. Additionally, for both LCA scenarios 2 to 5 have 4% of each type of biochar produced with different temperatures and 96% of the total cement. Each material, concrete and mortar, has different mix ratios, as elaborated in the methodology of Chapter 4 (Sections 4.1.1 and 4.1.2). Therefore, in Table 6.1, the amount required for each material to mix 1 m³ of both concrete and mortar is stated and taken into consideration when the inventory data is used. Furthermore, Table 6.2 is given to provide a clear understanding of which processes are taken into consideration in each scenario of both LCA studies.

Table 6.1 Labelling of the different scenarios and the quantity of materials used.

Scenario	Concrete	Mortar
Control Mix	SC1	SM1
Composite with 4% PKS Biochar at 500°C	SC2	SM2
Composite with 4% PKS Biochar at 409°C	SC3	SM3
Composite with 4% EFB Biochar at 455°C	SC4	SM4
Composite with 4% EFB Biochar at 500°C	SC5	SM5
Functional Unit	1 m ³ of Concrete	1 m ³ of Mortar
100% Cement (kg)	450	600
96% Cement (kg)	432	576
4% Biochar (kg)	18	24
Fine Aggregate (kg)	600	1200
Coarse Aggregate (kg)	1100	-

Table 6.2 Processes in each scenario.

	Scenario	Coarse Agg	Fine Agg	Cement	Pyrolysis	Landfill	Concrete Batching	T ¹ :POM ² to Pyrolysis	T ¹ :POM ² to Landfill	T ¹ :Cement to Concrete	T ¹ : Pyrolysis to Concrete
Concrete	SC1	✓	✓	✓	✗	✓	✓	✗	✓	✓	✗
	SC2	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	SC3	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	SC4	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
	SC5	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Mortar	SM1	✗	✓	✓	✗	✓	✗	✗	✗	✗	✗
	SM2	✗	✓	✓	✓	✓	✗	✗	✗	✗	✗
	SM3	✗	✓	✓	✓	✓	✗	✗	✗	✗	✗
	SM4	✗	✓	✓	✓	✓	✗	✗	✗	✗	✗
	SM5	✗	✓	✓	✓	✓	✗	✗	✗	✗	✗

T¹: Transport, POM²: Palm Oil Mill

6.1.2 Life Cycle Inventory and Assumptions

ISO 14044 states a few aspects to be covered when collecting inventory data, which are the geographical relevance, precision, completeness, and reproducibility. This stage of life cycle assessment process is usually the most challenging part due to the lack of

availability of specific data from biochar production sites. Taking this into account while collecting the LCI for this research, geographical relevance was considered. All LCI data are taken from previously published studies and referenced accordingly in Tables 6.3 and 6.4. This research pertains to the Malaysian construction and palm oil industries, much of the collected LCI information is relevant to the local context. Furthermore, since this research focusses on the potential environmental impact of the composite mixes tested and does not represent a specific case study, assumptions have been made and are outlined in the following statements:

- LCI of cement production, fine and coarse aggregate are collected from the same study (Gursel and Ostertag, 2016) . This study provided a complete set of LCI as the LCA was compared with the production and transport of the materials from different countries in Southeast Asia to Singapore. The detailed LCI is given in Table 6.3 with units for each energy, electricity, and emissions per ton of the material. Calculations required for each quantity from Table 6.1 are then made while keying in the software.
- The concrete batching plant and the heavy truck LCI have been obtained from a study conducted in Serbia (Marinković et al., 2021). The study was based on comparing the recycled and conventional aggregate used in the industry. However, as for the completeness of LCI data for transport and concrete batching, the information was adopted for this research. Similarly, other studies have also used this data for the same reason in Singapore, Malaysia, and Hong Kong (Aman et al., 2022; Hossain et al., 2016; Shan et al., 2017). The units of each energy, electricity, and emissions for concrete are per 1 m³, and for transport, “t km,” meaning the set distance parameter in km multiplied by each consumption and emission as given in Table 6.3.
- The LCI for biochar production through pyrolysis was collected from a study comparing the pyrolysis of different palm oil waste at different temperatures (Saharudin et al., 2024). The study was based on the different palm oil wastes in Malaysia, which include empty fruit bunch and palm kernel shells similar to this research. The LCI in the study was based on a simulated pyrolysis plant through Aspen Plus due to insufficient availability of pyrolysis plants and their recorded emissions and energy consumptions in Malaysia. Table 6.4 provides the energy and emissions for each pyrolysis temperature per ton of biochar

produced. Collected LCI data consists solely of temperatures at 500°C for EFB and PKS, as well as 400°C for both. These have been considered as the optimised temperatures of 409°C for PKS and 455°C for EFB, as determined by the first objective of this study.

- Data for the landfill LCI was gathered from research conducted at landfill sites in Selangor, Malaysia (Sanaz Saheri et al., 2012). The emissions data given in Table 6.4 are per ton of the deposited waste. In the context of this research, an assumption was made for the control scenarios to have a 100 kg waste. Moreover, for the other scenarios, the amount of biomass required for each temperature to produce the required biochar as stated in Table 6.1 is subtracted from the 100 kg; therefore, the rest of the biomass is then dumped at landfill sites. This entails that each temperature and material required for the biochar production play a critical role in the environmental impact or the pyrolysis process.

Table 6.3 LCI collected for cement, fine and coarse aggregate, transport truck and concrete plant.

Category	Fine Agg Production	Coarse Agg Production	Cement Production	Heavy Truck	Concrete Plant
	per ton			t km	1m ³
Country	Malaysia			Serbia	
Energy (MJ)	1.40E+02	2.10E+02	3.30E+03	-	-
Electricity (kWh)	2.50E+02	3.20E+02	1.50E+03	-	5.57E+00
Diesel	-	-	-	3.27E+00	-
Natural Gas	-	-	-	-	-
Coal	-	-	-	-	-
Emissions (kg)					
CO ₂	2.00E+00	3.60E+00	1.10E+03	2.35E+02	5.70E+03
CO	7.70E-03	1.20E-02	1.60E-01	9.03E-01	7.23E-01
SO _x	-	-	-	9.20E+05	9.88E+01
SO ₂	8.70E-03	1.20E-02	5.40E-01	-	-
NO _x	8.30E-03	1.20E-02	5.80E+00	1.94E+00	1.32E+01
CH ₄	6.40E-03	8.60E-03	7.40E-01	2.53E-01	4.33E-01
NM VOC	6.50E-04	8.50E-04	4.50E-02	4.96E-01	7.10E-01
VOC	1.10E-04	1.80E-04	8.30E-05	-	-
N ₂ O	1.20E-03	1.60E-03	7.90E-02	7.02E-03	2.91E-02
HCl	-	-	-	-	2.68E+00
HC	-	-	-	-	2.31E-02
PM10	2.60E-02	2.60E-02	1.40E+00	1.87E-01	1.20E+01
Reference	(Gursel and Ostertag, 2016)			(Marinković et al., 2021)	

Table 6.4 LCI collected for pyrolysis at each temperature and landfill site.

Category	Pyrolysis 400°C EFB	Pyrolysis 500°C EFB	Pyrolysis 400°C PKS	Pyrolysis 500°C PKS	Landfill
Unit of material	per ton	per ton	per ton	per ton	per ton
Country	Malaysia				
Energy (MJ)	-	-	-	-	-
Electricity (kWh)	5.43E+01	5.55E+01	4.86E+01	4.94E+01	-
Electricity fan (kWh)	2.75E+01	2.95E+01	2.41E+01	2.55E+01	-
Electricity N ₂ supply (kWh)	6.97E+00	7.12E+00	6.23E+00	6.34E+00	-
Nitrogen (kg)	1.82E+01	1.86E+01	1.63E+01	1.66E+01	-
Diesel	-	-	-	-	-
Natural Gas (MJ)	6.50E+00	6.30E+00	5.70E+00	5.50E+00	-
Coal	-	-	-	-	-
Water (kg)	2.44E+02	2.49E+02	2.18E+02	2.22E+02	-
Emissions (kg)					
CO ₂	1.47E+03	1.57E+03	1.25E+03	1.32E+03	1.38E+07
CO	1.07E+02	1.15E+02	9.10E+01	9.60E+01	-
SO _x	-	-	-	-	2.07E+04
SO ₂	2.49E+01	2.54E+01	1.86E+01	1.90E+01	-
SO ₃	7.50E-03	7.60E-03	5.60E-03	5.70E-03	-
NO _x	-	-	-	-	1.52E+05
NO ₂	5.65E-03	6.03E-03	4.97E-03	5.25E-03	-
NO	1.90E+01	2.02E+01	1.66E+01	1.75E+01	-
CH ₄	5.70E-13	5.70E-13	4.70E-13	4.70E-13	6.90E+05
NMVOC	-	-	-	-	-
VOC	-	-	-	-	-
N ₂ O	1.13E-03	1.12E-03	9.90E-04	1.05E-03	1.84E+02
HCl	1.34E+01	1.36E+01	1.16E+01	1.18E+01	-
H ₂ S	1.21E-04	1.19E-04	8.90E-05	8.70E-05	-
C ₂ H ₄	4.40E-22	4.43E-22	3.52E-22	3.53E-22	-
C ₂ H ₆	5.66E-28	5.51E-28	4.48E-28	4.37E-28	-
HC	-	-	-	-	3.36E+02
HCN	2.81E-07	2.97E-07	2.36E-07	2.48E-07	-
NH ₃	2.50E-05	2.60E-05	2.20E-05	2.20E-05	-
PM10	6.23E-07	6.57E-02	5.41E-02	5.65E-02	-
PCDD/F	8.31E-07	8.76E-07	7.21E-07	7.54E-07	-
PAH	2.22E-04	2.33E-04	1.92E-04	2.00E-04	-
NH ₄	-	-	-	-	1.05E+01
References	(Saharudin et al., 2024)				(Sanaz Saheri et al., 2012)

- The distances covered are directly taken from satellite image of Google Maps. The chosen locations are palm oil mills, cement plants, concrete plants, biochar production areas, and landfill sites. Measured distances from one location to another, was recorded and have been averaged for the purposes of this research and given in Table 6.5. These calculations have been adapted from another LCA study (Mah et al., 2018). According to the specified system in the previous section, transport and distances were only used for the concrete LCA. Details of the locations taken into account, marking them into Google Maps, and the distances measured are all provided in the Appendix G.

Table 6.5 Distances calculated for concrete LCA.

Distance	Symbol	Average (km)
Palm Oil Mills- Landfill	P-L	60.4
Palm Oil Mills- Biochar Plants	P-B	75.2
Cement Plants- Concrete Plants	C-CP	27.4
Biochar Plants- Concrete Plants	B-CP	40.1

6.1.3 Life Cycle Impact Assessment

This phase of the LCA identifies and evaluates the magnitude and significance of the environmental impacts from the LCI data (Guinée, 2001). The LCIA method used for this research is the Centre for Environmental Studies (CML) 2001 method. As there are many versions of the CML method, the one specifically used for this research is the CML2 baseline 2000, as it covers a wide range of environmental impact categories as stated in Table 6.6, which are expressed in terms of emissions to the environment. Each gas emission or energy usage in the LCI is classified to an impact category, and the software converts the emissions to their respective impact category units as expressed in Table 6.6.

Table 6.6 CML 2 baseline 2000.

Environmental Impact Categories	Unit	Classifications
Abiotic depletion	kg Sb eq	Energy
Acidification	kg SO ₂ eq	NH ₃ , NO ₂ , NO, NO _x , SO _x , HCl
Eutrophication	kg PO ₄ ⁻ eq	NH ₃ , NO _x , NO ₂ , NO,
Fresh water aquatic ecotox.	kg 1,4-DB eq	C ₂ H ₄ , PAH
Global warming (GWP100)	kg CO ₂ eq	CO ₂ , CH ₄ , CO, N ₂ O
Human toxicity	kg 1,4-DB eq	NH ₃ , C ₂ H ₄ , HCl, HS, NO _x , NO ₂ , PAH, PM10, SO _x
Marine aquatic ecotoxicity	kg 1,4-DB eq	C ₂ H ₄ , PAH
Photochemical oxidation	kg C ₂ H ₄ eq	CO, C ₂ H ₄ , CH ₄ , C ₂ H ₆ , NO ₂ , SO _x , NO
Terrestrial ecotoxicity	kg 1,4-DB eq	C ₂ H ₄ , HF

6.1.4 Open LCA Software

OpenLCA is an open-source software that makes it easier to do life cycle assessments (LCAs). With OpenLCA, users can model, analyse, and understand the environmental impacts of products, processes, and systems throughout their entire life cycles. The software is designed to be user friendly, so both beginners and experts in sustainability can use it easily. OpenLCA provides a smooth workflow for creating LCA models and generating detailed reports, streamlining the process of conducting thorough life cycle assessments. OpenLCA can assess environmental impacts across many different categories. This is because it supports multiple impact assessment methods. It is an important tool for people working to improve environmental sustainability. The software helps researchers, policymakers, and industry professionals make well-informed decisions about product design, process optimisation, and policy (“openLCA.org,” n.d.).

6.2 Results and Discussion

6.2.1 Environmental Impact Assessment

An overview of the life cycle environmental impact (EI) categories for each scenario was summarised for 1 m³ of biochar concrete composites and for 1 m³ of biochar mortar composites in Figure 6.3 (a) and (b) respectively. The figures show the results of the nine impact categories selected in Table 6.6. To provide a clear comparison of each scenario, the totals were calculated as percentages relative to the control mix, which is the first scenario for each material (mortar and concrete). This means that 100% in each diagram corresponds to the control mix without the addition of biochar. The results for each process and the sum of all scenarios for both materials can be found in [Appendix G](#). In Figure 6.3 all scenarios have a similar pattern of decrease in all impact categories except for abiotic depletion. With the highest impact by S3 with 409°C PKS, followed by S4 with 455°C EFB, S2 with 500°C PKS and the lowest percentage by S5 which uses 500°C EFB. The lowest percentage indicating the least environmental impact contributed by a scenario relative to the control mix. Accordingly, it can be reported that for both materials (concrete and mortar) S5 with 500°C EFB has caused the least environmental impact by taking into consideration all the processes in the scenario. Regarding abiotic depletion, the fact that there was no change in all scenarios shows that the type of biochar and the temperature had no influence on the impact, but the reduction in the amount of cement did.

It is noteworthy that both scenarios with 500°C PKS and EFB had a lower impact than the proposed optimised temperatures of the biochar. For this reason, it is important to recognise and break down the contribution of each process, which is explained later in Figure 6.5 to 6.8. For the concrete composites in Figure 6.3 (a), SC2 with 500°C PKS showed an EI reduction of 40.2%, while SC5 with 500°C EFB showed a reduction of 38.1% compared to SC1. At the optimised temperatures used in SC3 and SC4, there was a reduction of 50.2% and 47.3% at 409°C PKS and 455°C EFB respectively. As mentioned earlier, the same pattern followed for the mortar composites in Figure 6.3 (b) SM2 and SM5 showed a reduction of 20% and 17.2% respectively. For SM3 and SM4, the reduction was 33.3% and 29.4% respectively compared to the control mix. The different percentages of each scenario for both materials (despite the use of 4% biochar in all mixtures) are due to the different amounts of materials used, as indicated

in Table 6.1. This is evident throughout the discussion of the results in this chapter. The significance of each of these effects has been indicated in Table 2.5.

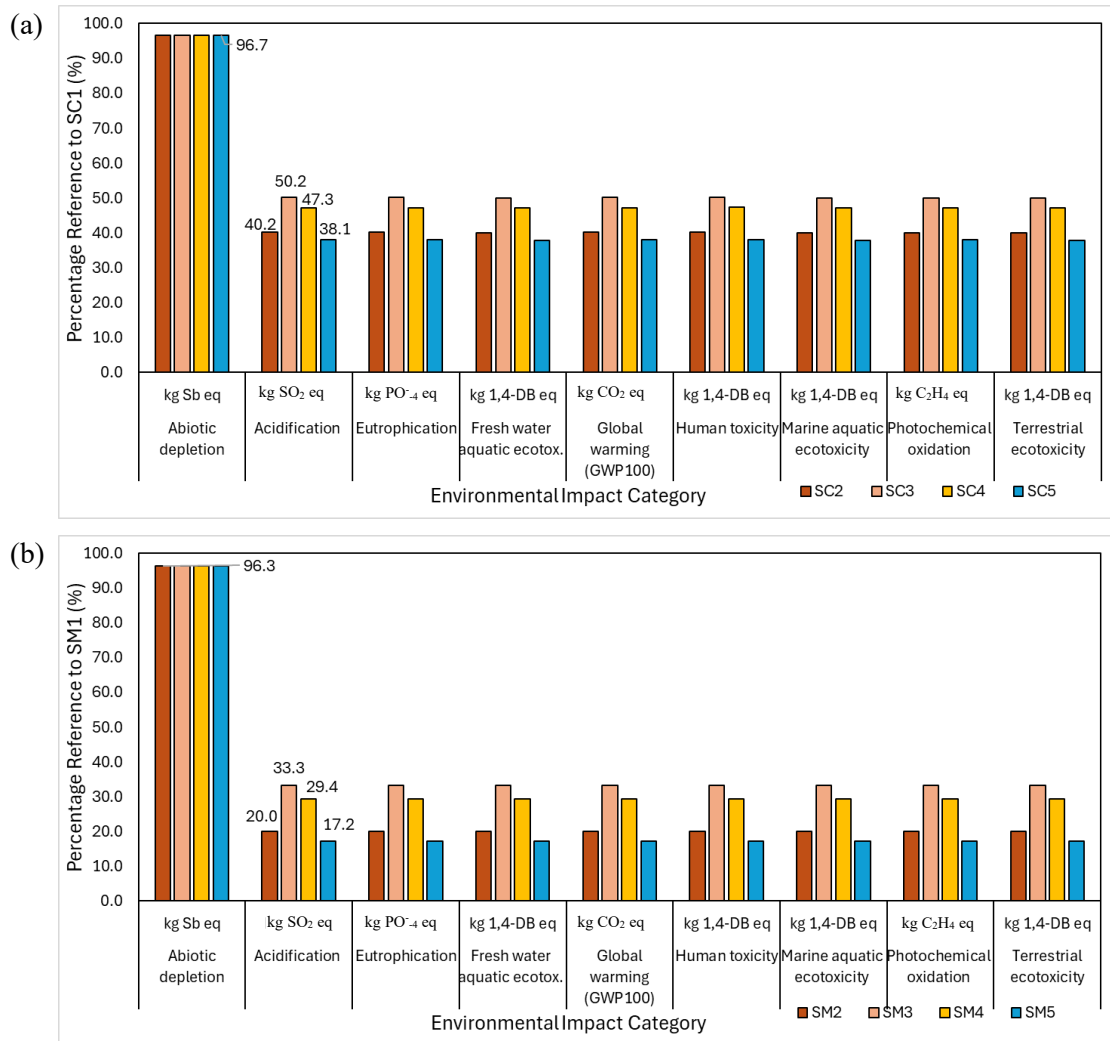


Figure 6.3 Environmental impact categories for scenarios 2, 3, 4 and 5 of biochar (a) concrete composites and (b) mortar composites.

