

Valorisation of e-waste by means of direct liquefaction

D Swanepoel

 **[orcid.org/ 0000-0001-6971-9054](https://orcid.org/0000-0001-6971-9054)**

Dissertation accepted in fulfilment of the requirements for the degree *Master of Engineering Chemical Engineering* at the North-West University

Supervisor:	Dr RJ Venter
Co-supervisor:	Prof FB Waanders
Co-supervisor	Prof S Marx

Graduation:	April 2024
-------------	------------

ABSTRACT

Global E-waste generation has increased rapidly in recent decades owing to a decrease in the lifespan of electronic equipment and an exponential increase in supply and demand. Due to inadequate treatment and disposal practices, the majority of e-waste is landfilled, polluting the air, soil, and water. E-waste can be a valuable source of secondary materials, with most end-processing methods aimed at recovering the valuable metals. However, many of these procedures are not feasible without government support and cause secondary pollution in the form of pollutants released by emissions and effluents. Furthermore, the presence of organic components and low metal concentrations in end-products impedes economic viability. As a result, there is a need to investigate novel end-processing routes that can overcome the drawbacks of present technologies and lead to a more environmentally friendly and economically viable treatment method for e-waste. One such novel route is the thermochemical depolymerisation process known as hydrothermal liquefaction or direct liquefaction. The potential depolymerisation and conversion of organic fractions into other valuable organics, as well as the potential immobilisation of metals through co-processing with lignocellulosic biomass, could result in liquefaction becoming a promising option for e-waste valorisation and end-stage treatment. This study aimed to determine the suitability of direct liquefaction as a treatment method for locally obtained printed circuit board (PCB) e-waste co-processed with lignosulphonate biomass.

The aim was achieved by studying the effect of hydrothermal liquefaction process conditions while co-processing PCB e-waste with lignosulphonate biomass in an SS-316 batch reactor. The effect of liquefaction temperature (250-330°C), residence time (20-80 min), and waste loading (0-100 wt.% of feed) was studied by analysing the recovery of metals and formation of organic compounds in the residues, and aqueous phases obtained from processing. The intertwining effect of residence time and temperature on the product yields was determined through calculated severity factors. The formation of organics was established by elemental analysis, proximate analysis, total phenolic analysis, Fourier-transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC), and Gas Chromatography-Mass Spectrometry (GC-MS). Metal recovery was determined through the digestion of reactor products, followed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine the concentration of metals and mineral elements.

This study found low yields of bio-oils at all process conditions, however, the oils mostly consisted of phenolic compounds. Residue products consisted of inorganics, such as ceramics and metals, as well as unreacted epoxy resin and heavy carbon molecules. Temperature influenced the yields and composition of products more than residence time. Generally, longer residence times mostly

affected the products by allowing HTL reactions to progress, whereas temperature heavily influenced the rate of these reactions. Both the bio-oil yield and the phenolic content increase with increasing temperature and reached a turning point as the rate of cracking reactions overtook the recombination. At 250°C, longer residence times increased the bio-oil and residue yields, however at 330°C a dynamic equilibrium between decomposition and repolymerisation reactions was reached. Furthermore, at lower temperatures, longer residence times increased the phenolic content of bio-oils. The optimum conditions for bio-oil production were determined as 300°C for 80 min.

Nearly all of the metals remained in a stable state within the residues, with only small concentrations detected in the bio-oils and aqueous phases after HTL. It was concluded that the migration from the residues was in relation to the initial concentration of each metal in the feedstock. Both temperature and residence time produced mostly inconsistent trends. At both short and long residence times, several metals (Au, Cu, Fe, Ni, Sn and Zn) showed high concentrations in the residues at 250°C, as a result of the slow decomposition rate of the waste PCBs. However, as the temperature increased, an initial decrease in concentration was noted as more metals were released, after which the concentrations slightly increased, possibly due to the adsorption from the biochar structures. Longer residence times at 250°C decreased most of the metal concentrations, however, no conclusive trends were seen at other temperatures.

It was observed that increasing the waste loading increased both the bio-oil and residue yields. The carbon content of the residues decreased from 49 wt.% at 0 wt.% PCB loading to 5 wt.% at a 100 wt.% PCB loading, confirming that almost all of the organic epoxy resin was depolymerised by HTL. Furthermore, the phenolic content of the bio-oils increased from 6 to 93 area%, confirming that the epoxy resin was primarily depolymerised and recombined into useful phenolic compounds. Increasing the waste loadings resulted in a non-linear increase for most metal concentrations, with the metal concentrations in the residues at 90 and 100 wt.% waste loadings being significantly higher than the original feedstock concentrations, with less than 6 wt.% carbon.