Of all the EIs, the global warming potential (GWP) had the highest values, which are stated [Appendix G](#) (Tables E.7 and E.11). Evidently, it is important to discuss the overall impact of each scenario in Figure 6.4 (a) and (b). Emphasising the overall impact on GWP is crucial to show that all biochar composites have a lower GWP than the conventional control mix. Even if only a small amount of biochar is used, a large difference in GWP can occur.

For both materials, scenario 1 shows the highest GWP of 36% (3.52×10^6 kg CO₂-eq/m³) for concrete and 50% for mortar (3.51×10^6 kg CO₂-eq/m³) for the control mix. Another study, in which cement was replaced with rice husk ash, found that the most sustainable mix had low compressive strength. Nevertheless, the mix was recommended due to its

low GWP impact (54% less CO₂-eq/m³) and durability properties (Gursel et al., 2016). In Figures 6.4 (a) the SC3 attributes to 18% (1.76×10^6 kg CO₂-eq/m³), SC4 17% (1.66×10^6 kg CO₂-eq/m³), SC2 15% (1.41×10^6 kg CO₂-eq/m³), SC5 14% (1.34×10^6 kg CO₂-eq/m³). In Figure 6.4 (b) the SM3 attributes to 17% (1.17×10^6 kg CO₂-eq/m³), SM4 15% (1.03×10^6 kg CO₂-eq/m³), SM2 10% (7.02×10^5 kg CO₂-eq/m³), SM5 8% (6.04×10^5 kg CO₂-eq/m³). Similar to this research, another LCA compared biochar as a cement replacement using 5% of alum sludge (Mekky et al., 2024). Their LCA also included landfill and reported an overall decrease of GWP by 32.3% from the control mix. A study that only calculated the CO₂-eq/kg reported that used 2% areca nut husk biochar (produced at 500°C) reduced CO₂-eq by 22% for mortar composites (Manjunath et al., 2024). As mentioned in Table 6.2 an additional difference between the impact by both materials is dependent on the processes used in the concrete LCA are distances covered which always attributes to high GWP impact (Campos et al., 2020; Estanqueiro et al., 2018; Gursel et al., 2016; Shan et al., 2017).

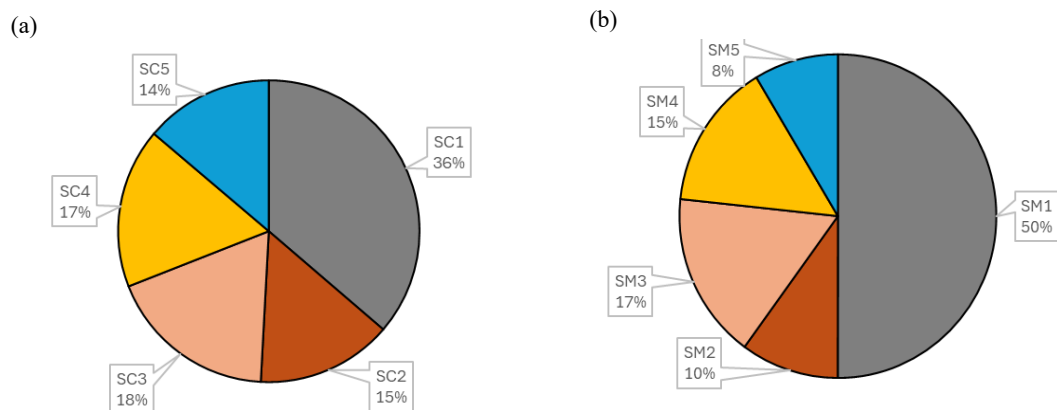


Figure 6.4 Global warming potential (a) concrete composites and (b) mortar composites.

6.2.2 Individual Process Impact Analysis

In this section, the overall significance of each process is elaborated for each EI, regardless of the scenario. Figures 6.5 (a) and (b) show the overall significance of the impact for each process in biochar concrete and mortar composites. The results of all processes for each environmental impact can be found in [Appendix G](#). A prior LCA study conducted on different waste disposal methods in Malaysia highlighted that landfilling is not preferable as it causes a high negative environmental impact (Sanaz Saheri et al., 2012). Therefore, any decision to decrease landfill is valuable. The result

of this research highlights that the highest emissions in all processes for both materials are landfill.

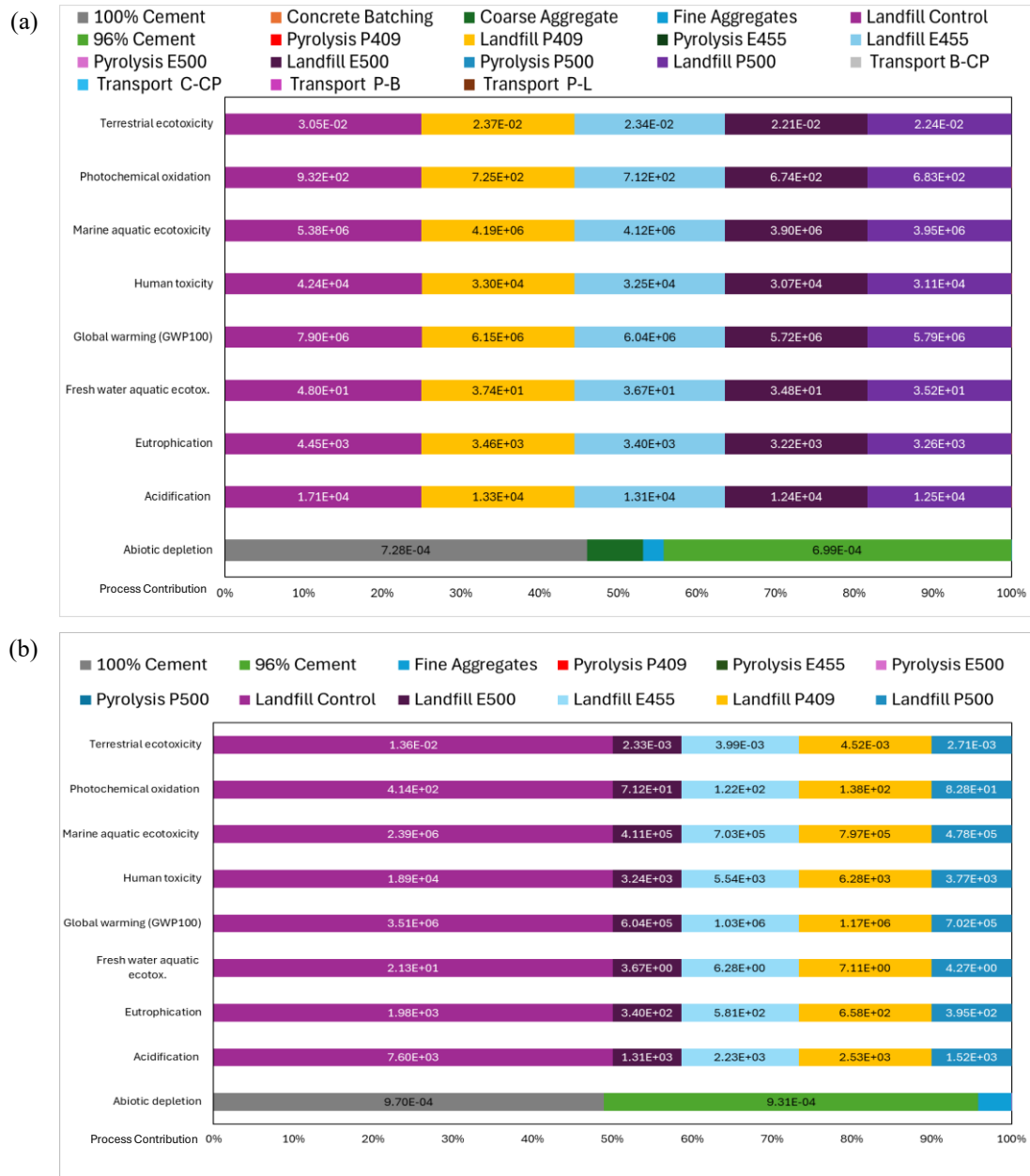


Figure 6.5 Environmental impact categories of ingredients and phases for biochar (a) concrete composites' and (b) mortar composites.

Figure 6.5 shows that for all impacts except abiotic depletion, landfill has the highest environmental impact. It was indicated under Section 6.1.2 that for each scenario a different amount of material deposited in landfill is calculated. The higher the biomass needed to provide the amount of biochar for each mixture, the lower the amount of biomass that is disposed of in the landfill sites. This means that the higher the temperature of the biochar, the more biomass is used to yield the same amount of

biochar as at lower temperatures. For this reason, the overall impacts for each scenario with 500°C PKS (S2) and EFB (S5) are lower for both materials than the scenarios for temperatures of 409°C (S3) and 455°C (S4). This means that the overall impact is determined more by the landfill process than by the rest. Another study in Malaysia using EFB biomass for pellet production also reported that this would reduce EFB to landfill sites by 62.74% (Chew et al., 2023). Highlighting the aim of this research as to avoid the deposit of biomass to landfill sites. Figure 6.5 shows that landfills have the greatest impact on GWP, followed by marine aquatic ecotoxicity, human toxicity, acidification, eutrophication, photochemical oxidation, freshwater aquatic ecotoxicity and least of all terrestrial ecotoxicity. Abiotic depletion is mainly influenced by cement production and the processing of coarse and fine aggregate process as shown in Figure 6.5. This EI is measured by the energy consumption of fossil fuels. The most energy-consuming process in cement production is the pyro-processing (use of high temperatures) to produce clinker (Gursel et al., 2014).

Having established that landfill has the greatest impact on the scenarios, it is important to examine the impact of other processes in more detail. Figure 6.6 shows the impact of other processes excluding landfill for concrete composites. The process of producing fine and coarse aggregates has not been considered as they are constant for all scenarios. Figure 6.6 clearly shows which EI is highly affected by transport, namely human toxicity, eutrophication and acidification. However, for global warming potential and photochemical oxidation, the impacts of the different pyrolysis processes are also remarkable (less than 5% each). Due to its significant environmental impact, transport is a recurring topic in life cycle assessments (Estanqueiro et al., 2018; Gursel et al., 2016; Shan et al., 2017). As it can be seen from the calculated distances in Table 6.5, the longest average distance is travelled from the palm oil mill to the biochar plant (P-B), followed by the palm oil mill to the landfill (P-L), the biochar plant to the concrete plant (B-CP) and the least distance from the cement to the concrete plant (C-CP). The results of this research confirm that the longer the distance travelled, the higher the EI, regardless of the destination. To reduce the EI, the literature always recommends taking the shortest distances (Aman et al., 2022; Estanqueiro et al., 2018; Gursel et al., 2016; Gursel and Ostertag, 2016; Shan et al., 2017). However, this research is not a specific case study, but only determines average distances between destinations. Furthermore, as indicated in Table 6.2, all distances are considered for all scenarios, with the

exception of SC1, which excludes (P-B) and (B-CP). It is important to emphasise that although SC1 does not consider all distances, it still has the highest EI of all other scenarios due to the amount of biomass deposited in the landfill. Another LCA study was conducted on biochar as a partial cement replacement for concrete from different regions of the Philippines (Campos et al., 2020). The authors reported that the focus of the study was on the biochar collection area (distance covered) and percentage replacement. Their results indicated that distance covered had a higher overall EI than the percentage replacement from 5 to 20% of biochar.

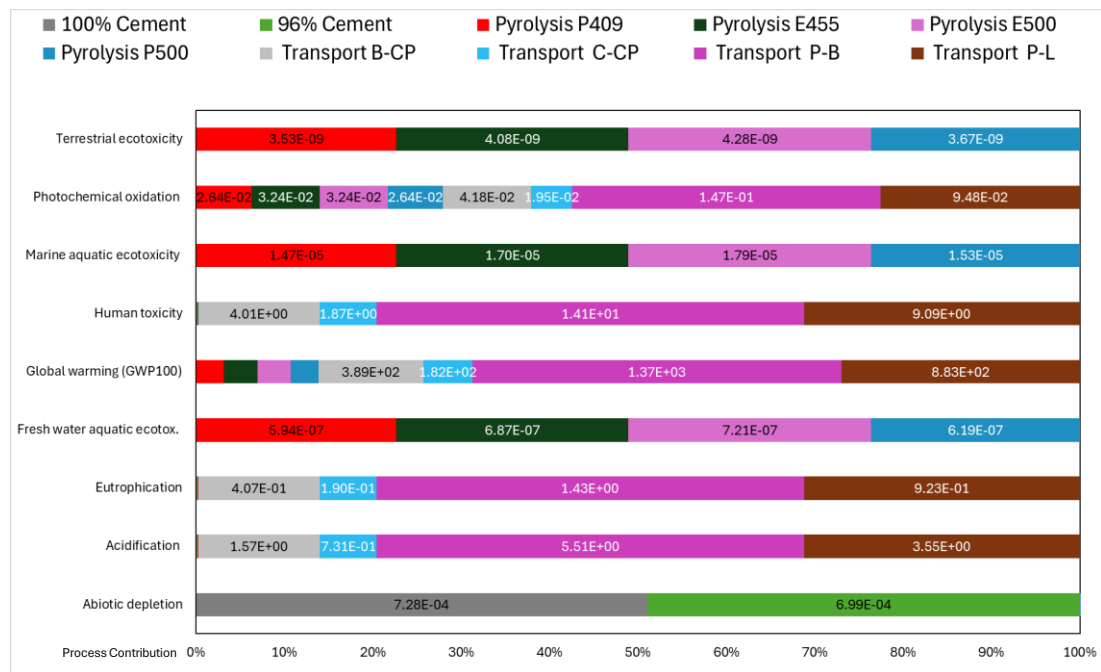


Figure 6.6 Environmental impact categories of cement, transport and pyrolysis for concrete composites.

Figure 6.6 also shows that the cement production process only has a noticeable impact on abiotic depletion and not on other EI. For this reason, further detailed impact differences are required, which are shown in Figure 6.7 (a) and (b) for concrete and mortar composites of only cement and biochar production. It is important to note that the values of these impacts are calculated directly for 1 m³ of mortar and concrete composites, which is why they are minimal. The LCA study conducted highlights the differences between each process and their impacts. Figures 6.7 (a) and (b) show that cement production has the greatest impact in terms of human toxicity, eutrophication, acidification and abiotic depletion compared to the pyrolysis processes.

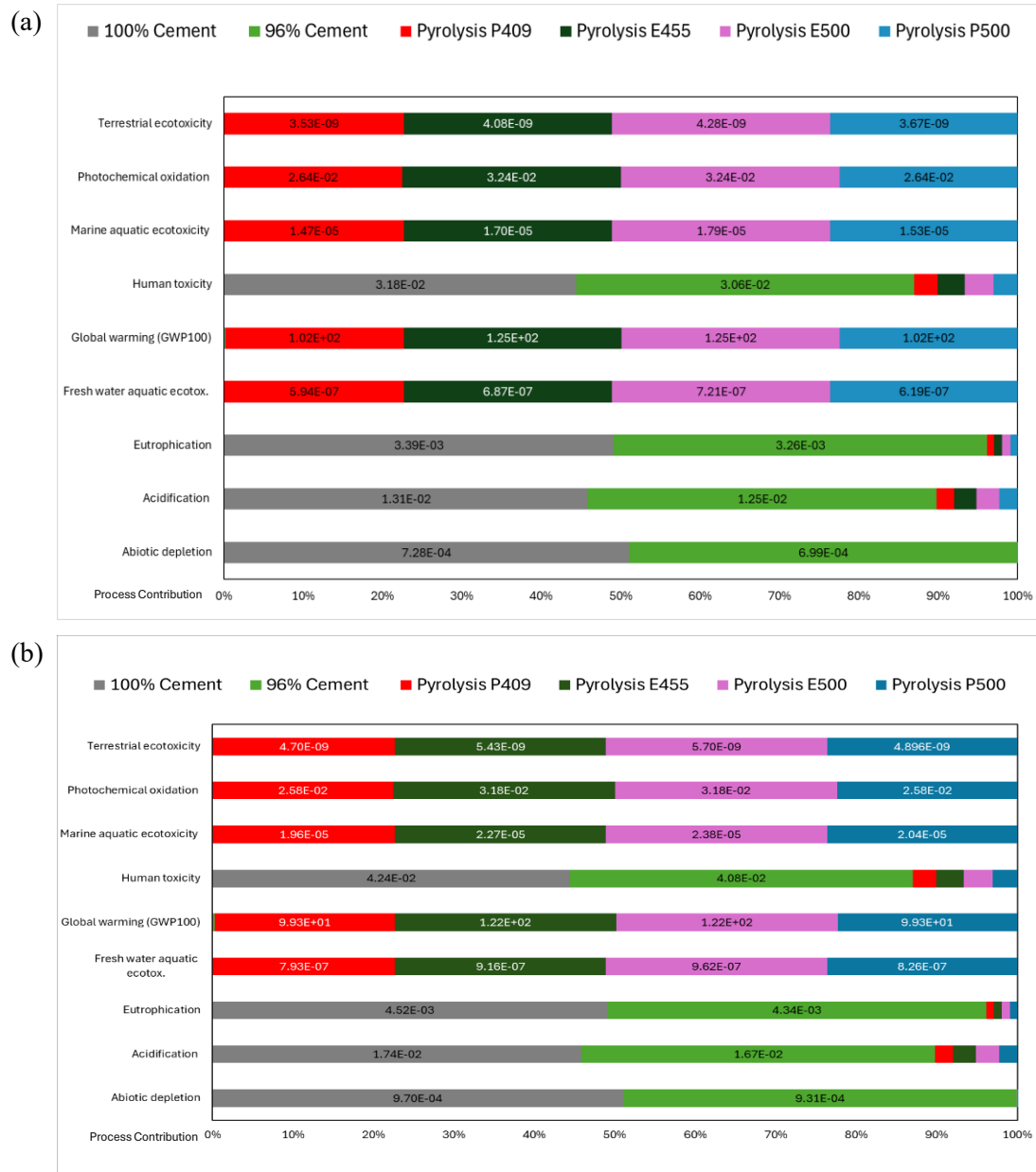


Figure 6.7 Environmental impact categories of cement and pyrolysis for (a) concrete composites and (b) mortar composites.