This study revealed that hydrothermal liquefaction is an effective treatment approach for waste PCBs by confirming the organics in waste PCBs transform to valuable phenolic compounds while the majority of metals remain stable during processing, resulting in the production of metal-rich residues.

Keywords: E-waste, Hydrothermal liquefaction, PCB, Recovery, Valorisation

DECLARATION

I, Dian Swanepoel, hereby declare that I am the sole author of this dissertation entitled:

Valorisation of e-waste by means of direct liquefaction

Potchefstroom

November 2023

Dian Swanepoel

The original text was edited by a recognised and experienced freelance language editing practitioner (specialising in scientific texts).

Dr Margie J Hurndall

PhD (Polymer science, SU); Dipl Translation, Afr/Eng, cum laude (UNISA)

ACKNOWLEDGEMENTS

The author would like to acknowledge the following people for their support, insights, and guidance:

- Prof. Sanette Marx for accepting me as a master's student. Her extensive knowledge and experience were vital towards the research topic.
- Dr. Roelf Venter for his insightful guidance, knowledge, and supervision. His contributions were vital to the completion of this study.
- Prof. Frans Waanders for his assistance in completing this dissertation.
- My parents, Andre Swanepoel and Mari Swanepoel, for their support and belief in me.
- Mr. Jan Kroeze for his expertise and technical support in the design and maintenance of the experimental setup.
- Mrs. Rene Bekker for her continuing support and knowledge throughout all experimental phases.
- Frans Roodt, for his assistance in preparing samples for GPC analysis.
- The staff at the North-west University School of Chemical and Minerals Engineering.
- The North-West University for financial support throughout the course of this study.

TABLE OF CONTENTS

ABSTRACT	I
DECLARATION.....	III
ACKNOWLEDGEMENTS.....	IV
TABLE OF CONTENTS	V
LIST OF TABLES.....	XII
LIST OF FIGURES	XVI
LIST OF ABBREVIATIONS.....	XIX
 CHAPTER 1	 1
INTRODUCTION	1
1.1 General.....	1
1.2 Background and motivation	1
1.3 Problem statement.....	5
1.4 Aim	6
1.5 Objectives.....	6
1.6 Scope of study	6
1.7 Outline of dissertation	7
 CHAPTER 2	 9
LITERATURE REVIEW	9
2.1 Introduction	9
2.2 Electrical waste	10
2.2.1 Categorisation and legislation	10
2.2.2 Characterisation of e-waste and PCBs.....	12
2.3 Recycling methods for waste PCBs	17
2.3.1 Mechanical separation	18

2.3.2	Bio-metallurgy	18
2.3.3	Hydrometallurgy	19
2.3.4	Pyrometallurgy	19
2.4	HTL.....	20
2.4.1	HTL feedstocks	21
2.4.1.1	Lignocellulosic biomass and lignosulphonate	21
2.4.1.2	Waste materials	22
2.4.1.3	Microalgae	23
2.4.2	HTL products	23
2.4.2.1	Biocrude-oil	23
2.4.2.2	Biochar and residue	24
2.4.2.3	Aqueous phase	25
2.4.2.4	Gas	25
2.4.3	HTL reaction mechanisms.....	26
2.4.3.1	Reaction mechanism for biomass and lignin	26
2.4.3.2	Reaction mechanism for PCB epoxy resin	27
2.4.4	HTL operating parameters	29
2.4.4.1	Temperature	29
2.4.4.2	Residence time	30
2.4.4.3	Liquid-to-solid ratio.....	30
2.4.4.4	Pressure.....	31
2.4.4.5	Heating rate	31
2.5	Severity factor	32
2.6	Hydrothermal treatment of non-metallic PCB fractions	32
2.7	Metal recovery through hydrothermal treatment	33
2.8	Metal sorption.....	35
2.8.1	Chemical speciation of metals.....	35
2.8.2	Biochar adsorption	36

2.8.3	Mechanisms for metal sorption.....	37
2.9	Conclusion	38
CHAPTER 3		40
MATERIALS AND METHODS.....		40
3.1	Introduction	40
3.2	Materials	40
3.2.1	Raw materials	40
3.2.2	Chemicals and gases	41
3.3	Experimental sets	42
3.4	Experimental methods.....	43
3.4.1	HTL	43
3.4.1.1	Experimental setup	43
3.4.1.2	Reactor preparation	45
3.4.1.3	Sleeve loading.....	45
3.4.1.4	Experimental procedure	45
3.4.1.5	Product separation and recovery.....	46
3.4.2	Metal recovery.....	46
3.5	Analytical methods	47
3.5.1	Product yields	47
3.5.2	Severity analysis	48
3.5.3	Compositional analyses	48
3.5.3.1	Elemental analysis	48
3.5.3.2	Proximate analysis	49
3.5.3.3	HHV analysis	49
3.5.3.4	Total phenolic content analysis	49
3.5.3.5	GC-MS analysis	50
3.5.3.6	GPC analysis	50

3.5.3.7	FTIR analysis	51
3.5.3.8	ICP-OES analysis	51
3.5.3.9	XRF analysis	52
CHAPTER 4		53
RESULTS AND DISCUSSION		53
4.1	Introduction	53
4.2	Characterisation of waste PCBs and lignosulphonate	53
4.2.1	Elemental composition	53
4.2.2	Proximate composition	54
4.2.3	FTIR analysis	55
4.2.4	Metal composition	56
4.3	Effect of operating parameters on product yields	58
4.3.1	Reaction temperature	60
4.3.2	Residence time	62
4.3.3	Waste loading	64
4.4	Effects of operating parameters on the chemical properties of products ..	65
4.4.1	Reaction temperature	65
4.4.1.1	Elemental composition	65
4.4.1.2	Energy content	67
4.4.1.3	Proximate composition	68
4.4.1.4	Molecular weight and PDI	68
4.4.2	Residence time	70
4.4.2.1	Elemental composition	70
4.4.2.2	Energy content	71
4.4.2.3	Proximate composition	71
4.4.2.4	Molecular weight and PDI	72
4.4.3	Waste loading	73

4.4.3.1	Elemental composition	73
4.4.3.2	Energy content.....	75
4.4.3.3	Proximate composition	75
4.4.3.4	Molecular weight and PDI	76
4.5	Effect of operating parameters on the organic compounds in products	77
4.5.1	Reaction temperature.....	77
4.5.1.1	Water-soluble phenolic compounds.....	77
4.5.1.2	Functional groups of bio-oils and residues	78
4.5.1.3	Compounds in bio-oils.....	82
4.5.2	Residence time	84
4.5.2.1	Water-soluble phenolic compounds.....	84
4.5.2.2	Functional groups of bio-oils and residues	85
4.5.2.3	Compounds in bio-oils.....	87
4.5.3	Waste loading	88
4.5.3.1	Water-soluble phenolic compounds.....	88
4.5.3.2	Functional groups of bio-oils and residues	89
4.5.3.3	Compounds in bio-oils.....	91
4.6	Effect of operating parameters on the metal recovery	93
4.6.1	Reaction temperature.....	93
4.6.2	Residence time	99
4.6.3	Waste loading	103
4.7	Summary of results.....	106
CHAPTER 5		107
CONCLUSIONS AND RECOMMENDATIONS		107
5.1	Introduction	107
5.2	Conclusion	107
5.3	Limitations and recommendations	109

REFERENCES	111
 APPENDIX A: ADDITIONAL DATA	 125
A.1 Temperature profiles for HTL experiments.....	125
A.2 Pressure profiles for HTL experiments.....	127
A.3 HTL product yields	129
A.4 Severity factors	130
A.5 Elemental analysis	131
A.6 Energy content	133
A.7 Proximate analysis.....	135
A.8 GPC analysis	136
A.9 FTIR analysis	136
A.10 GC-MS analysis	139
A.11 Total phenolic analysis	141
A.12 ICP-OES analysis.....	141
 APPENDIX B: ADDITIONAL INFORMATION	 147
B.1 Hazardous materials in e-waste	147
B.2 Metal content in waste PCBs and metal ores	148
B.3 Molecular structure of lignin	148
B.4 Calibration curve for total phenolic analysis.....	149
B.5 List of metals detected by ICP-OES analysis	149
B.6 FTIR spectrum functional group ranges.....	150
APPENDIX C: EXPERIMENTAL ERRORS.....	151
C.1 Experimental error calculations	151
C.2 Experimental errors of product yields	152
C.3 Experimental errors of elemental analysis	152
C.4 Experimental errors of proximate analysis.....	153