One study reports relatively high impacts during cement production, especially clinker calcination, which is mainly responsible for abiotic depletion and human toxicity and GWP (Guo et al., 2023). The authors of the study also acquired weight coefficients for each EI in cement production abiotic depletion (0.3), human toxicity (0.25), GWP (0.27), photochemical oxidation (0.057) eutrophication (0.033). However, an important finding from this research is that the GWP for 1 m³ of mortar and concrete is higher for pyrolysis than for cement production. This is due to the additional methane and dinitrogen monoxide emissions from the pyrolysis reactors during the thermal

decomposition of the biomass. It is important to note that these results are highly subjective to the type of pyrolysis reactors used.

An additional in-depth comparison between the pyrolysis process at different temperatures and different biomass is essential. Figures 6.8 (a) and (b) show the EI categories of the different pyrolysis carried out for the required amount of 4% biochar as cement replacement for biochar concrete and mortar composites. As already stated, the GWP has reached the highest impact for all pyrolysis processes. This is followed by photochemical oxidation, human toxicity, acidification, eutrophication, aquatic ecotoxicity in marine and freshwater, abiotic depletion and terrestrial ecotoxicity. The intensity of the individual effects is higher for the mortar composite than for the concrete composite, as the amount of biochar required for each material is different, as shown in Table 6.1. From the results in Figure 6.8 (a) and (b), the pyrolysis of EFB biomass is higher than that of PKS for all EI. Furthermore, regardless of the temperature used, GWP and photochemical oxidation were found to have the same effects. In Figure 6.12 it was 1.25×10^2 kg CO₂-eq and 3.42×10^{-2} kg C₂H₄-eq by EFB and 1.02×10^2 kg CO₂-eq and 2.64×10^{-2} kg C₂H₄-eq by PKS composites. This is due to the additional biomass processing steps required for EFB in the form of heating, washing and grinding prior to the pyrolysis process. As it is a more fibrous and bulky material compared to the granular nature of PKS (Chan et al., 2016). LCA study conducted in Malaysia reported that EFB biomass processing releases more carbon emissions (in MY) than oil palm trucks due to the washing (169.2–439.0 kg CO₂-eq/tonne_{pellet} per hour) and drying processes (534.7–732.3 kg CO₂-eq/tonne_{pellet} per hour) (Chew et al., 2023). Similarly, another LCA conducted in Brazil, it was reported that the use of EFB has disadvantages as its moisture content is above 50% and its tough lignocellulosic structure reduces energy efficiency (Vaskan et al., 2018).

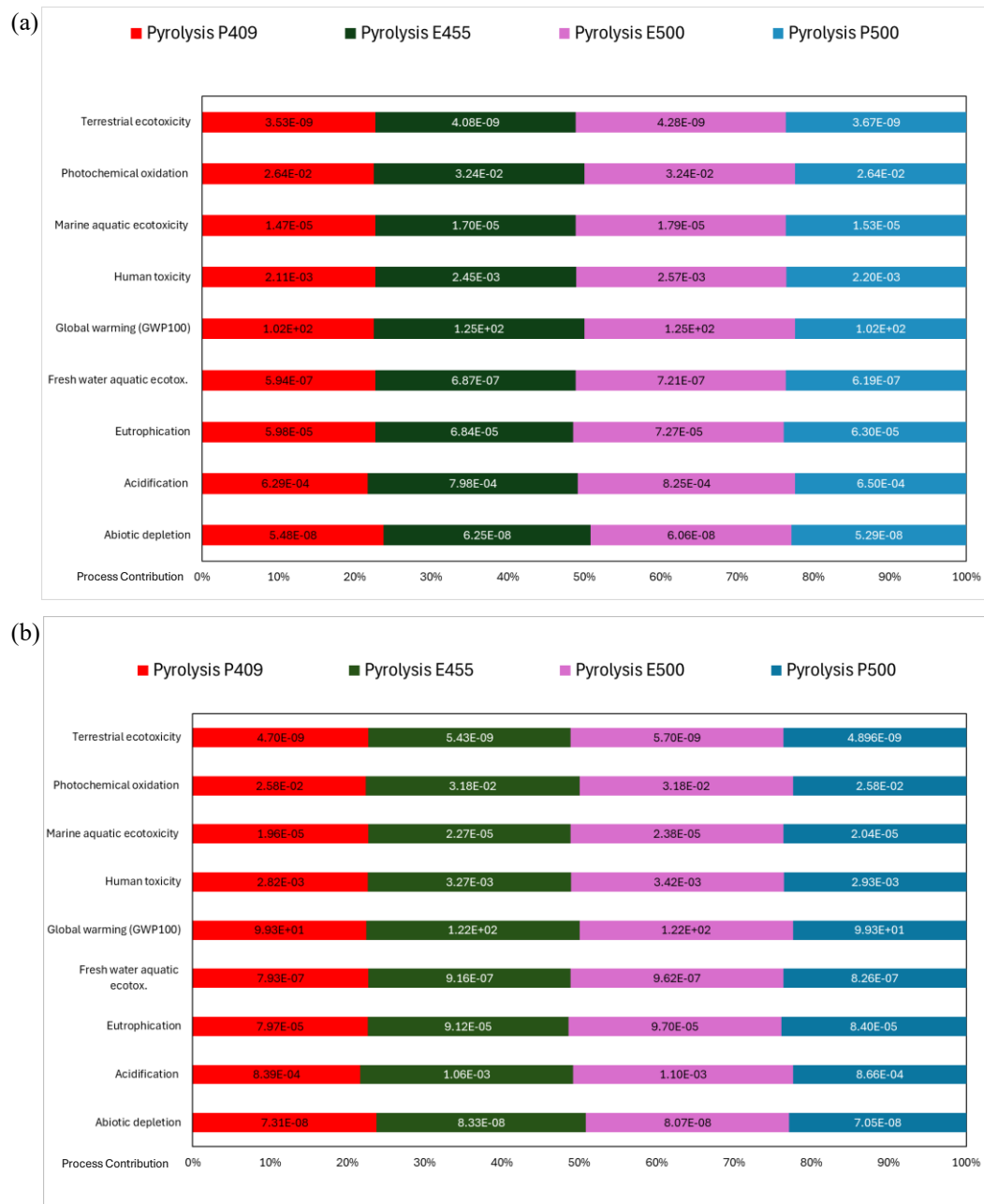


Figure 6.8 Environmental impact categories of pyrolysis for (a) concrete composites and for (b) mortar composites.

All EI (except GWP and photochemical oxidation) are consistent with the common conception of the higher the temperature used for pyrolysis, the higher the EI. This is the reason why a lower temperature was preferred when optimising biochar production in the first objective. A study comparing different processes for converting EFB into bio-oil found that the global warming potential is always higher and the other impacts such as acidification, eutrophication, toxicity and photo-oxidants are always less severe (Chan et al., 2016). An alternative study on optimised pyrolysis parameters of different biomasses (wood and corn stover) was conducted in Canada to investigate soil carbon

sequestration versus use as a fuel source (Dutta and Raghavan, 2014). They reported that pyrolysis had the highest GHG emissions (51.2% for wood and 47.3% for corn fodder) compared to other processes such as feedstock and transport. In another LCA for the use of biochar for soil application, it was mentioned that the reactor used for pyrolysis plays a crucial role in the EI of the process (Roberts et al., 2010). Pyrolysis was carried out at a temperature of 450°C and the reactor used allowed the gases to flow into a thermal oxidiser to achieve clean combustion. The heat generated by this system was used to dry the biomass prior to pyrolysis. Another study used a combination of LCA and machine learning to evaluate the performance of slow pyrolysis across multiple feedstocks and processing conditions. The authors pointed out that slow pyrolysis of crop residues and woody wastes has the potential for an energy-generating technology with negative emissions, with GWP reductions ranging from -200 to -1050 kg CO₂-eq/t (Cheng et al., 2020). They also reported that the best overall energy and climate change performances are achieved via pyrolysis of lignocellulosic biomass at high temperature, but only when taking into account the amount of stable carbon in biochar and the fuel properties of other by-products (bio-oil and syngas from pyrolysis). This emphasises that when assessing the environmental impact of a material, its application is very important to determine its positive or negative impact.

6.3 Summary of Findings

This chapter addresses the final objective of this research, which is to assess the environmental impact of using different palm oil waste biochar as a cement replacement for mortar and concrete composites. It is important to note that LCA study is highly dependent on the inventory data used and the system boundaries established. The uniqueness of the LCA study conducted for this research is the combination of composites' materials and landfills, which has rarely been considered in the literature. The LCA system boundary considered for the LCA of concrete was from cradle to gate and for the LCA of mortar from gate to gate. A general conclusion about the least environmental impact by palm oil waste biochar is scenario 5 with 4% 500°C EFB, this was highly dependent on the landfill emissions. However, taking into consideration the optimal mechanical properties established for each material, scenario 3 for concrete LCA using 4% 409°C PKS and scenario 4 for mortar LCA which is 4% of 455°C EFB are suggested as they both have a much lower impact than the control scenarios.

Chapter 7 Conclusions

7.1 Research Conclusions

Research into effective supplementary cementitious materials has increased, as most of them have shown to have better mechanical properties and are environmentally friendly in the long term. This would lead to the development and production of sustainable concrete and mortar mixes. As mentioned in the collected literature, biochar has been tested with different approaches and has proven to be an effective supplementary cementitious material. In this research, biochar was produced from palm oil waste and used as cement replacement, which was then tested and analysed for various mechanical tests. The biochar, the mortar and concrete mixes were then tested for their ability to adsorb carbon dioxide. These developed sustainable mixes were then assessed for their environmental impact through life cycle assessments.

Below are the conclusions on the objectives achieved:

- Pyrolysis parameters that were optimised for the production of biochar, include temperature, heating rate and residence time using the response surface methodology. The optimum parameters were determined so that the biochar can be used as cement replacement. 409°C, 15°C/min, 120 min for palm kernel shell and 455°C, 15°C/min, 20 min for empty fruit bunch were the finalised optimum parameters.
- Optimal percentage of cement replacement from 1 to 8% was evaluated based on compressive and flexural strengths, hardened density, water absorption, and porosity of mortar composites with different types of biochar: 409°C PKS, 500°C PKS, 455°C EFB and 500°C EFB. It was concluded that 4% cement replacement was the most effective replacement percentage, especially for the mortar mix with 4% 455°C EFB.
- As for the concrete composites, 4% of each biochar was used as a cement replacement. The mechanical properties of the composites were compared and evaluated. The optimal type of biochar that showed less significant decrease in properties compared to the control samples was 4% 409°C PKS.
- After 24 hours of exposure to concentrated CO₂, all biochar types showed significant potential to sequester CO₂. Biochar that showed the highest

sequestration was 409°C PKS. Mortars and concrete composites made from palm oil waste showed a potential to sequester CO₂. However, this was mainly due to physical adsorption rather than chemical reaction with the composites in the time frame tested.

- Life cycle assessment study was conducted on all 4% biochar mortar and concrete composites under different scenarios. All composites have shown a decrease in environmental impact in comparison to the control. Among them, the composite containing 4% EFB biochar produced at 500°C exhibited the lowest environmental impact when considering all processes, largely influenced by landfill emissions. Based on the combined evaluation of mechanical properties and carbon sequestration potential, the optimised biochar from both biomass sources, EFB and PKS are proposed as an environmentally beneficial option.

An overall conclusion for this research states that optimised palm kernel shell and empty fruit bunch biochar have shown improvement in mechanical properties when used as a cement replacement. These composites showed potential to be utilised as carbon sink material.

7.2 Research Limitations and Future Recommendations

The limitations that were faced in this research include:

- The amount of biochar produced in a single pyrolysis run for PKS and EFB using the dedicated pyrolysis reactor is small. This is compared to the amount of material required for mortar and concrete composites. This consequently affected the time required to produce the amount of biochar that was needed for each composite.
- The pressure and moisture could not be controlled for the carbon dioxide sequestering experimental set up which limited the time frame of the experiment.
- The life cycle assessment conducted is highly dependent on the life cycle inventory used, as literature lacks accurate inventory data on pyrolysis that is specific to Malaysia.

Although a considerable amount of research has been conducted on biochar as a cement replacement, further research can still be conducted on various palm oil

waste biochar to improve their efficiency and promote their further industrial utilisation:

- Long term durability and mechanical tests on palm oil waste biochar mortar and concrete composites over different curing durations.
- Carbon sequestration capabilities of palm oil waste biochar concrete composites made with pre-treated biochar. Biochar properties such as surface area, mineral content and porosity could be altered with different chemical treatments. Such as potassium, calcium and sodium solutions.
- Testing of palm oil waste biochar concrete composites for the ability to absorb pollutants, such as CO, NO, NO₂ and SO₂ while keeping time as a dependent variable, and without affecting the mechanical properties such as compressive strength, density and porosity.

References

- Abdullah, N., Sulaiman, F., Abdullah, N., Sulaiman, F., 2013. The Oil Palm Wastes in Malaysia. *Biomass Now - Sustainable Growth and Use*.
- Ahmad, S., Khushnood, R.A., Jagdale, P., J.M., Ferro, G.A., 2015. High performance self-consolidating cementitious composites by using micro carbonized bamboo particles. *Mater Des* 76, 223–229.
- Ahmed, M., Bashar, I., Alam, S.T., Wasi, A.I., Jerin, I., Khatun, S., Rahman, M., 2021. An overview of Asian cement industry: Environmental impacts, research methodologies and mitigation measures. *Sustain Prod Consum* 28, 1018–1039.
- Akhtar, A., Sarmah, A.K., 2018a. Novel biochar-concrete composites: Manufacturing, characterization and evaluation of the mechanical properties. *Science of The Total Environment* 616–617, 408–416.
- Akhtar, A., Sarmah, A.K., 2018b. Strength improvement of recycled aggregate concrete through silicon rich char derived from organic waste. *J Clean Prod* 196, 411–423.
- Akinyemi, B.A., Adesina, A., 2020. Recent advancements in the use of biochar for cementitious applications: A review. *Journal of Building Engineering* 32, 101705.
- Al Arni, S., 2018. Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renew Energy* 124, 197–201.
- Alvarenga, K.P., Cordeiro, G.C., 2024. Evaluating sugarcane bagasse fly ash as a sustainable cement replacement for enhanced performance. *Clean Eng Technol* 20, 100751.
- Aman, A.M.N., Selvarajoo, A., Chong, S., Teo, F.Y., 2022. Comparative life cycle assessment of pervious concrete production in Malaysia with natural and recycled aggregate. *Innovative Infrastructure Solutions* 7, 1–16.
- Arif, M., Jan, T., Riaz, M., Fahad, S., Adnan, M., Amanullah, Ali, K., Mian, I.A., Khan, B., Rasul, F., 2020. Biochar; a Remedy for Climate Change. *Environment, Climate, Plant and Vegetation Growth* 151–171.

-
- Asadi Zeidabadi, Z., Bakhtiari, S., Abbaslou, H., Ghanizadeh, A.R., 2018. Synthesis, characterization and evaluation of biochar from agricultural waste biomass for use in building materials. *Constr Build Mater* 181, 301–308.
- ASTM C1585, 2020. Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic- Cement Concretes. ASTM.
- Azunna, S.U., 2019. Compressive strength of concrete with palm kernel shell as a partial replacement for coarse aggregate. *SN Appl Sci* 1, 1–10.
- Baby, R., Saifullah, B., Hussein, M.Z., 2019. Palm Kernel Shell as an effective adsorbent for the treatment of heavy metal contaminated water. *Scientific Reports* 2019 9:1 9, 1–11.
- Barbhuiya, S., Bhusan Das, B., Kanavaris, F., 2024. Biochar-concrete: A comprehensive review of properties, production and sustainability. *Case Studies in Construction Materials* 20, e02859.
- Barranco, R., Cooper, M., Hanson, S., Lee, K.U., Low, K.S., Teo, C.H., 2007. Gasification Behaviour of Malaysian Biomass: Sugarcane Waste. 1st Engineering Conference on Energy & Environment 131–135.
- Bazargan, A., Kostić, M.D., Stamenković, O.S., Veljković, V.B., McKay, G., 2015. A calcium oxide-based catalyst derived from palm kernel shell gasification residues for biodiesel production. *Fuel* 150, 519–525.
- Bediako, M., Gawu, S.K., Adjaottor, A.A., Solomon Ankrah, J., Atiemo, E., 2016. Analysis of co-fired clay and palm kernel shells as a cementitious material in Ghana. *Case Studies in Construction Materials* 5, 46–52.
- Belaadi, A., Boumaaza, M., Alshahrani, H., Bouchak, M., 2023. Optimization of Palm Rachis Biochar Waste Content and Temperature Effects on Predicting Bio-Mortar : ANN and RSM Modelling. *Journal of Natural Fibers* 20.
- Ben Salem, I., El Gamal, M., Sharma, M., Hameedi, S., Howari, F.M., 2021. Utilization of the UAE date palm leaf biochar in carbon dioxide capture and sequestration processes. *J Environ Manage* 299, 113644.