C.5 Experimental errors of HHV	154
C.6 Experimental errors of GPC analysis.....	154
C.7 Experimental errors of total phenolic analysis.....	155
C.8 Experimental errors of GC-MS analysis.....	155
C.9 Experimental errors of ICP-OES analysis.....	155

LIST OF TABLES

Table 2-1: Categorisation of EEE adopted by the EU-WEEE directives (adapted from Forti <i>et al.</i> , 2018, 2020; Mihai <i>et al.</i> , 2019).....	11
Table 2-2: The composition of plastics, ceramics, and metals in waste PCBs as reported in several studies (adapted from Duan <i>et al.</i> , 2011; Kaya, 2016)	15
Table 3-1: Materials used during HTL and product recovery	41
Table 3-2: Materials used during product preparation for compositional analyses.....	42
Table 3-3: Compositional analyses for the characterisation of feedstocks.....	42
Table 3-4: Analyses of HTL products	43
Table 3-5: Combined severity factors for temperatures and residence times used in this study	48
Table 4-1: Elemental analysis of lignosulphonate, sieved waste PCB, and milled waste PCB feedstock	53
Table 4-2: Proximate analysis of lignosulphonate, sieved waste PCB, and milled waste PCB feedstock	54
Table 4-3: ICP-OES concentrations of metals in sieved waste PCB and lignosulphonate feedstock.....	57
Table 4-4: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C	66
Table 4-5: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C	67
Table 4-6: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C	68
Table 4-7: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C	69
Table 4-8: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min.....	70
Table 4-9: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min	71
Table 4-10: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min	72
Table 4-11: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min	72

Table 4-12: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %.....	74
Table 4-13: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %.....	75
Table 4-14: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %	76
Table 4-15: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %	77
Table 4-16: Total phenol analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C	78
Table 4-17: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C.....	83
Table 4-18: Total phenolic analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min.....	84
Table 4-19: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min	87
Table 4-20: Total phenolic analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %.....	89
Table 4-21: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %	92
Table 4-22: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C	94
Table 4-23: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C.....	96
Table 4-24: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C	98
Table 4-25: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min.....	99
Table 4-26: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min.....	100
Table 4-27: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min	102
Table 4-28: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt. %	103

Table 4-29: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%	104
Table 4-30: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%.....	105
Table 5-1: Product mass yields for HTL experiments at all operating temperatures and residence times	129
Table 5-2: Product mass yields for HTL experiments at all waste PCB mass loadings.....	129
Table 5-3: Elemental analysis of bio-oils and residues at all temperatures and residence times .	132
Table 5-4: HHV of bio-oils at all temperatures and residence times	134
Table 5-5: Proximate analysis of residues at all temperatures and residence times	135
Table 5-6: GPC analysis of bio-oils at all temperatures and residence times	136
Table 5-7: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min	139
Table 5-8: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C.....	140
Table 5-9: Total phenolic analysis of aqueous phases at all temperatures and residence times .	141
Table 5-10: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min.....	142
Table 5-11: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C.....	142
Table 5-12: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min.....	143
Table 5-13: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C	144
Table 5-14: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min	144
Table 5-15: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C	145
Table 5-16: ICP-OES and XRF analysis of sieved waste PCBs	146
Table 5-17: List of potentially hazardous materials and elements in e-waste with examples of EEE, sources, and routes to human exposure (adapted from Perkins <i>et al.</i> , 2014)	147
Table 5-18: Metal contents of ores compared to the waste PCBs (adapted from Bizzo <i>et al.</i> , 2014)	148
Table 5-19: List of categories and elements analysed by ICP-OES	149

Table 5-20: Notations, wavenumbers, and functional groups used for the assignment of FTIR spectrum peaks	150
Table 5-21: Experimental errors on HTL product yields	152
Table 5-22: Experimental errors for the elemental analysis on bio-oils.....	152
Table 5-23: Experimental errors for the elemental analysis on residues.....	152
Table 5-24: Experimental errors for the elemental analysis on milled waste PCB feedstock	152
Table 5-25: Experimental errors for the elemental analysis on sieved waste PCB feedstock	153
Table 5-26: Experimental errors for the elemental analysis on lignosulphonate feedstock	153
Table 5-27: Experimental errors for the proximate analysis on residues	153
Table 5-28: Experimental errors for the proximate analysis on milled waste PCB feedstock	153
Table 5-29: Experimental errors for the proximate analysis on sieved waste PCB feedstock	154
Table 5-30: Experimental errors for the proximate analysis on lignosulphonate feedstock	154
Table 5-31: Experimental error for the HHV on bio-oils	154
Table 5-32: Experimental errors for the GPC analysis on bio-oils	154
Table 5-33: Experimental error for the total phenolic analysis on Aqueous phases	155
Table 5-34: Experimental error for the GC-MS analysis on bio-oils	155
Table 5-35: Experimental error for the ICP-OES analysis on residues	155
Table 5-36: Experimental error for the ICP-OES analysis on bio-oils	156
Table 5-37: Experimental error for the ICP-OES analysis on aqueous phases.....	156
Table 5-38: Experimental error for the ICP-OES analysis on sieved waste PCB feedstock.....	157
Table 5-39: Experimental error for the ICP-OES analysis on lignosulphonate feedstock.....	158