-
- Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., Escaleira, L.A., 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta* 76, 965–977.
- Biochar Malaysia Association 2023. URL <http://biocharmalaysia.com/> (accessed 5.27.23).
- Bixapathi, G., Saravanan, M., 2022. Strength and durability of concrete using Rice Husk ash as a partial replacement of cement. *Mater Today Proc* 52, 1606–1610.
- Bong, H.K., Selvarajoo, A., Arumugasamy, S.K., 2022. Stability of biochar derived from banana peel through pyrolysis as alternative source of nutrient in soil: feedforward neural network modelling study. *Environ Monit Assess* 194, 1–29.
- Boumaaza, M., Belaadi, A., Alshahrani, H., Bouchak, M., Jawaid, M., 2023. Response Surface Methodology Optimization of Palm Rachis Biochar Content and Temperature Effects on Predicting Bio-Mortar Compressive Strength, Porosity and Thermal Conductivity. *Journal of Natural Fibers* 20.
- Boumaaza, M., Belaadi, A., Bouchak, M., Jawaid, M., Hamid, S., 2022. Comparative study of flexural properties prediction of *Washingtonia filifera* rachis biochar bio-mortar by ANN and RSM models. *Constr Build Mater* 318, 125985.
- BS EN 1015-11, 2019. Methods of test for mortar for masonry. Determination of flexural and compressive strength of hardened mortar.
- BS EN 12390-3, 2019. Compressive strength of test specimens for testing hardened concrete.
- Campos, J., Fajilan, S., Lualhati, J., Mandap, N., Clemente, S., Campos, J., Fajilan, S., Lualhati, J., Mandap, N., Clemente, S., 2020. Life Cycle Assessment of Biochar as a Partial Replacement to Portland Cement. *E&ES* 479, 012025.
- Chan, Y.H., Tan, R.R., Yusup, S., Lam, H.L., Quitain, A.T., 2016. Comparative life cycle assessment (LCA) of bio-oil production from fast pyrolysis and hydrothermal liquefaction of oil palm empty fruit bunch (EFB). *Clean Technol Environ Policy* 18, 1759–1768.
- Chang, C.F., Chen, J.W., 2006. The experimental investigation of concrete carbonation depth. *Cem Concr Res* 36, 1760–1767.

-
- Chen, L., Wang, L., Zhang, Y., Ruan, S., Mechtcherine, V., Tsang, D.C.W., 2022a. Roles of biochar in cement-based stabilization/solidification of municipal solid waste incineration fly ash. *Chemical Engineering Journal* 430.
- Chen, L., Zhang, Y., Wang, L., Ruan, S., Chen, J., Li, H., Yang, J., Mechtcherine, V., Tsang, D.C.W., 2022b. Biochar-augmented carbon-negative concrete. *Chemical Engineering Journal* 431.
- Cheng, F., Luo, H., Colosi, L.M., 2020. Slow pyrolysis as a platform for negative emissions technology: An integration of machine learning models, life cycle assessment, and economic analysis. *Energy Convers Manag* 223, 113258.
- Chew, Z.L., Tan, E.H., Palaniandy, S.A.L., Woon, K.S., Phuang, Z.X., 2023. An integrated life-cycle greenhouse gas protocol accounting on oil palm trunk and empty fruit bunch biofuel production. *Science of The Total Environment* 856, 159007.
- Choi, W.C., Yun, H. Do, Lee, J.Y., 2012. Mechanical Properties of Mortar Containing Bio-Char From Pyrolysis. *Journal of the Korea institute for structural maintenance and inspection* 16, 67–74.
- Colangelo, F., Forcina, A., Farina, I., Petrillo, A., 2018. Life Cycle Assessment (LCA) of Different Kinds of Concrete Containing Waste for Sustainable Construction. *Buildings* 8, 70.
- Creamer, A.E., Gao, B., Zhang, M., 2014. Carbon dioxide capture using biochar produced from sugarcane bagasse and hickory wood. *Chemical Engineering Journal* 249, 174–179.
- Danish, A., Ali Mosaberpanah, M., Usama Salim, M., Ahmad, N., Ahmad, F., Ahmad, A., 2021. Reusing biochar as a filler or cement replacement material in cementitious composites: A review. *Constr Build Mater* 300, 124295.
- Ding, E., Jiang, J., Lan, Y., Zhang, L., Gao, C., Jiang, K., Qi, X., Fan, X., 2023. Optimizing Cd²⁺ adsorption performance of KOH modified biochar adopting response surface methodology. *J Anal Appl Pyrolysis* 169, 105788.

-
- Ding, Y., Guo, C., Qin, S., Wang, B., Zhao, P., Cui, X., 2022. Effects of process water recirculation on yields and quality of hydrochar from hydrothermal carbonization process of rice husk. *J Anal Appl Pyrolysis* 166, 105618.
- Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., Zheng, B., 2016. Biochar to improve soil fertility. A review. *Agronomy for Sustainable Development* 36:2 36, 1–18.
- Dissanayake, P.D., You, S., Igalavithana, A.D., Xia, Y., Bhatnagar, A., Gupta, S., Kua, H.W., Kim, S., Kwon, J.H., Tsang, D.C.W., Ok, Y.S., 2020. Biochar-based adsorbents for carbon dioxide capture: A critical review. *Renewable and Sustainable Energy Reviews* 119, 109582.
- Dixit, A., Gupta, S., Pang, S.D., Kua, H.W., 2019. Waste Valorisation using biochar for cement replacement and internal curing in ultra-high performance concrete. *J Clean Prod* 238, 117876.
- Duan, S., He, J., Xin, X., Li, L., Zou, X., Zhong, Y., Zhang, J., Cui, X., 2023. Characteristics of digested sludge-derived biochar for promoting methane production during anaerobic digestion of waste activated sludge. *Bioresour Technol* 129245.
- Dutta, B., Raghavan, V., 2014. A life cycle assessment of environmental and economic balance of biochar systems in Quebec. *International Journal of Energy and Environmental Engineering* 5, 1–11.
- Endut, A., Abdullah, S.H.Y.S., Hanapi, N.H.M., Hamid, S.H.A., Lananan, F., Kamarudin, M.K.A., Umar, R., Juahir, H., Khatoon, H., 2017. Optimization of biodiesel production by solid acid catalyst derived from coconut shell via response surface methodology. *Int Biodeterior Biodegradation* 124, 250–257.
- Estanqueiro, B., Dinis Silvestre, J., de Brito, J., Duarte Pinheiro, M., 2018. Environmental life cycle assessment of coarse natural and recycled aggregates for concrete. *European Journal of Environmental and Civil Engineering* 22, 429–449.
- Fang, Z., Gao, Y., Bolan, N., Shaheen, S.M., Xu, S., Wu, X., Xu, X., Hu, H., Lin, J., Zhang, F., Li, J., Rinklebe, J., Wang, H., 2020. Conversion of biological solid

-
- waste to graphene-containing biochar for water remediation: A critical review. *Chemical Engineering Journal* 390, 124611.
- Fawzy, S., Osman, A.I., Yang, H., Doran, J., Rooney, D.W., 2021. Industrial biochar systems for atmospheric carbon removal: a review. *Environmental Chemistry Letters* 2021 19:4 19, 3023–3055.
- Ferreira, M.F.P., Oliveira, B.F.H., Pinheiro, W.B.S., Correa, N.F., França, L.F., Ribeiro, N.F.P., 2020. Generation of biofuels by slow pyrolysis of palm empty fruit bunches: Optimization of process variables and characterization of physical-chemical products. *Biomass Bioenergy* 140, 105707.
- Flórez, E., Acelas, N., Ramirez, A.P., Giraldo, S., Rodríguez, B., Correa, E., Echeverría, F., 2019. Small additions of activated Biochar from palm oil shells to Portland cement mortar. *J Phys Conf Ser* 1247, 012052.
- Friedlingstein, P., O.M., J.M.W., A.R.M., 2021. Annual CO₂ emissions (Malaysia) Global Carbon Project. URL <https://www.globalcarbonproject.org/> (accessed 5.26.23).
- GaBi Handbook, 2012. GaBi Paper Clip Tutorial. Lca 1–75.
- Ge, S., Foong, S.Y., Ma, N.L., Liew, R.K., Wan Mahari, W.A., Xia, C., Yek, P.N.Y., Peng, W., Nam, W.L., Lim, X.Y., Liew, C.M., Chong, C.C., Sonne, C., Lam, S.S., 2020. Vacuum pyrolysis incorporating microwave heating and base mixture modification: An integrated approach to transform biowaste into eco-friendly bioenergy products. *Renewable and Sustainable Energy Reviews* 127, 109871.
- Groves, G.W., Rodway, D.I., Richardson, I.G., 1990. The carbonation of hardened cement pastes. *Advances in Cement Research* 3, 117–125.
- Guinée, J. et. al, 2001. Handbook on Life Cycle Assessment - Operational Guide to the ISO Standards. Centre of Environmental Science, Leiden University (CML); The Netherlands, 200.
- Guo, X., Li, Y., Shi, H., She, A., Guo, Y., Su, Q., Ren, B., Liu, Z., Tao, C., 2023. Carbon reduction in cement industry - An indigenized questionnaire on environmental impacts and key parameters of life cycle assessment (LCA) in China. *J Clean Prod* 426.

-
- Gupta, S., 2021. Carbon sequestration in cementitious matrix containing pyrogenic carbon from waste biomass: A comparison of external and internal carbonation approach. *Journal of Building Engineering* 43, 102910.
- Gupta, S., Kashani, A., 2021. Utilization of biochar from unwashed peanut shell in cementitious building materials – Effect on early age properties and environmental benefits. *Fuel Processing Technology* 218, 106841.
- Gupta, Souradeep, Kashani, A., Mahmood, A.H., 2022a. Carbon sequestration in engineered lightweight foamed mortar – Effect on rheology, mechanical and durability properties. *Constr Build Mater* 322, 126383.
- Gupta, S., Kashani, A., Mahmood, A.H., Han, T., 2021a. Carbon sequestration in cementitious composites using biochar and fly ash – Effect on mechanical and durability properties. *Constr Build Mater* 291, 123363.
- Gupta, S., Kua, H.W., 2017. Factors Determining the Potential of Biochar As a Carbon Capturing and Sequestering Construction Material: Critical Review. *Journal of Materials in Civil Engineering* 29, 04017086.
- Gupta, S., Kua, H.W., 2018a. Effect of water entrainment by pre-soaked biochar particles on strength and permeability of cement mortar. *Constr Build Mater* 159, 107–125.
- Gupta, S., Kua, H.W., 2019. Carbonaceous micro-filler for cement: Effect of particle size and dosage of biochar on fresh and hardened properties of cement mortar. *Science of The Total Environment* 662, 952–962.
- Gupta, S., Kua, H.W., 2020. Combination of Biochar and Silica Fume as Partial Cement Replacement in Mortar: Performance Evaluation Under Normal and Elevated Temperature. *Waste Biomass Valorization* 11, 2807–2824.
- Gupta, S., Kua, H.W., Dai Pang, S., 2018a. Biochar-mortar composite: Manufacturing, evaluation of physical properties and economic viability.
- Gupta, S., Kua, H.W., Koh, H.J., 2018b. Application of biochar from food and wood waste as green admixture for cement mortar. *Science of The Total Environment* 619–620, 419–435.

-
- Gupta, S., Kua, H.W., Low, C.Y., 2018c. Use of biochar as carbon sequestering additive in cement mortar. *Cem Concr Compos* 87, 110–129.
- Gupta, S., Kua, W., Dai Pang, S., 2019. Biochar-concrete composite: manufacturing, characterization and performance evaluation at elevated temperature. *Academic Journal of Civil Engineering* 37, 507–513.
- Gupta, S., Muthukrishnan, S., Kua, H.W., 2021b. Comparing influence of inert biochar and silica rich biochar on cement mortar – Hydration kinetics and durability under chloride and sulfate environment. *Constr Build Mater* 268, 121142.
- Gupta, Shubhi, Patel, P., Mondal, P., 2022. Biofuels production from pine needles via pyrolysis: Process parameters modeling and optimization through combined RSM and ANN based approach. *Fuel* 310, 122230.
- Gupta, Souradeep, Tulliani, J.M., Kua, H.W., 2022b. Carbonaceous admixtures in cementitious building materials: Effect of particle size blending on rheology, packing, early age properties and processing energy demand. *Science of the Total Environment* 807.
- Gursel, A.P., Maryman, H., Ostertag, C., 2016. A life-cycle approach to environmental, mechanical, and durability properties of “green” concrete mixes with rice husk ash. *J Clean Prod* 112, 823–836.
- Gursel, A.P., Masanet, E., Horvath, A., Stadel, A., 2014. Cement & Concrete Composites Life-cycle inventory analysis of concrete production: A critical review. *Cem Concr Compos* 51, 38–48.
- Gursel, A.P., Ostertag, C.P., 2016. Impact of Singapore’s importers on life-cycle assessment of concrete. *J Clean Prod* 118, 140–150.
- Haris Javed, M., Ali Sikandar, M., Ahmad, W., Tariq Bashir, M., Alrowais, R., Bilal Wadud, M., 2022. Effect of various biochars on physical, mechanical, and microstructural characteristics of cement pastes and mortars. *Journal of Building Engineering* 57, 104850.
- Harsono, S.S., Grundman, P., Lau, L.H., Hansen, A., Salleh, M.A.M., Meyer-Aurich, A., Idris, A., Ghazi, T.I.M., 2013. Energy balances, greenhouse gas emissions and

-
- economics of biochar production from palm oil empty fruit bunches. *Resour Conserv Recycl* 77, 108–115.
- Horgnies, M., Dubois-Brugger, I., Gartner, E.M., 2012. NO_x de-pollution by hardened concrete and the influence of activated charcoal additions. *Cem Concr Res* 42, 1348–1355.
- Hossain, M.U., Poon, C.S., Lo, I.M.C., Cheng, J.C.P., 2016. Comparative environmental evaluation of aggregate production from recycled waste materials and virgin sources by LCA. *Resour Conserv Recycl* 109, 67–77.
- Huggins, T.M., Haeger, A., Biffinger, J.C., Ren, Z.J., 2016. Granular biochar compared with activated carbon for wastewater treatment and resource recovery. *Water Res* 94, 225–232.
- Hussain, A., Kumar, S., Fohad, ., Husain, M., Kumar, V., Vlaskin, M.S., Alajmi, M.F., Wu, T.Y., 2023. Numerical optimization of hydrothermal liquefaction process for the production of bio-oil and bio-char from *Citrus maxima* peel waste and product characterization. *Environmental Science and Pollution Research* 2023 1, 1–12.
- Idris, R., Chong, C.T., Asik, J.A., Ani, F.N., 2020. Optimization studies of microwave-induced co-pyrolysis of empty fruit bunches/waste truck tire using response surface methodology. *J Clean Prod* 244, 118649.
- International Biochar Initiative 2024. URL <https://biochar-international.org/carbon-gold/> (accessed 5.27.23).
- Ismail, H.Y., Fayyad, S., Ahmad, M.N., Leahy, J.J., Naushad, Mu., Walker, G.M., Albadarin, A.B., Kwapinski, W., 2021. Modelling of yields in torrefaction of olive stones using artificial intelligence coupled with kriging interpolation. *J Clean Prod* 326, 129020.
- Jafri, N., Yoon, L.W., Wong, W.Y., Cheah, K.H., 2020. Power generation from palm kernel shell biochar in a direct carbon fuel cell. *SN Appl Sci* 2, 1–8.
- Jiang, Z., Zheng, H., Xing, B., 2021. Environmental life cycle assessment of wheat production using chemical fertilizer, manure compost, and biochar-amended manure compost strategies. *Science of The Total Environment* 760, 143342.

-
- Jung, K.A., Nam, C.W., Woo, S.H., Park, J.M., 2016. Response surface method for optimization of phenolic compounds production by lignin pyrolysis. *J Anal Appl Pyrolysis* 120, 409–415.
- Kalderis, D., Anastasiou, E., Petrakis, E., Konopisi, S., 2024. Utilization of biochar from olive tree pruning as additive to cement mortars. *J Clean Prod* 469, 143137.
- Kant Bhatia, S., Palai, A.K., Kumar, A., Kant Bhatia, R., Kumar Patel, A., Kumar Thakur, V., Yang, Y.-H., 2021. Trends in renewable energy production employing biomass-based biochar. *Bioresour Technol* 340, 125644.
- Kazemi Targhi, N., Tavakoli, O., Nazemi, A.H., 2022. Co-pyrolysis of lentil husk wastes and *Chlorella vulgaris*: Bio-oil and biochar yields optimization. *J Anal Appl Pyrolysis* 165, 105548.
- Khushnood, R.A., Ahmad, S., Restuccia, L., Spoto, C., Jagdale, P., Tulliani, J.M., Ferro, G.A., 2016. Carbonized nano/microparticles for enhanced mechanical properties and electromagnetic interference shielding of cementitious materials. *Frontiers of Structural and Civil Engineering* 10, 209–213.
- Kiliç, M., Pütün, E., Pütün, A.E., 2014. Optimization of *Euphorbia rigida* fast pyrolysis conditions by using response surface methodology. *J Anal Appl Pyrolysis* 110, 163–171.
- Kim Hoang Pham, L., Kongparakul, S., Guan, G., Chanlek, N., Vo, D.V.N., Van Cuong, N., Watanabe, A., Samart, C., 2024. CO₂-assisted fast pyrolysis of palm kernel shells over a Ni–Ce/CN catalyst for the selective production of bio-oil. *Fuel* 371, 132038.
- Klasson, K.T., Uchimiya, M., Lima, I.M., 2015. Characterization of narrow micropores in almond shell biochars by nitrogen, carbon dioxide, and hydrogen adsorption. *Ind Crops Prod* 67, 33–40.
- Klinghoffer, N.B., Castaldi, M.J., Nzihou, A., 2015. Influence of char composition and inorganics on catalytic activity of char from biomass gasification. *Fuel* 157, 37–47.
- Krou, N.J., Batonneau-Gener, I., Belin, T., Mignard, S., Horgnies, M., Dubois-Brugger, I., 2013. Mechanisms of NO_x entrapment into hydrated cement paste containing
-

-
- activated carbon — Influences of the temperature and carbonation. *Cem Concr Res* 53, 51–58.
- Kurniawan, T.A., Othman, M.H.D., Liang, X., Goh, H.H., Gikas, P., Chong, K.K., Chew, K.W., 2023. Challenges and opportunities for biochar to promote circular economy and carbon neutrality. *J Environ Manage* 332, 117429.
- Kushwah, S., Singh, S., Agarwal, R., Nighot, N.S., Kumar, R., Athar, H., Naik B, S., 2024. Mixture of biochar as a green additive in cement-based materials for carbon dioxide sequestration. *Journal of Materials Science: Materials in Engineering* 2024 19:1 19, 1–15.
- Lahijani, P., Mohammadi, M., Mohamed, A.R., 2018. Metal incorporated biochar as a potential adsorbent for high capacity CO₂ capture at ambient condition. *Journal of CO₂ Utilization* 26, 281–293.
- Lee, T., Zubir, Z.A., Jamil, F.M., Matsumoto, A., Yeoh, F.Y., 2014. Combustion and pyrolysis of activated carbon fibre from oil palm empty fruit bunch fibre assisted through chemical activation with acid treatment. *J Anal Appl Pyrolysis* 110, 408–418.
- Lee, X.J., Lee, L.Y., Hiew, B.Y.Z., Gan, S., Thangalazhy-Gopakumar, S., Ng, H.K., 2020. Valorisation of oil palm wastes into high yield and energy content biochars via slow pyrolysis: Multivariate process optimisation and combustion kinetic studies. *Mater Sci Energy Technol* 3, 601–610.
- Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jung, J., Hyun, S., 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C. *Bioresour Technol* 148, 196–201.
- Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2019. Biochar stability assessment methods: A review. *Science of The Total Environment* 647, 210–222.
- Li, K., Wang, J., Zhuang, Y., Yuan, G., Li, Y., Zhu, X., 2023. Glucose-Histidine Heyns compound: Preparation, characterization and fragrance enhancement. *Carbohydr Res* 532, 108922.
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G., 2006. Black
-

-
- Carbon Increases Cation Exchange Capacity in Soils. Soil Science Society of America Journal 70, 1719–1730.
- Lim, X.Y., Yek, P.N.Y., Liew, R.K., Chiong, M.C., Wan Mahari, W.A., Peng, W., Chong, C.T., Lin, C.Y., Aghbashlo, M., Tabatabaei, M., Lam, S.S., 2022. Engineered biochar produced through microwave pyrolysis as a fuel additive in biodiesel combustion. Fuel 312, 122839.
- Liu, J., Liu, G., Zhang, W., Li, Z., Jin, H., Xing, F., 2023. A new approach to CO₂ capture and sequestration: A novel carbon capture artificial aggregates made from biochar and municipal waste incineration bottom ash. Constr Build Mater 398.
- Liu, S.H., Huang, Y.Y., 2018. Valorization of coffee grounds to biochar-derived adsorbents for CO₂ adsorption. J Clean Prod 175, 354–360.
- Liu, W., Li, K., Xu, S., 2022. Utilizing bamboo biochar in cement mortar as a bio-modifier to improve the compressive strength and crack-resistance fracture ability. Constr Build Mater 327.
- Loy, A.C.M., Alhazmi, H., Lock, S.S.M., Yiin, C.L., Cheah, K.W., Chin, B.L.F., How, B.S., Yusup, S., 2021. Life-cycle assessment of hydrogen production via catalytic gasification of wheat straw in the presence of straw derived biochar catalyst. Bioresour Technol 341, 125796.
- Lü, F., Zhou, Q., Wu, D., Wang, T., Shao, L., He, P., 2015. Dewaterability of anaerobic digestate from food waste: Relationship with extracellular polymeric substances. Chemical Engineering Journal 262, 932–938.
- Ma, Z., Yang, Y., Ma, Q., Zhou, H., Luo, X., Liu, X., Wang, S., 2017. Evolution of the chemical composition, functional group, pore structure and crystallographic structure of bio-char from palm kernel shell pyrolysis under different temperatures. J Anal Appl Pyrolysis 127, 350–359.
- Mah, C.M., Fujiwara, T., Ho, C.S., 2018. Life cycle assessment and life cycle costing toward eco-efficiency concrete waste management in Malaysia. J Clean Prod 172, 3415–3427.

-
- Maljaee, H., Madadi, R., Paiva, H., Tarelho, L., Ferreira, V.M., 2021a. Incorporation of biochar in cementitious materials: A roadmap of biochar selection. *Constr Build Mater* 283, 122757.
- Maljaee, H., Paiva, H., Madadi, R., Tarelho, L.A.C., Morais, M., Ferreira, V.M., 2021b. Effect of cement partial substitution by waste-based biochar in mortars properties. *Constr Build Mater* 301, 124074.
- Manjunath, B., Ouellet-Plamondon, C.M., Das, B.B., Rao, S., Bhojaraju, C., Rao, M., 2024. Areca nut husk biochar as a sustainable carbonaceous filler for cement: Pyrolysis temperature and its effect on characterization, strength, and hydration. *Ind Crops Prod* 222, 119883.
- Manyà, J.J., Roca, F.X., Perales, J.F., 2013. TGA study examining the effect of pressure and peak temperature on biochar yield during pyrolysis of two-phase olive mill waste. *J Anal Appl Pyrolysis* 103, 86–95.
- Marinković, S., Carević, V., Dragaš, J., 2021. The role of service life in Life Cycle Assessment of concrete structures. *J Clean Prod* 290, 125610.
- Md Said, M.S., Azni, A.A., Wan Ab Karim Ghani, W.A., Idris, A., Ja'afar, M.F.Z., Mohd Salleh, M.A., 2022. Production of biochar from microwave pyrolysis of empty fruit bunch in an alumina susceptor. *Energy* 240, 122710.
- Mekky, K.M., Ibrahim, M.G., Sharobim, K., Fujii, M., Nasr, M., 2024. Evaluating environmental and economic benefits of using biochar in concrete: A life cycle assessment and multi-criteria decision-making framework. *Case Studies in Construction Materials* 21.
- Mensah, R.A., Shanmugam, V., Narayanan, S., Razavi, S.M.J., Ulfberg, A., Blanksvärd, T., Sayahi, F., Simonsson, P., Reinke, B., Försth, M., Sas, G., Sas, D., Das, O., 2021. Biochar-Added Cementitious Materials—A Review on Mechanical, Thermal, and Environmental Properties. *Sustainability* 2021, Vol. 13, Page 9336 13, 9336.
- Michalak, I., Baśladyńska, S., Mokrzycki, J., Rutkowski, P., 2019. Biochar from a freshwater macroalga as a potential biosorbent for wastewater treatment. *Water (Switzerland)* 11.
-

-
- Mishra, G., Danoglidis, P.A., Shah, S.P., Konsta-Gdoutos, M.S., 2023. Carbon capture and storage potential of biochar-enriched cementitious systems. *Cem Concr Compos* 140.
- Mohamad, N., Muthusamy, K., Embong, R., Kusbiantoro, A., Hashim, M.H., 2021. Environmental impact of cement production and Solutions: A review. *Mater Today Proc.*
- MPOC, 2023. Malaysian Palm Oil Council (MPOC) URL <http://mpoc.org.my/about-palm-oil/>
- Mubarak, N.M., Sahu, J.N., Abdullah, E.C., Jayakumar, N.S., 2016. Plam oil empty fruit bunch based magnetic biochar composite comparison for synthesis by microwave-assisted and conventional heating. *J Anal Appl Pyrolysis* 120, 521–528.
- Mukherjee, A., Borugadda, V.B., Dynes, J.J., Niu, C., Dalai, A.K., 2021. Carbon dioxide capture from flue gas in biochar produced from spent coffee grounds: Effect of surface chemistry and porous structure. *J Environ Chem Eng* 9, 106049.
- Muthukrishnan, S., Gupta, S., Kua, H.W., 2019. Application of rice husk biochar and thermally treated low silica rice husk ash to improve physical properties of cement mortar. *Theoretical and Applied Fracture Mechanics* 104, 102376.
- Nam, W.L., Phang, X.Y., Su, M.H., Liew, R.K., Ma, N.L., Rosli, M.H.N. Bin, Lam, S.S., 2018. Production of bio-fertilizer from microwave vacuum pyrolysis of palm kernel shell for cultivation of Oyster mushroom (*Pleurotus ostreatus*). *Science of The Total Environment* 624, 9–16.
- Nasmech Technology Sdn Bhd, n.d. Nasmech [WWW Document]. URL https://www.nasmech.com.my/index.php?ws=pages&pages_id=16369
- Neville A. M., 2011. *Properties of Concrete*, 5th ed. Pearson .
- Nisticò, R., Lavagna, L., Versaci, D., Ivanchenko, P., Benzi, P., 2020a. Chitosan and its char as fillers in cement-base composites: A case study. *Boletín de la Sociedad Española de Cerámica y Vidrio* 59, 186–192.

-
- Nochaiya, T., Wongkeo, W., Chaipanich, A., 2010. Utilization of fly ash with silica fume and properties of Portland cement-fly ash-silica fume concrete. *Fuel* 89, 768–774.
- Ofori-Boadu, A.N., Kelley, R., Aryeetey, F., Fini, E., Akangah, P., 2017. The Influence of Swine-Waste Biochar on the Early-Age Characteristics of Cement Paste. *Int. Journal of Engineering Research and Application* www.ijera.com 7, 1–07.
- Ogundipe, K.E., Ogunbayo, B.F., Olofinnade, O.M., Amusan, L.M., Aigbavboa, C.O., 2021. Affordable housing issue: Experimental investigation on properties of eco-friendly lightweight concrete produced from incorporating periwinkle and palm kernel shells. *Results in Engineering* 9, 100193.
- Oh, S.-J., Choi, G.-G., Kim, J.-S., 2016. Characteristics of bio-oil from the pyrolysis of palm kernel shell in a newly developed two-stage pyrolyzer. *Energy* 113, 108–115.
- Omar, R., Idris, A., Yunus, R., Khalid, K., Aida Isma, M.I., 2011. Characterization of empty fruit bunch for microwave-assisted pyrolysis. *Fuel* 90, 1536–1544.
- openLCA.org n.d. URL <https://www.openlca.org/> (accessed 3.29.24).
- Praneeth, S., Guo, R., Wang, T., Dubey, B.K., Sarmah, A.K., 2020a. Accelerated carbonation of biochar reinforced cement-fly ash composites: Enhancing and sequestering CO₂ in building materials. *Constr Build Mater* 244, 118363.
- Praneeth, S., Saavedra, L., Zeng, M., Dubey, B.K., Sarmah, A.K., 2021. Biochar admixed lightweight, porous and tougher cement mortars: Mechanical, durability and micro computed tomography analysis. *Science of The Total Environment* 750, 142327.
- Praneeth, S., Zameer, A., Zhang, N., Dubey, B.K., Sarmah, A.K., 2022. Biochar admixture cement mortar fines for adsorptive removal of heavy metals in single and multimetal solution: Insights into the sorption mechanisms and environmental significance. *Science of The Total Environment* 839, 155992.
- Promraksa, A., Rakmak, N., 2020a. Biochar production from palm oil mill residues and application of the biochar to adsorb carbon dioxide. *Heliyon* 6, e04019.

-
- Pua, F.-L., Subari, M.S., Ean, L.-W., Krishnan, S.G., 2020. Characterization of biomass fuel pellets made from Malaysia tea waste and oil palm empty fruit bunch. *Mater Today Proc* 31, 187–190.
- Qin, Y., Pang, X., Tan, K., Bao, T., 2021a. Evaluation of pervious concrete performance with pulverized biochar as cement replacement. *Cem Concr Compos* 119, 104022.
- Quah, R.V., Tan, Y.H., Mubarak, N.M., Kansedo, J., Khalid, M., Abdullah, E.C., Abdullah, M.O., 2020. Magnetic biochar derived from waste palm kernel shell for biodiesel production via sulfonation. *Waste Management* 118, 626–636.
- RAHEEM, A.A., ORIOLA, K.O., KAREEM, M.A., ABDULWAHAB, R., 2021. Investigation on thermal properties of rice husk ash-blended palm kernel shell concrete. *Environmental Challenges* 5, 100284.
- Rajendiran, N., Ganesan, S., Weichgrebe, D., Srinivasan, ., Venkatachalam, S., 2023. Optimization of pyrolysis process parameters for the production of biochar from banana peduncle fibrous waste and its characterization. *Clean Technologies and Environmental Policy* 2023 1, 1–13.
- Restuccia, L., Ferro, G.A., 2016a. Promising low cost carbon-based materials to improve strength and toughness in cement composites. *Constr Build Mater* 126, 1034–1043.
- Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R., Lehmann, J., 2010. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. *Environ Sci Technol* 44, 827–833.
- Rodier, L., Bilba, K., Onésippe, C., Arsène, M.-A., 2019. Utilization of bio-chars from sugarcane bagasse pyrolysis in cement-based composites. *Ind Crops Prod* 141, 111731.
- Saharudin, D.M., Jeswani, H.K., Azapagic, A., 2024. Biochar from agricultural wastes: Environmental sustainability, economic viability and the potential as a negative emissions technology in Malaysia. *Science of The Total Environment* 919, 170266.
- Sahoo, K., Upadhyay, A., Runge, T., Bergman, R., Puettmann, M., Bilek, E., 2021. Life-cycle assessment and techno-economic analysis of biochar produced from

-
- forest residues using portable systems. *International Journal of Life Cycle Assessment* 26, 189–213.
- Sahoo, S.S., Vijay, V.K., Chandra, R., Kumar, H., 2021. Production and characterization of biochar produced from slow pyrolysis of pigeon pea stalk and bamboo. *Clean Eng Technol* 3, 100101.
- Salleh, A., Hang Lau, L., Mukhlesur Rahman, M., Azlina Wan Ab Karim Ghani, W., Thaiyiba Shafie, S., Amran Mohd Salleh, M., Lek Hang, L., Azlina Wan Abdul Karim Ghani, W., Info, A., 2012. Effect of pyrolysis temperature on the biochar nutrient and water retention capacity. *researchgate.net* ST Shafie, MM Salleh, LL Hang, M Rahman, W Ghani *Journal of purity, utility reaction and environment*, 2012•*researchgate.net* 1, 323–337.
- Samsuri, A.W., Sadegh-Zadeh, F., Seh-Bardan, B.J., 2013. Adsorption of As(III) and As(V) by Fe coated biochars and biochars produced from empty fruit bunch and rice husk. *J Environ Chem Eng* 1, 981–988.
- Sanaz Saheri, Masoud Aghajani Mir, Noor Ezlin Ahmad Basri, Noor Zalina Binti Mahmood, Rawshan Ara Begum, 2012. Life Cycle Assessment for Solid Waste Disposal Options in Malaysia. *Pol J Environ Stud* 21, 1377–1382.
- Sari, N.A., Ishak, C.F., Bakar, R.A., 2014. CHARACTERIZATION OF OIL PALM EMPTY FRUIT BUNCH AND RICE HUSK BIOCHARS AND THEIR POTENTIAL TO ADSORB ARSENIC AND CADMIUM. *Am J Agric Biol Sci* 9, 450–456.
- Šavija, B., Luković, M., 2016a. Carbonation of cement paste: Understanding, challenges, and opportunities. *Constr Build Mater* 117, 285–301.
- Selvarajoo, A., 2021. Slow pyrolysis of *Durio zibethinus* rind and the influence of carbonization temperature on biochar properties. *IOP Conf Ser Mater Sci Eng* 1092, 012042.
- Selvarajoo, A., Oochit, D., 2020. Effect of pyrolysis temperature on product yields of palm fibre and its biochar characteristics. *Mater Sci Energy Technol* 3, 575–583.

-
- Senadheera, S.S., Gupta, S., Kua, H.W., Hou, D., Kim, S., Tsang, D.C.W., Ok, Y.S., 2023. Application of biochar in concrete – A review. *Cem Concr Compos* 143, 105204.
- Sevilla, M., Maciá-Agulló, J.A., Fuertes, A.B., 2011. Hydrothermal carbonization of biomass as a route for the sequestration of CO₂: Chemical and structural properties of the carbonized products. *Biomass Bioenergy* 35, 3152–3159.
- Shaaban, A., Se, S.M., Dimin, M.F., Juoi, J.M., Mohd Husin, M.H., Mitan, N.M.M., 2014. Influence of heating temperature and holding time on biochars derived from rubber wood sawdust via slow pyrolysis. *J Anal Appl Pyrolysis* 107, 31–39.
- Shafawi, A.N., Mohamed, A.R., Lahijani, P., Mohammadi, M., 2021. Recent advances in developing engineered biochar for CO₂ capture: An insight into the biochar modification approaches. *J Environ Chem Eng* 9, 106869.
- Shan, X., Zhou, J., Chang, V.W.C., Yang, E.H., 2017. Life cycle assessment of adoption of local recycled aggregates and green concrete in Singapore perspective. *J Clean Prod* 164, 918–926.
- Singh Pali, H., Sharma, A., Kumar, M., Anand Annakodi, V., Nhanh Nguyen, V., Kumar Singh, N., Singh, Y., Balasubramanian, D., Deepanraj, B., Hai Truong, T., Quy Phong Nguyen, P., 2023. Enhancement of combustion characteristics of waste cooking oil biodiesel using TiO₂ nanofluid blends through RSM. *Fuel* 331, 125681.
- Sirico, A., Bernardi, P., Belletti, B., Malcevski, A., Dalcanale, E., Domenichelli, I., Fornoni, P., Moretti, E., 2020a. Mechanical characterization of cement-based materials containing biochar from gasification. *Constr Build Mater* 246, 118490.
- Song, S., Liu, Z., Liu, G., Cui, X., Sun, J., 2023. Application of biochar cement-based materials for carbon sequestration. *Constr Build Mater*.
- Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Manag* 1, 289–303.
- Suarez-Riera, D., Restuccia, L., Ferro, G.A., 2020. The use of Biochar to reduce the carbon footprint of cement-based materials. *Procedia Structural Integrity* 26, 199–210.
-

-
- Syahida Adnan, Z., Ariffin, N.F., Syed Mohsin, S.M., Abdul Shukor Lim, N.H., 2021. Review paper: Performance of rice husk ash as a material for partial cement replacement in concrete. *Mater Today Proc.*
- Tag, A.T., Duman, G., Ucar, S., Yanik, J., 2016. Effects of feedstock type and pyrolysis temperature on potential applications of biochar. *J Anal Appl Pyrolysis* 120, 200–206.
- Tak, S., Gupta, P., Kumar, A., Sofi, A., Mei Yun, C., 2023. Effect of using silica fume as a partial replacement of cement in concrete. *Mater Today Proc.*
- Tan, K., Pang, X., Qin, Y., Wang, J., 2020. Properties of cement mortar containing pulverized biochar pyrolyzed at different temperatures. *Constr Build Mater* 263, 120616.
- Tan, K., Qin, Y., Wang, J., 2022. Evaluation of the properties and carbon sequestration potential of biochar-modified pervious concrete. *Constr Build Mater* 314, 125648.
- Tomczyk, A., Sokołowska, Z., Boguta, P., 2020. Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. *Reviews in Environmental Science and Bio/Technology* 2020 19:1 19, 191–215.
- United Nations Development Programme, 2021. Climate Promise MALAYSIA (Asia and the Pacific) <https://climatepromise.undp.org/what-we-do/where-we-work/malaysia>.
- Vaskan, P., Pachón, E.R., Gnansounou, E., 2018. Techno-economic and life-cycle assessments of biorefineries based on palm empty fruit bunches in Brazil. *J Clean Prod* 172, 3655–3668.
- Vasudevan, G., Marimuthu, N., 2021. Evaluation of Mechanical Properties of Eggshell Powder and Palm Kernel Shell Powder as Partial Replacement of Cement. *Lecture Notes in Civil Engineering* 139 LNCE, 21–30.
- Wan Mahari, W.A., Nam, W.L., Sonne, C., Peng, W., Phang, X.Y., Liew, R.K., Yek, P.N.Y., Lee, X.Y., Wen, O.W., Show, P.L., Chen, W.H., Chang, J.S., Lam, S.S., 2020a. Applying microwave vacuum pyrolysis to design moisture retention and pH neutralizing palm kernel shell biochar for mushroom production. *Bioresour Technol* 312, 123572.