LIST OF FIGURES

Figure 1-1: Energy savings from recycled materials present in e-waste compared to virgin material production (adapted from Cui & Forssberg, 2003).....	3
Figure 2-1: Composition and common materials found in waste PCBs (adapted from Chauhan <i>et al.</i> , 2018; Kaya, 2016).....	14
Figure 2-2: Condensation reaction of epichlorohydrin and BPA to form DGEBA epoxy resin	16
Figure 2-3: Polymerisation reaction between DGEBA epoxy resin and TBBPA to produce a fire retarded epoxy resin	17
Figure 2-4: Molecular structure of the three main monolignols present in lignin: A) sinapyl alcohol, B) coniferyl alcohol and C) <i>p</i> -courmaryl alcohol (adapted from Kumar <i>et al.</i> , 2020)	21
Figure 2-5: The partial chemical structure of sodium lignosulphonate produced via the sodium sulphite pulping process (reused from Megiatto <i>et al.</i> (2016) with permission from Elsevier, obtained through RightsLink)	22
Figure 2-6: Basic reaction scheme for the decomposition of lignin through hydrolysis (reused from Toor <i>et al.</i> (2011) with permission from Elsevier, obtained through RightsLink)	27
Figure 2-7: Thermal decomposition of BER at high temperatures (reused from Yin <i>et al.</i> (2011) with permission from Elsevier, obtained through RightsLink).....	28
Figure 2-8: Hydrolysis of BER (reused from Yin <i>et al.</i> (2011) with permission from Elsevier, obtained through RightsLink)	29
Figure 2-9: Biochar adsorption mechanisms of metals (reused from Li <i>et al.</i> (2017) with permission from Elsevier, obtained through RightsLink).....	38
Figure 3-1: Pre-processing steps for waste PCB feedstock (left) with milled sample (middle), smeared metals (top right) and sieved sample (bottom right).....	40
Figure 3-2: HTL reactor vessel (left), temperature indicator and controller, and pressure gauge (right)	44
Figure 3-3: Schematic of reactor setup	44
Figure 3-4: Microwave digester (left), lip-sealed digestion vessel (middle), and digested sample (right)	47
Figure 4-1: FTIR spectrum of sieved waste PCB feedstock	55
Figure 4-2: FTIR spectrum of lignosulphonate feedstock	56
Figure 4-3: Aqueous phase, residue, bio-oil, and gas yields for HTL experiments with varying temperatures (250°C-330°C) and residence times (20-80 min).....	58

Figure 4-4: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 20 min at 250, 275, 300, and 330°C	60
Figure 4-5: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 80 min at 250, 275, 300, and 330°C	61
Figure 4-6: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 250°C at 20, 40, 60, and 80 min	62
Figure 4-7: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 330°C at 20, 40, 60, and 80 min	63
Figure 4-8: Aqueous phase, residue, bio-oil, and gas yields for HTL experiments with waste PCB mass loadings of 0 to 100 wt.%	64
Figure 4-9: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 80 min for 250, 275, 300, and 330°C	79
Figure 4-10: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 80 min for 250, 275, 300, and 330°C	81
Figure 4-11: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C for 20, 40, 60, and 80 min	85
Figure 4-12: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 250°C for 20, 40, 60, and 80 min	86
Figure 4-13: FTIR spectrum for bio-oils from the HTL of waste PCBs and lignosulphonate at 0, 30, 50, 70, and 100 wt.% PCB mass loading	90
Figure 4-14: FTIR spectrum for residues from the HTL of waste PCBs and lignosulphonate at 0, 30, 50, 70, and 100 wt.% PCB mass loading	90
Figure 5-1: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 20 min at 250, 275, 300, and 330°C	125
Figure 5-2: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 40 min at 250, 275, 300, and 330°C	125
Figure 5-3: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 60 min at 250, 275, 300, and 330°C	126
Figure 5-4: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 80 min at 250, 275, 300, and 330°C	126
Figure 5-5: Reactor temperature profile for HTL of waste PCBs and lignosulphonate at 300°C for 80 min with 0, 50, and 100 wt.% waste PCB loading	126
Figure 5-6: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 20 min at 250, 275, 300, and 330°C	127