-
- Wan Mahari, W.A., Nam, W.L., Sonne, C., Peng, W., Phang, X.Y., Liew, R.K., Yek, P.N.Y., Lee, X.Y., Wen, O.W., Show, P.L., Chen, W.-H., Chang, J.-S., Lam, S.S., 2020b. Applying microwave vacuum pyrolysis to design moisture retention and pH neutralizing palm kernel shell biochar for mushroom production. *Bioresour Technol* 312, 123572.
- Wang, L., Chen, L., Tsang, D.C.W., Guo, B., Yang, J., Shen, Z., Hou, D., Ok, Y.S., Poon, C.S., 2020a. Biochar as green additives in cement-based composites with carbon dioxide curing. *J Clean Prod* 258, 120678.
- Wang, L., Chen, L., Tsang, D.C.W., Kua, H.W., Yang, J., Ok, Y.S., Ding, S., Hou, D., Poon, C.S., 2019. The roles of biochar as green admixture for sediment-based construction products. *Cem Concr Compos* 104, 103348.
- Wijeyawardana, P., Law, D., Gunasekara, C., Nanayakkara, N., Karunarathna, A., Pramanik, B.K., 2024. Assessing the life cycle and economic impact of cement-modified biochar compared to conventional adsorbents for heavy metal removal in stormwater. *Process Safety and Environmental Protection* 192, 244–256.
- Winters, D., Boakye, K., Simske, S., 2022. Toward Carbon-Neutral Concrete through Biochar–Cement–Calcium Carbonate Composites: A Critical Review. *Sustainability* 2022, Vol. 14, Page 4633 14, 4633.
- Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., Pokomeda, K., 2014. Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. *Bioresour Technol* 160, 150–160.
- Xiang, W., Zhang, X., Chen, J., Zou, W., He, F., Hu, X., Tsang, D.C.W., Ok, Y.S., Gao, B., 2020. Biochar technology in wastewater treatment: A critical review. *Chemosphere* 252, 126539.
- Xie, T., Sadasivam, B.Y., Reddy, K.R., Wang, C., Spokas, K., 2016. Review of the Effects of Biochar Amendment on Soil Properties and Carbon Sequestration. *J Hazard Toxic Radioact Waste* 20.
- Xuan, D., Zhan, B., Poon, C.S., 2016. Development of a new generation of eco-friendly concrete blocks by accelerated mineral carbonation. *J Clean Prod* 133, 1235–1241.

-
- Yaashikaa, P.R., Kumar, P.S., Varjani, S., Saravanan, A., 2020. A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. *Biotechnology Reports* 28, e00570.
- Yadav, K., Jagadevan, S., 2021. Effect of Pyrolysis of Rice Husk–Derived Biochar on the Fuel Characteristics and Adsorption of Fluoride from Aqueous Solution. *Bioenergy Res* 14, 964–977.
- Yadav, K., Tyagi, M., Kumari, S., Jagadevan, S., 2019. Influence of Process Parameters on Optimization of Biochar Fuel Characteristics Derived from Rice Husk: a Promising Alternative Solid Fuel. *Bioenergy Res* 12, 1052–1065.
- Yang, F., Zhang, S., Sun, Y., Tsang, D.C.W., Cheng, K., Ok, Y.S., 2019. Assembling biochar with various layered double hydroxides for enhancement of phosphorus recovery. *J Hazard Mater* 365, 665–673.
- Yang, S., Wi, S., Lee, J., Lee, H., Kim, S., 2019. Biochar-red clay composites for energy efficiency as eco-friendly building materials: Thermal and mechanical performance. *J Hazard Mater* 373, 844–855.
- Yang, X., Wang, X.Y., 2021. Hydration-strength-durability-workability of biochar-cement binary blends. *Journal of Building Engineering* 42, 103064.
- Ye, P., Guo, B., Qin, H., Wang, C., Li, J., Chen, Y., Lu, D., Wang, L., Gao, P., Ma, P., Zhan, B., Yu, Q., 2024. Investigation of the properties and sustainability of modified biochar-doped cement-based composite. *Cem Concr Compos* 153, 105684.
- You, S., Ok, Y.S., Tsang, D.C.W., Kwon, E.E., Wang, C.-H., 2018. Towards practical application of gasification: a critical review from syngas and biochar perspectives. <https://doi.org/10.1080/10643389.2018.1518860> 48, 1165–1213.
- Zhang, C., Ji, Y., Li, C., Zhang, Y., Sun, S., Xu, Y., Jiang, L., Wu, C., 2023. The Application of Biochar for CO₂ Capture: Influence of Biochar Preparation and CO₂ Capture Reactors. *Ind Eng Chem Res* 62, 17168–17181.
- Zhang, X., Zhang, P., Yuan, X., Li, Y., Han, L., 2020. Effect of pyrolysis temperature and correlation analysis on the yield and physicochemical properties of crop residue biochar. *Bioresour Technol* 296, 122318.
-

-
- Zhao, S.X., Ta, N., Wang, X.D., 2017. Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies (Basel)* 10.
- Zhao, W., Yang, H., He, S., Zhao, Q., Wei, L., 2021. A review of biochar in anaerobic digestion to improve biogas production: Performances, mechanisms and economic assessments. *Bioresour Technol* 341, 125797.
- Zhou, R., Zhang, M., Li, J., Zhao, W., 2020. Optimization of preparation conditions for biochar derived from water hyacinth by using response surface methodology (RSM) and its application in Pb²⁺ removal. *J Environ Chem Eng* 8, 104198.
- Zhu, X., Labianca, C., He, M., Luo, Z., Wu, C., You, S., Tsang, D.C.W., 2022. Life-cycle assessment of pyrolysis processes for sustainable production of biochar from agro-residues. *Bioresour Technol* 360, 127601.

Appendices

Appendix A: Compressive and Flexural Strength of Literature Studies

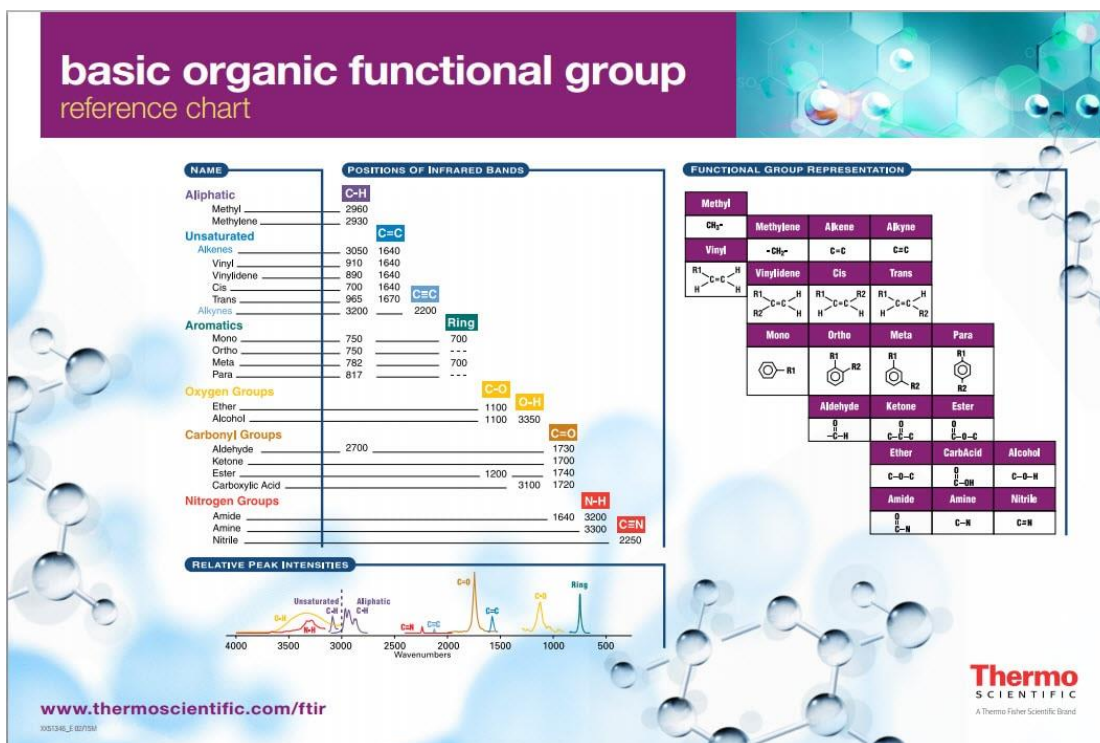
Table A.1

Biomass	Sample	Pyrolysis Temp (°C)	BC ^a (%)	Compressive Strength (MPa)	Flexural Strength (MPa)	Ref
Rice Husk	RH0.1	500	0.1	≈34.5	≈4.8	(Akhtar and Sarmah, 2017)
	RH0.75		0.75	≈26.5	≈4.2	
	RH1		1	≈29	≈4.7	
Pulp and Papermill	PP0.1		0.1	≈35	≈4.2	
	PP1		1	≈28.5	≈3.8	
Poultry litter	PL0.1	450	0.1	≈33	≈4.9	
	PL0.75		0.75	≈29	≈3.7	
	Control	-	0	≈39	≈3.8	
Eucalyptus Plywood	G3	500	3.2	≈11	N/A	(Qin et al., 2021b)
	G4		6.5	≈12.2		
	G5		9.5	≈8		
	G6		13.5	≈6.8		
	Control	-	0	≈9		
Wood Waste (saw dust) (Moist Curing)	Dry BC300_M	300	2	≈59	≈12.1	(Gupta and Kua, 2018b)
	Presoak BC300_M			≈67	≈12.8	
	Dry BC500_M	500		≈63	≈12	
	Presoak BC500_M			≈72	≈13	
	Control		0	≈57	≈12.2	
Wood Waste (saw dust) (Air Curing)	Dry BC300_M	300	2	≈47	≈10	
	Presoak BC300_M			≈61	≈10.8	
	Dry BC500_M	500		≈49	≈9.5	
	Presoak BC500_M			≈64	≈11	
	Control	-	0	≈43	≈9	
Waste wood sawdust (Masson pine wood)	500-1	500	1	≈71	N/A	(Wang et al., 2020b)
	500-2		2	≈69		
	500-5		5	≈64		
	700-1	700	1	≈72		
	700-2		2	≈71		
	700-5		5	≈63		
	Control		0	≈67		
Mixed saw dust (MW), Food Waste (FW), Rice waste (RW)	MWBC	500	1	58.80	12.80	(Gupta et al., 2018b)
			2	54.09	12.10	
			5	49.25	11.48	
	FWBC		1	53.56	11.92	

	RWBC		2	46.93	11.16			
			5	41.10	10.56			
			2	45.40	10.99			
			5	43.01	10.00			
	Mortar Control		0	48.816	12.23			
Rice husk (RH), bagasse (BB) treated biochar samples (TBB & TRHB), treated rice husk ash (TRHA)	RHB	700	5	≈43.4	N/A	(Asadi Zeidabadi et al., 2018)		
			10	≈36.0				
	TRHB		5	≈48.3				
			10	≈33.4				
	TRHA		5	≈45.3				
			10	≈49.6				
	TBB		5	≈ 53.1				
			10	≈41.3				
	BB		5	≈42.7				
			10	≈42.0				
	Control		0	≈36.5				
Olive Stone (OSB), Rice Husk (RHB), Wood Chips (FWB)	OSB_0.5	500	0.5	26.84	6.95	(Maljaee et al., 2021)		
	OSB_1		1	27.90	6.96			
	OSB_2		2	28.44	7.11			
	OSB_4		4	26.87	7.00			
	FWB_0.5		0.5	26.09	6.80			
	FWB_1		1	27.53	7.04			
	FWB_2		2	26.45	6.83			
	FWB_4		4	25.89	6.61			
	RHB_0.5		0.5	25.06	7.12			
	RHB_1		1	27.87	7.21			
	RHB_2		2	26.67	7.39			
	RHB_4		4	27.24	7.16			
	Control		0	26.03	6.83			
Corn Stover (cement and Fly ash)	M20	550	2	≈38.5	N/A	(Praneeth et al., 2020b)		
			4	≈38.8				
			6	≈40.5				
			8	≈39.4				
	M40	550	0	≈38.0				
			2	≈35.8				
			4	≈37.5				
			6	≈34.5				
		550	8	≈34.8				
			0	≈35.0				
			M50	550			2	≈36.5
							4	≈36.5
	6	≈35.0						
	8	≈34.5						

			0	≈36.0		
Rice Husk	B2-M	550	2	42.33	N/A	(Yang and Wang, 2021)
	B5-M		5	42.07		
	Control		0	44.52		
	A0	-	0	≈95	≈6.2	(Sirico et al., 2020b)
Wood Chips	A1	500	1.0	≈90	≈6.1	
	A2.5		2.5	≈83	≈5.9	
	B0	-	0	≈43	≈4.5	
Wood Chips	B1	500	1	≈42	≈4.7	
	B2.5		2.5	≈41	≈4.3	
	C0	-	0	≈71	≈6.1	
Wood Chips	C1	500	1	≈68	≈5.7	
	C2.5		2.5	≈61	≈5.3	
Coffee Powder (CP), Hazelnut shells (HS)	PY-HS 0.5%	800	0.5	55.09	3.96	(Restuccia and Ferro, 2016b)
	PY-HS 0.8%		0.8	45.51	4.02	
	PY-HS 1.0%		1.0	36.95	2.85	
	PY-CP 0.5%		0.5	57.79	3.71	
	PY-CP 0.8%		0.8	56.84	3.57	
	PY-CP 1.0%		1.0	52.37	2.73	
	Control	-	0	33.59	2.74	(Nisticò et al., 2020b)
Chitosan	C800	800	0.1	≈16.0	≈2.00	
	Control	-	0	≈22.0	≈3.00	
Peanut Shells (PS), Hazelnut Shells (HS)	0.025 wt% HS	850	0.025	N/A	3.44±0.20	(Khushnood et al., 2016)
	0.05 wt% HS		0.05		3.91±0.21	
	0.2 wt% HS		0.2		5.44±0.91	
	0.5 wt% HS		0.5		5.19±0.08	
	1.0 wt% HS		1		4.21±0.16	
	0.025 wt% PS	850	0.025		3.15±0.36	
	0.05 wt% PS		0.05		3.88±0.20	
	0.2 wt% PS		0.2		5.43±0.94	
	0.5 wt% PS		0.5		3.61±0.25	
	1.0 wt% PS		1		2.77±0.30	
	Control		0		2.96±0.03	
Sugarcane bagasse	CLA 2B	200	2	N/A	2.77±0.29	(Rodier et al., 2019)
	CLA 4B		4		1.39±0.17	
	CLA 6B		6		2.02±0.28	

Appendix B: Basic Organic Functional Group Chart



Appendix C: Trial Mixes of Biochar Composites

Multiple trials with varying cement quantities and water-to-cement ratios were conducted to achieve adequate consistency, flowability, and the target strength of 25 MPa for both concrete and mortar samples. Table C1 presents the different trial mixes, highlighting the final mix selected for this research. An initial trial mix was adapted from the design sheet provided on the following page. Based on experimental observations during mixing, adjustments were made to improve the consistency and flowability, resulting in a second trial mix, which was tested for 7-day strength. As this mix exhibited low early strength, the cement content was increased, and two additional trial mixes were prepared and evaluated for consistency. The mix exhibiting the desirable consistency, flowability, and strength was selected and used in this study. Similarly, for the mortar mix the cement quantity was further increased and the ratios of water and aggregate were optimised for flowability and consistency.

Table C1. Trial Mixes of Concrete and Mortar control samples.