Figure 5-7: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 40 min at 250, 275, 300, and 330°C	127
Figure 5-8: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 60 min at 250, 275, 300, and 330°C	128
Figure 5-9: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 80 min at 250, 275, 300, and 330°C	128
Figure 5-10: Reactor pressure profile for HTL of waste PCBs and lignosulphonate at 300°C for 80 min with 0, 50, and 100 wt.% waste PCB loading.....	128
Figure 5-11: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 40 min at 250, 275, 300, and 330°C	130
Figure 5-12: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 60 min at 250, 275, 300, and 330°C	130
Figure 5-13: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 275°C at 20, 40, 60 and 80 min	131
Figure 5-14: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 300°C at 20, 40, 60, and 80 min	131
Figure 5-15: The van Krevelen plot for bio-oils produced at all temperatures and residence times	133
Figure 5-16: The van Krevelen plot for bio-oils produced at all waste PCB loadings	133
Figure 5-17: FTIR spectrum of sieved waste PCB feedstock compared to conventional epoxy resin used in EEE	137
Figure 5-18: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 330°C for 20, 40, 60, and 80 min	137
Figure 5-19: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min for 250, 275, 300, and 330°C	137
Figure 5-20: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 330°C for 20, 40, 60, and 80 min	138
Figure 5-21: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 20 min for 250, 275, 300, and 330°C	138
Figure 5-22: FTIR spectrum of residue from the HTL of waste PCBs at 100 wt.% PCB mass loading compared to glass	138
Figure 5-23: The structure of a lignin molecule	148
Figure 5-24: Gallic acid calibration curve for total phenolic analysis	149

LIST OF ABBREVIATIONS

Abbreviation	Meaning
BCR	Community bureau of reference
BDL	Below detection limit
BER	Brominated epoxy resin
BFR	Brominated flame retardant
BPA	Bisphenol A
CEM	Composite epoxy material
DEA	Department of Environmental Affairs
DGEBA	Diglycidyl ether of bisphenol A
EEE	Electrical and electronic equipment
ERA	E-waste recycling authority
E-waste	Electronic waste
FR	Fire retardant
FTIR	Fourier-transform infrared
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GPC	Gel permeation chromatography
HHV	Higher heating value
HTL	Hydrothermal liquefaction
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IR	Infrared
Mn	Number average molecular weight
Mw	Weight average molecular weight
ND	Not detected
PC	Polycarbonate
PCBs	Printed circuit boards
PDI	Polydispersity index
PTFE	Polytetrafluoroethylene
SF	Severity factor

STD	Standard deviation
TBBPA	Tetrabromobisphenol A
TIC	Temperature indicator and controller
VOCs	Volatile organic compounds
WEEE / e-waste	Waste electrical and electronic equipment
wt.%	Mass fraction
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 General

This chapter provides a background to and subsequent motivation for this study (Section 1.2), followed by the problem statement (Section 1.3). The overall aim and specific objectives of the study are described in Sections 1.4 and 1.5, respectively. The scope and the outline of the dissertation are described in Sections 1.6 and 1.7, respectively.

1.2 Background and motivation

Excessive industrial and household waste is a decades-long issue plaguing modern society. It has been estimated that the global waste generation in 2010 was approximately 3.5 million tonnes per day, with trends indicating an increase to 6 million tonnes per day in 2024 (Hoornweg & Bhada-Tata, 2012). The massive volumes of untreated solid waste, along with the inadequacy of most waste management systems in developing nations, has led to a decline in environmental and human health (Adeleke *et al.*, 2021). According to a report on waste published by the Department of Environmental Affairs (DEA), South Africa produced approximately 54.2 million tonnes of general waste in 2017, with only about 38.6% of this waste being recycled. Furthermore, in that year, South Africa produced approximately 66.9 million tonnes of hazardous waste, with only 6% of this waste reused or recycled. Furthermore, 360,000 tonnes of this hazardous waste was attributed to waste electrical and electronic equipment (WEEE), otherwise known as 'e-waste'. Only 9.7% of e-waste was recycled, the remainder was landfilled (DEA, 2018). In 2019, global e-waste generation reached 53.6 million tonnes, with only 17.4% documented and recycled (Forti *et al.*, 2020). It is estimated that global e-waste generation will reach 75 million tonnes by 2030. As a result of a higher disposable income, industrialisation, and urbanisation in developing countries like South Africa, the generation of e-waste is set to rise considerably (Baldé *et al.*, 2015).

Although e-waste can be a valuable source of secondary materials, it can be very toxic when not managed and disposed of in a suitable manner—thus it is classified as hazardous waste. Various toxic substances are present; however, it is the heavy metals that are of notable concern due to the ease of soil and water contamination as a result of their mobility and non-biodegradability (Wu *et al.*, 2015). Heavy metals can accumulate in the soil, resulting in soil pollution that is hazardous to both the environment and human health (Ilić *et al.*, 2020). The interference with microbial activities, nutrient availability, and plant uptake can lead to a reduction in crop yields. Furthermore, heavy metals can be taken up by plants, thus creating a source of exposure for both humans and

animals (Usman *et al.*, 2022). Exposure to elevated levels of heavy metals can lead to chronic and acute toxicity that damages the peripheral and central nervous system, liver, lungs, kidneys, and blood composition (Lanphear & Roghmann, 1997).

E-waste can be described as waste from any equipment that requires electromagnetic fields or electric currents to function, along with any equipment used for the measurement, transfer, or generation of the mentioned fields or currents (RSA, 2014). This includes industrial and household appliances, communication and information equipment, entertainment and consumer electronics, lighting appliances, electronic tools, health equipment, security equipment, and mixed e-waste (RSA, 2012). According to the E-waste Recycling Authority (ERA), the South African chain of recovery and recycling comprises collectors, refurbishers, pre-processors, and processors. Collectors refer to companies offering e-waste collection and replacement services to other businesses, drop-off points, and waste pickers on landfill sites. Refurbishes refer to companies that repair or refurbish e-waste for reintegration into the market. Pre-processors dismantle, sort, and separate recyclable parts of e-waste. Lastly, processors purchase the pre-processed e-waste to then recycle certain valuable fractions, for example, plastics, aluminium, or various other metals (ERA, 2018). Common recycling systems implemented globally revolve around two methods: pre-processing and end-processing.

As mentioned, pre-processing refers to manually dismantling e-waste into waste, metal, plastic, and glass fractions. Thereafter, shredding reduces particle size for further processing. Lastly, mechanical separation is implemented to separate various fractions from the shredded e-waste. This can be achieved by magnetic separation, density separators, and eddy currents. These methods of recovery have several disadvantages: it is time consuming, the capital investment is high, and there is loss of material as dust during shredding. The increasing complexity of e-waste also complicates the dismantling process (Kumar *et al.*, 2017).

End-processing refers to processes capable of recovering valuable metals and/or organic fractions from pre-processed e-waste. These processes have been implemented to recover metals from waste printed circuit boards (PCBs) as the concentrations of precious metals, such as silver, gold, palladium, and platinum, are reportedly ten-fold higher than in their respective commercially mined minerals (Ghosh *et al.*, 2015; Hadi *et al.*, 2015). Typical PCBs also contain considerable amounts of Fe, Cu, Al, and Zn, as well as numerous other heavy metals, such as lead and cadmium (Cui & Zhang, 2008). Besides the economic attraction of precious metal recovery, sustainable end-processing should also aim to serve as an environmentally friendly treatment method for heavy metals in e-waste. Recycling materials from e-waste results in considerable energy savings, compared to the production of virgin materials, as seen in Figure 1-1.