Mix	Cement	Water	Fine Agg	Coarse Agg	Ratio (C:W:FA:CA)	7 Day Strength
Unit	(kg/m³)					(MPa)
Concrete						
Trial	350	245	580	1175	1:0.57:2.1:2.81	-
Trial	370	210	780	1040	1:0.7:1.66:3.36	11.25
Used	450	250	600	1100	1:0.56:1.33:2.44	20.34
Trial	460	215	650	1075	1:0.47:1.41:2.33	-
Mortar						
Trial	600	270	1200	-	1:0.45:2	18.90
Used	600	309	1200	-	1:0.51:2	19.70

Concrete Mix Trial Design Sheet

Table 1 Concrete mix design form

Job title

Trial Mix

Stage	Item	Reference or calculation	Values		
1	1.1 Characteristic strength	Specified	25 N/mm ² at 2.8 days		
			Proportion defective 5 %		
	1.2 Standard deviation	Fig 3	8 N/mm ² or no data N/mm ²		
	1.3 Margin	C1 or Specified	(k = 1.64) 1.64 × 8 = 13.12 N/mm ²		
	1.4 Target mean strength	C2	25 + 13.12 = 38.12 N/mm ²		
	1.5 Cement type	Specified	OPC/SRPC/RHPC		
	1.6 Aggregate type: coarse Aggregate type: fine		Crushed/uncrushed Crushed/uncrushed		
	1.7 Free-water/cement ratio	Table 2, Fig 4	0.7 0.57		
	1.8 Maximum free-water/cement ratio	Specified	0.7 Use the lower value 0.57		
2	2.1 Slump or Vebe time	Specified	Slump 50 mm or Vebe time s		
	2.2 Maximum aggregate size	Specified	20 mm		
	2.3 Free-water content	Table 3	210 kg/m ³		
3	3.1 Cement content	C3	210 ÷ 0.57 = 370 kg/m ³		
	3.2 Maximum cement content	Specified	kg/m ³		
	3.3 Minimum cement content	Specified	240 kg/m ³		
			use 3.1 if ≤ 3.2 use 3.3 if > 3.1		
	3.4 Modified free-water/cement ratio		370 kg/m ³		
4	4.1 Relative density of aggregate (SSD)		known/assumed		
	4.2 Concrete density	Fig 5	2400 kg/m ³		
	4.3 Total aggregate content	C4	2400 - 210 - 370 = 1820 kg/m ³		
5	5.1 Grading of fine aggregate	Percentage passing 600 µm sieve	35 %		
	5.2 Proportion of fine aggregate	Fig 6	43 %		
	5.3 Fine aggregate content	C5	(43% × 1820) = 780 kg/m ³		
	5.4 Coarse aggregate content		1820 - 780 = 1040 kg/m ³		
Quantities		Cement (kg)	Water (kg or L)	Fine aggregate (kg)	Coarse aggregate (kg) 10 mm 20 mm 40 mm
per m ³ (to nearest 5 kg)		370	210	780	1040
per trial mix of m ³					

Items in *italics* are optional limiting values that may be specified (see Section 7)

1 N/mm² = 1 MN/m² = 1 MPa (see footnote to Section 3).

OPC = ordinary Portland cement; SRPC = sulphate-resisting Portland cement; RHPC = rapid-hardening Portland cement.

Relative density = specific gravity (see footnote to Para 5.4).

SSD = based on a saturated surface-dry basis.

15

Appendix D: Slump Test Results

Figure D.1: Concrete mix with 4% 500°C EFB.



Figure D.2: Concrete mix with 4% 500°C PKS.



Figure D.3: Concrete mix with 4% 409°C PKS.



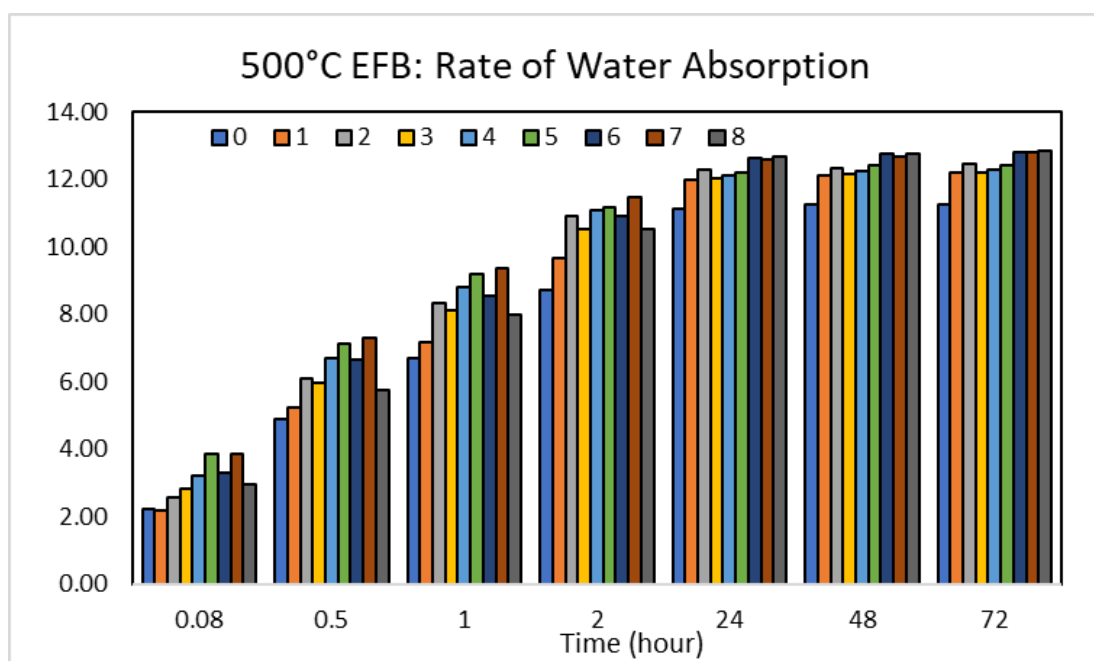
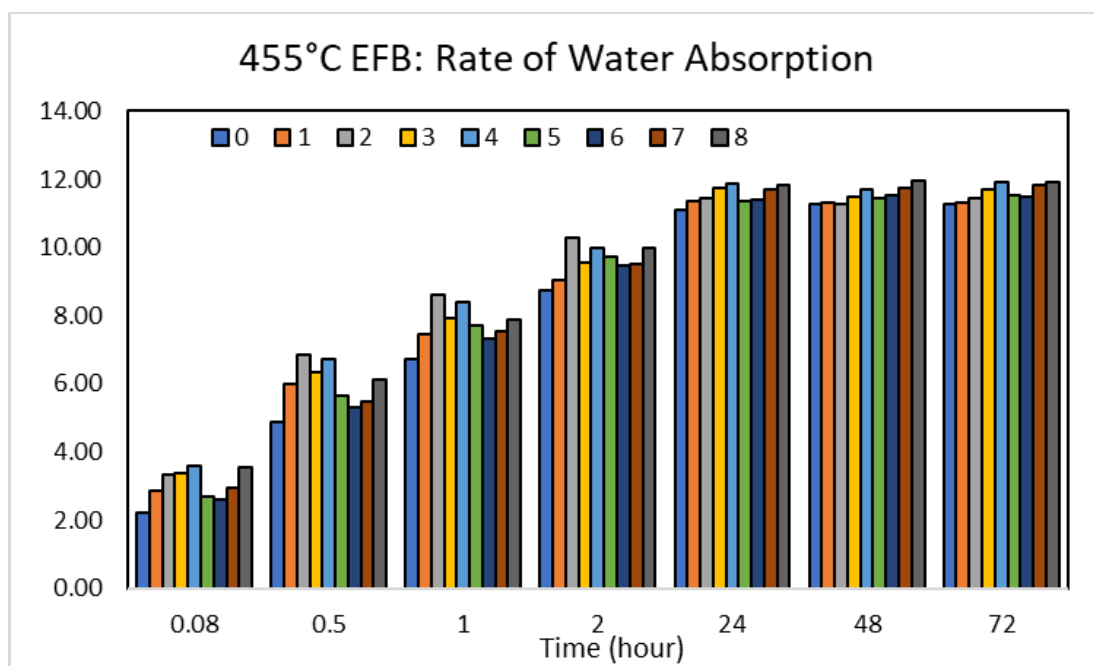
Figure D.4: Concrete mix with 4% 455°C EFB.

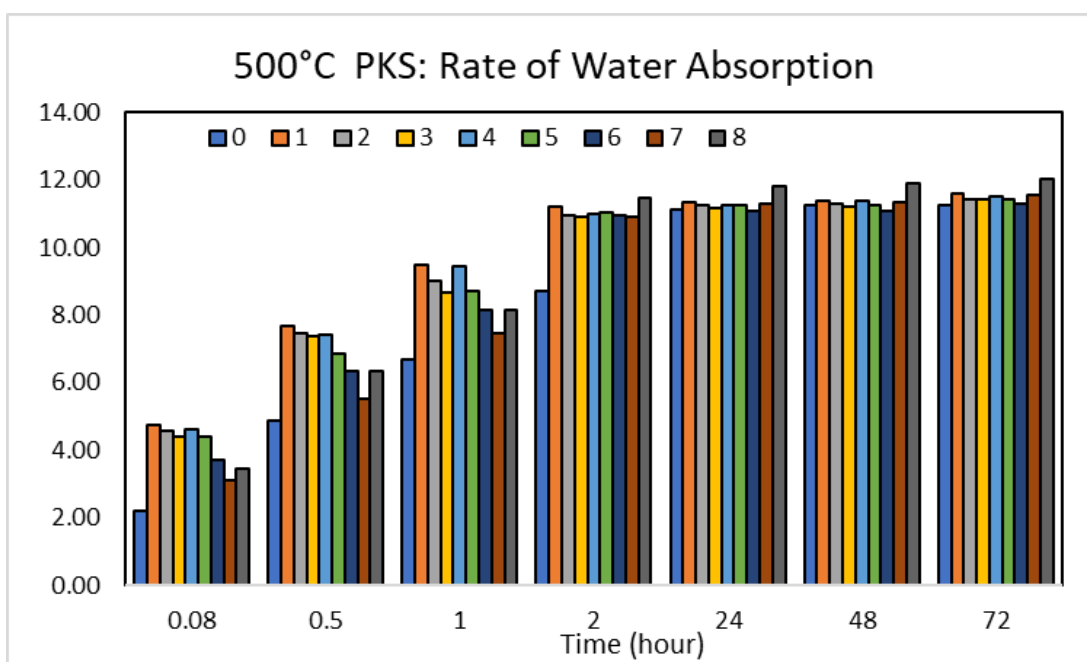
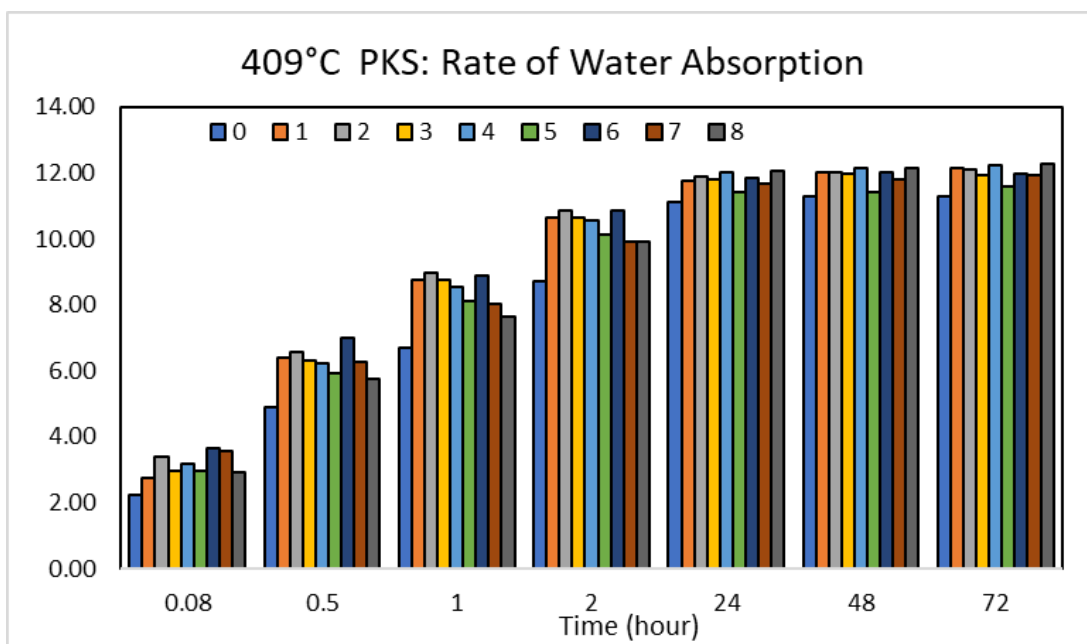


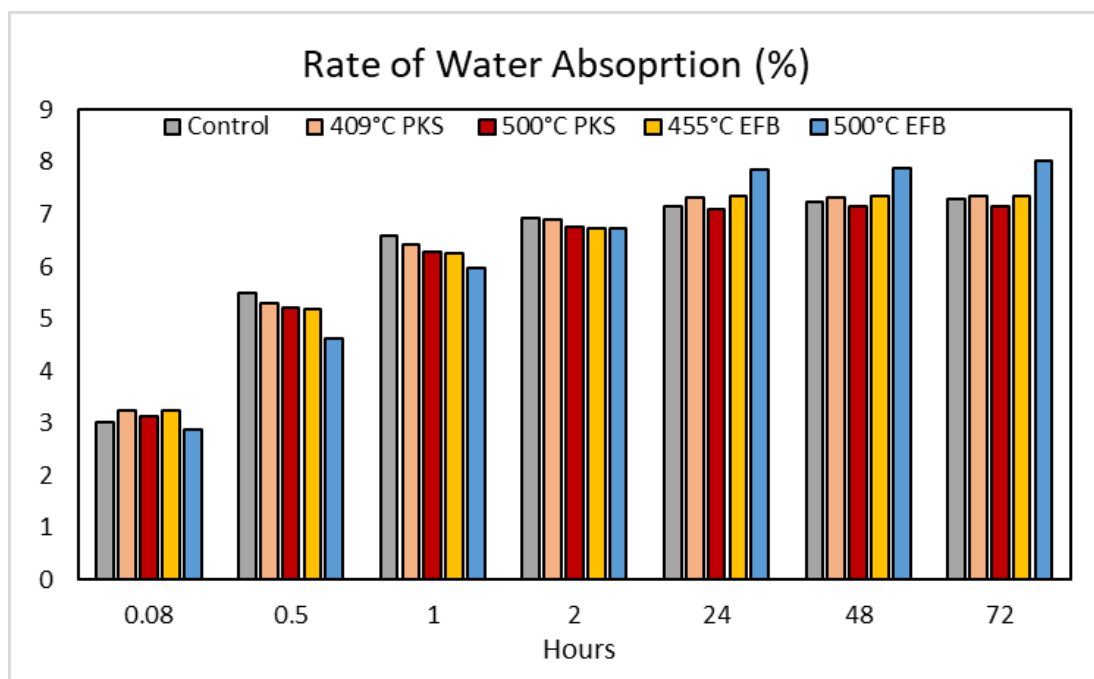
Figure D.5: Control concrete mix.



Appendix E: Water Absorption Results of Biochar Composites

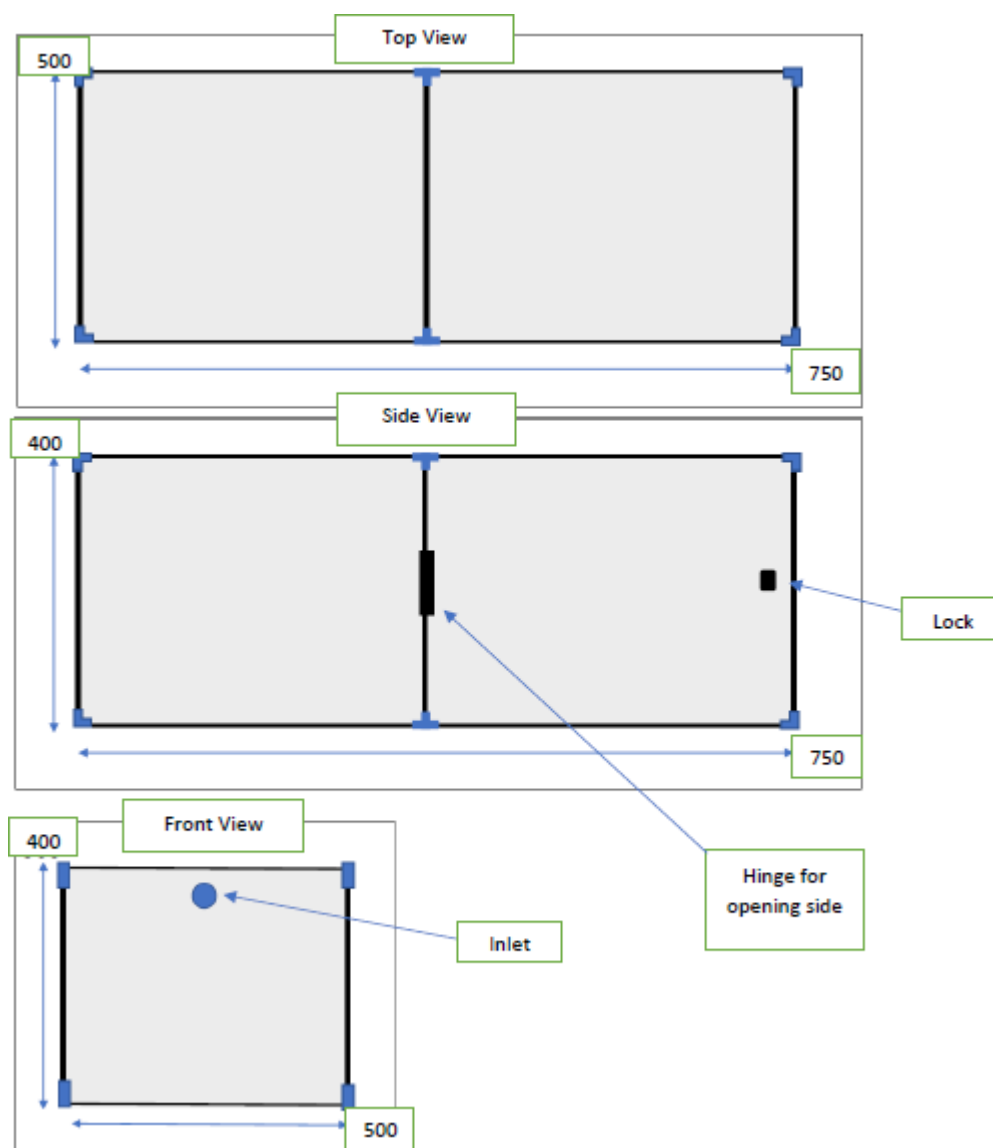






Appendix F: Design of Experimental Set up

Design drawn for out sourcing the making of the sealed box used for carbon sequestering study.



Appendix G: LCA Results

Table G.1 Places taken into consideration for averaging the distance:

Company Name	Address	Label
Palm Oil Mill		
Seri Bandar Palm Oil Mill Sdn Bhd	Jalan Tok Mujir, Kampung Sungai Buaya, 42700 Banting, Selangor	P1
Sime Plantations Sdn Bhd (Tennamaram Palm Oil Mill)	Kilang Kelapa Sawit Tennamaram, K/B No. 211, 45600 Bestari Jaya, Selangor	P2
Tuan Mee Palm Oil Mill	Batu 24, Jln Kuala Selangor, Kepong, 47000 Sungai Buloh, Selangor	P3
LBF OIL PALM SDN BHD	LOT 334 Jalan Kepong, MUKIM, 45600 Batang Berjuntai, Selangor	P4
Sin Huat Hin Palm Oil Mill	Lot 4636, Jalan Kampung Kuantan, 45600 Bestari Jaya, Selangor	P5
Biochar Plant		
Pakar B2E Sdn Bhd-Biochar Manufacturing and Trading	8942, Jalan Telok Gong, Kampung Telok Gong, 42000 Pelabuhan Klang, Selangor	B1
Nasmech Technology Sdn Bhd	No.31-5, Jalan SP 2/1, Serdang Perdana (Seksyen 2), 43300 Seri Kembangan, Selangor	B2
REVOGANIX Sdn Bhd	Biotechnolgy Incubation Centre, Technology Park Malaysia,, Bukit Jalil, 57000 Kuala Lumpur, Wilayah Persekutuan Kuala Lumpur	B3
BIO AGROTECH TRADING	960a, Jalan Besar, Kampung Ulu Chuchoh, 43950 Sungai Pelek, Selangor	B4
Cement Production Plant		
YTL Cement, USJ Plant	207, Jalan Subang 6, Taman Perindustrian Subang, 47500 Subang Jaya, Selangor	C1
Wisma YTL Cement	No. 2, Jalan Kilang 51/206, Pjs 51, 46050 Petaling Jaya, Selangor	C2
Cement Industries of Malaysia Bhd	Cima Cement Depot, Jln. Station, 48050 Kuang, Selangor	C3
Concrete Batching Plant		
MDC Ready Mix Concrete Plant	Jalan Dua, Chan Sow Lin, 55200 Kuala Lumpur, Wilayah Persekutuan Kuala Lumpur	CP1
CEMIX Concrete Malaysia	17, Jalan Tiga, Chan Sow Lin, 55200 Kuala Lumpur, Wilayah Persekutuan Kuala Lumpur	CP2

Buildcon Concrete Sdn Bhd - Sungai Buloh Plant	1558, Jalan Kusta, Kawasan Industri Kampung Jaya, 47000 Sungai Buloh, Selangor	CP3
Hanson Balakong Plant	Jalan Perindustrian Balakong, Taman Balakong Jaya, 43000 Seri Kembangan, Selangor	CP4
Lafarge Concrete Chan Sow Lin Plant	18, Jalan Empat, Chan Sow Lin, 55200 Kuala Lumpur, Wilayah Persekutuan Kuala Lumpur	CP5
Landfill		
Tanjung Dua Belas Sanitary Landfill	Tanjung Duabelas Sanitary Landfill, Mukim Tg. Duabelas, Selangor	L1
JK Waste Disposal sdn bhd	No 2-2C Jalan ppk1 taman kinara puchong Selangor Puchong, 47100 Subang Jaya, Selangor	L2
Kuala Lumpur Transfer Station (Taman Beringin)	52000 Kuala Lumpur, Federal Territory of Kuala Lumpur	L3
Kuang Inert Waste Landfill	Kuang Inert Waste Landfill, Mukim, 48050 Kuang, Selangor	L4

Table G.2 Average Distances

From	To	Distance (km)
Cement – Concrete		
C1	CP1	27.6
	CP2	22.9
	CP3	26.3
	CP4	31
	CP5	22.5
C2	CP1	13.7
	CP2	13.7
	CP3	23.8
	CP4	24.1
	CP5	31.3
C3	CP1	34.4
	CP2	35.2
	CP3	4.7
	CP4	64.6
	CP5	34.9
	Avg	27.4
Palm Oil to Landfill		
P1	L1	40.4
	L2	45.8
	L3	67.9
	L4	75.1
P2	L1	98.1
	L2	65.9
	L3	57.6
	L4	33.6
P3	L1	81.6

	L2	49.9
	L3	41.1
	L4	20.1
P4	L1	99.8
	L2	58.2
	L3	49.4
	L4	28.4
P5	L1	115
	L2	72.8
	L3	64
	L4	43
	Avg	60.4
Palm Oil Mill- Biochar		
P1	B1	26.3
	B2	52.4
	B3	50.1
	B4	50.4
P2	B1	81.0
	B2	76.6
	B3	73.3
	B4	115
P3	B1	58.2
	B2	60.1
	B3	56.7
	B4	98.5
P4	B1	67.1
	B2	68.4
	B3	65
	B4	117
P5	B1	72.5
	B2	83
	B3	86
	B4	131
	Avg	75.2
Biochar Plant -Concrete Plant		
B1	CP1	47.1
	CP2	47.3
	CP3	49.9
	CP4	50.6
	CP5	47.0
B2	CP1	14.4
	CP2	14.4
	CP3	37.1
	CP4	5.8
	CP5	14.2
B3	CP1	13
	CP2	13.2
	CP3	35.3
	CP4	11
	CP5	12.9
B4	CP1	80.9
	CP2	74.4
	CP3	92.5

	CP4	60.1
	CP5	80.7
	Avg	40.1

Google maps

LCA

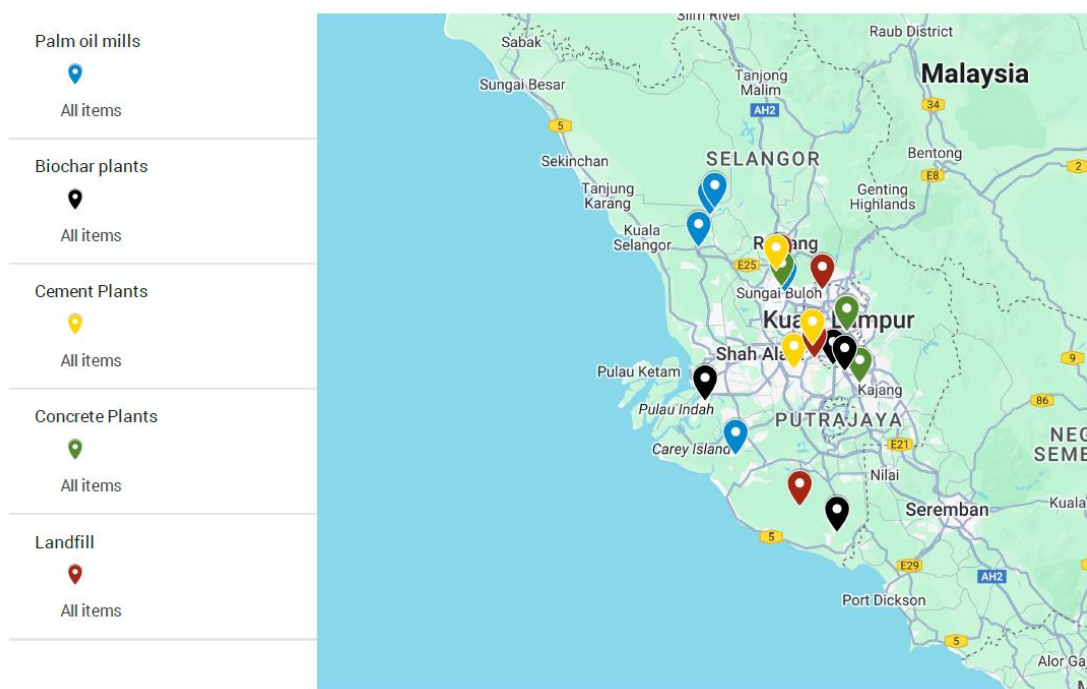


Table G. 3 Environmental Impact Category for Concrete Production Processes

Concrete						
Process		100% Cement	Concrete Batching	Coarse Aggregate	Fine Aggregate	Landfill Control
Impact category	Unit					
Abiotic depletion	kg Sb eq	7.28E-04		1.13E-04	4.12E-05	
Acidification	kg SO ₂ eq	1.31E-02	6.61E+00	2.24E-05	8.75E-06	1.71E+04
Eutrophication	kg PO ₄ --- eq	3.39E-03	1.72E+00	1.72E-06	6.47E-07	4.45E+03
Fresh water aquatic ecotox.	kg 1,4-DB eq					4.80E+01
Global warming (GWP100)	kg CO ₂ eq	5.13E-01	5.72E+03	4.72E-03	1.51E-03	7.90E+06
Human toxicity	kg 1,4-DB eq	3.18E-02	2.70E+01	4.06E-05	1.93E-05	4.24E+04
Marine aquatic ecotoxicity	kg 1,4-DB eq					5.38E+06
Photochemical oxidation	kg C ₂ H ₄ eq	3.94E-06	2.21E-02	1.05E-06	3.98E-07	9.32E+02
Terrestrial ecotoxicity	kg 1,4-DB eq					3.05E-02

Table G.4

Concrete						
Process		96% Cement	Pyrolysis PKS409	Landfill PKS409	Pyrolysis EFB455	Landfill EEB455
Impact category	Unit					
Abiotic depletion	kg Sb eq	6.99E-04	5.48E-08		6.25E-08	
Acidification	kg SO2 eq	1.25E-02	6.29E-04	1.33E+04	7.98E-04	1.31E+04
Eutrophication	kg PO4--- eq	3.26E-03	5.98E-05	3.46E+03	6.84E-05	3.40E+03
Fresh water aquatic ecotox.	kg 1,4-DB eq		5.94E-07	3.74E+01	6.87E-07	3.67E+01
Global warming (GWP100)	kg CO2 eq	4.93E-01	1.02E+02	6.15E+06	1.25E+02	6.04E+06
Human toxicity	kg 1,4-DB eq	3.06E-02	2.11E-03	3.30E+04	2.45E-03	3.25E+04
Marine aquatic ecotoxicity	kg 1,4-DB eq		1.47E-05	4.19E+06	1.70E-05	4.12E+06
Photochemical oxidation	kg C2H4 eq	3.78E-06	2.64E-02	7.25E+02	3.24E-02	7.12E+02
Terrestrial ecotoxicity	kg 1,4-DB eq		3.53E-09	2.37E-02	4.08E-09	2.34E-02

Table G.5

Concrete					
Process		Pyrolysis EFB500	Landfill EFB500	Pyrolysis PKS500	Landfill PKS500
Impact category	Unit				
Abiotic depletion	kg Sb eq	6.06E-08		5.29E-08	
Acidification	kg SO2 eq	8.25E-04	1.24E+04	6.50E-04	1.25E+04
Eutrophication	kg PO4--- eq	7.27E-05	3.22E+03	6.30E-05	3.26E+03
Fresh water aquatic ecotox.	Kg 1,4-DB eq	7.21E-07	3.48E+01	6.19E-07	3.52E+01
Global warming (GWP100)	kg CO2 eq	1.25E+02	5.72E+06	1.02E+02	5.79E+06
Human toxicity	kg 1,4-DB eq	2.57E-03	3.07E+04	2.20E-03	3.11E+04
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.79E-05	3.90E+06	1.53E-05	3.95E+06
Photochemical oxidation	kg C2H4 eq	3.24E-02	6.74E+02	2.64E-02	6.83E+02
Terrestrial ecotoxicity	kg 1,4-DB eq	4.28E-09	2.21E-02	3.67E-09	2.24E-02

Table G.6

Concrete					
Process		Transport B-CP	Transport C-CP	Transport P-B	Transport P-L
Impact category	Unit				
Abiotic depletion	kg Sb eq				
Acidification	kg SO2 eq	1.57E+00	7.31E-01	5.51E+00	3.55E+00
Eutrophication	kg PO4--- eq	4.07E-01	1.90E-01	1.43E+00	9.23E-01

Fresh water aquatic ecotox.	kg 1,4-DB eq				
Global warming (GWP100)	kg CO2 eq	3.89E+02	1.82E+02	1.37E+03	8.83E+02
Human toxicity	kg 1,4-DB eq	4.01E+00	1.87E+00	1.41E+01	9.09E+00
Marine aquatic ecotoxicity	kg 1,4-DB eq				
Photochemical oxidation	kg C2H4 eq	4.18E-02	1.95E-02	1.47E-01	9.48E-02
Terrestrial ecotoxicity	kg 1,4-DB eq				

Table G.7 Sum of all processes in each scenario.

Concrete			P5	p4	E4	E5
		SC1	SC2	SC3	SC4	SC5
Impact category	Unit					
Abiotic depletion	kg Sb eq	8.82E-04	8.53E-04	8.53E-04	8.53E-04	8.53E-04
Acidification	kg SO2 eq	7.61E+03	3.06E+03	3.82E+03	3.60E+03	2.90E+03
Eutrophication	kg PO4--- eq	1.98E+03	7.95E+02	9.93E+02	9.36E+02	7.54E+02
Fresh water aquatic ecotox.	kg 1,4-DB eq	2.13E+01	8.54E+00	1.07E+01	1.01E+01	8.09E+00
Global warming (GWP100)	kg CO2 eq	3.52E+06	1.41E+06	1.76E+06	1.66E+06	1.34E+06
Human toxicity	kg 1,4-DB eq	1.89E+04	7.60E+03	9.49E+03	8.94E+03	7.20E+03
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.39E+06	9.57E+05	1.20E+06	1.13E+06	9.07E+05
Photochemical oxidation	kg C2H4 eq	4.14E+02	1.66E+02	2.07E+02	1.95E+02	1.57E+02
Terrestrial ecotoxicity	kg 1,4-DB eq	1.36E-02	5.43E-03	6.79E-03	6.39E-03	5.14E-03

Table G.8 Environmental Impact Category for Mortar Production Processes

Mortar		100% Cement	96% Cement	Fine Aggregate	Pyrolysis PKS409
Impact category	Unit				
Abiotic depletion	kg Sb eq	9.70E-04	9.31E-04	8.23E-05	7.31E-08
Acidification	kg SO2 eq	1.74E-02	1.67E-02	1.75E-05	8.39E-04
Eutrophication	kg PO4--- eq	4.52E-03	4.34E-03	1.29E-06	7.97E-05
Fresh water aquatic ecotox.	kg 1,4-DB eq				7.93E-07
Global warming (GWP100)	kg CO2 eq	6.84E-01	6.57E-01	3.02E-03	9.93E+01
Human toxicity	kg 1,4-DB eq	4.24E-02	4.08E-02	3.85E-05	2.82E-03
Marine aquatic ecotoxicity	kg 1,4-DB eq				1.96E-05
Photochemical oxidation	kg C2H4 eq	5.26E-06	5.05E-06	7.97E-07	2.58E-02
Terrestrial ecotoxicity	kg 1,4-DB eq				4.70E-09

Table G.9

Mortar		Pyrolysis EFB455	Pyrolysis EFB500	Pyrolysis PKS500
Impact category	Unit			
Abiotic depletion	kg Sb eq	8.33E-08	8.07E-08	7.05E-08
Acidification	kg SO2 eq	1.06E-03	1.10E-03	8.66E-04
Eutrophication	kg PO4--- eq	9.12E-05	9.70E-05	8.40E-05
Fresh water aquatic ecotox.	kg 1,4-DB eq	9.16E-07	9.62E-07	8.26E-07
Global warming (GWP100)	kg CO2 eq	1.22E+02	1.22E+02	9.93E+01
Human toxicity	kg 1,4-DB eq	3.27E-03	3.42E-03	2.93E-03
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.27E-05	2.38E-05	2.04E-05
Photochemical oxidation	kg C2H4 eq	3.18E-02	3.18E-02	2.58E-02
Terrestrial ecotoxicity	kg 1,4-DB eq	5.43E-09	5.70E-09	4.896E-09

Table G.10

Mortar		Landfill Control	Landfill E500	Landfill E455	Landfill P409	Landfill P500
Impact category	Unit					
Abiotic depletion	kg Sb eq					
Acidification	kg SO2 eq	7.60E+03	1.31E+03	2.23E+03	2.53E+03	1.52E+03
Eutrophication	kg PO4--- eq	1.98E+03	3.40E+02	5.81E+02	6.58E+02	3.95E+02
Fresh water aquatic ecotox.	kg 1,4-DB eq	2.13E+01	3.67E+00	6.28E+00	7.11E+00	4.27E+00
Global warming (GWP100)	kg CO2 eq	3.51E+06	6.04E+05	1.03E+06	1.17E+06	7.02E+05
Human toxicity	kg 1,4-DB eq	1.89E+04	3.24E+03	5.54E+03	6.28E+03	3.77E+03
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.39E+06	4.11E+05	7.03E+05	7.97E+05	4.78E+05
Photochemical oxidation	kg C2H4 eq	4.14E+02	7.12E+01	1.22E+02	1.38E+02	8.28E+01
Terrestrial ecotoxicity	kg 1,4-DB eq	1.36E-02	2.33E-03	3.99E-03	4.52E-03	2.71E-03

Table G.11 Sum of all processes in each scenario.

Mortar			P5	P4	E4	E5
		SM1	SM2	SM3	SM4	SM5
Impact category	Unit					
Abiotic depletion	kg Sb eq	1.05E-03	1.01E-03	1.01E-03	1.01E-03	1.01E-03
Acidification	kg SO2 eq	7.60E+03	1.52E+03	2.53E+03	2.23E+03	1.31E+03
Eutrophication	kg PO4--- eq	1.98E+03	3.95E+02	6.58E+02	5.81E+02	3.40E+02
Fresh water aquatic ecotox.	kg 1,4-DB eq	2.13E+01	4.27E+00	7.11E+00	6.28E+00	3.67E+00
Global warming (GWP100)	kg CO2 eq	3.51E+06	7.02E+05	1.17E+06	1.03E+06	6.04E+05
Human toxicity	kg 1,4-DB eq	1.89E+04	3.77E+03	6.28E+03	5.54E+03	3.24E+03
Marine aquatic ecotoxicity	kg 1,4-DB eq	2.39E+06	4.78E+05	7.97E+05	7.03E+05	4.11E+05
Ozone layer depletion (ODP)	kg CFC-11 eq	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Photochemical oxidation	kg C2H4 eq	4.14E+02	8.28E+01	1.38E+02	1.22E+02	7.12E+01
Terrestrial ecotoxicity	kg 1,4-DB eq	1.36E-02	2.71E-03	4.52E-03	3.99E-03	2.33E-03