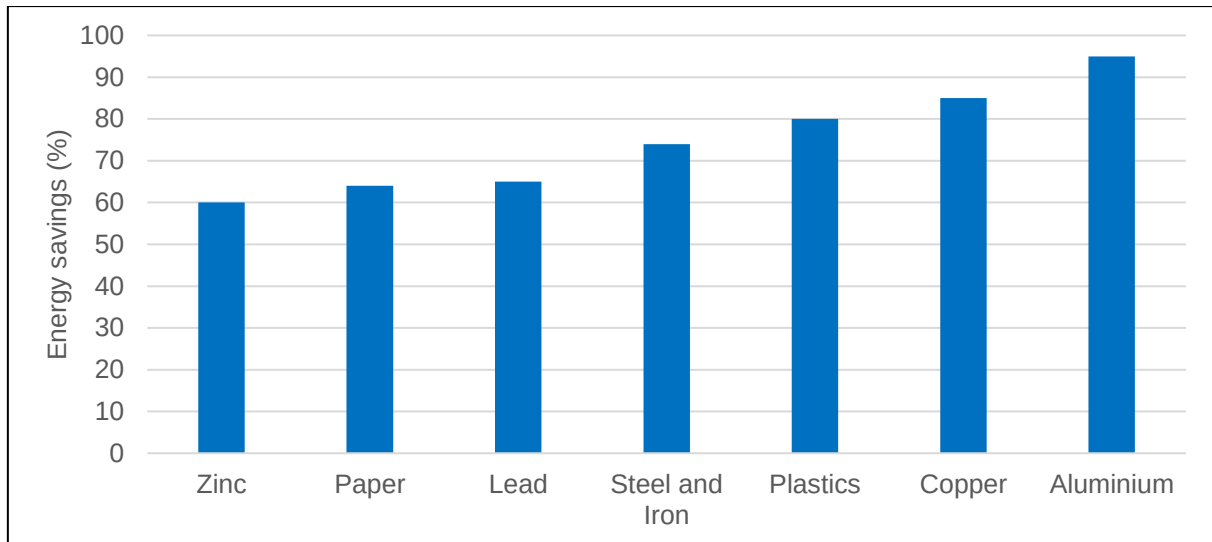


Figure 1-1: Energy savings from recycled materials present in e-waste compared to virgin material production (adapted from Cui & Forssberg, 2003)

The energy savings also have a significant impact on pollutant generation. For example, the recycling of iron and steel, instead of producing these from the original ores, results in a 40% decrease in water usage, an 86% decrease in air pollution, a 76% decrease in water pollution, and a 97% decrease in waste, along with 74% energy savings (Cui & Forssberg, 2003).

Widely used end-processes include bio-metallurgy, hydrometallurgy, and pyrometallurgy. Bio-metallurgy is a new environmentally friendly process in which metals are leached from the e-waste with microbes. This is a slow process and it has not been fully developed for the increasing complexity of metal distribution in e-waste (Namias, 2013). Hydrometallurgy is a treatment option in which various chemicals are used to leach and dissolve specific metals into a solution; however, this process is associated with high costs, high toxicity, and high reagent consumption, along with large and complex waste effluent streams (Kumar *et al.*, 2017). Lastly, pyrometallurgy involves melting pre-processed e-waste under high temperatures to retain a mixture of valuable metals (Namias, 2013). This process has a high energy demand and the emissions contain volatile metals, furans, and dioxins that present health and safety issues (Khaliq *et al.*, 2014). Pyrometallurgical processing cannot completely separate all metals, therefore additional hydrometallurgical processes are required to extract the valuable metals (Namias, 2013).

One pyrometallurgical method used for the recovery of metals from e-waste is pyrolysis. Although this method has been subject to in-depth study, it has not been fully industrialised. It involves the thermochemical decomposition of the organic materials at high temperatures, between 450 and 1100°C, in the absence of oxygen, to produce valuable liquid, gas, and char products that can be used as fuel or chemical feedstock. Pyrolysis has been proven as a suitable method for e-waste recycling in laboratory-scale experiments. It has been established that pyrolysis can direct inorganic materials in e-waste, such as metals and glass, to a solid char fraction through

disentanglement facilitated by the removal of organics (Andooz *et al.*, 2022). Furthermore, co-pyrolysis of e-waste with biomass has resulted in a synergetic effect that improves both product quality and yield (Andooz *et al.*, 2022; Ebin & Isik, 2016). However, pyrolysis produces brominated and other halogenic compounds, as well as dioxins, which are toxic to the environment (Arun & Gopinath, 2020). Consequently, further research into novel methods for e-waste treatment is necessary before green and economic end-processing can be fully industrialised.

Hydrothermal liquefaction (HTL), also known as direct liquefaction, is a thermochemical depolymerisation process similar to pyrolysis. HTL operates under lower temperatures and high pressures in the presence of a solvent, usually water, which serves as a hydrogen donor. Organic materials are converted into liquid biocrude-oil and char, with small amounts of gas emissions (Zhang & Chen, 2018). Various feedstocks have been processed via HTL, and high carbon efficiency and energy recovery with minimal secondary waste in the form of aqueous wastewater and gas have been achieved (Elliott *et al.*, 2015). When compared to co-pyrolysis with biomass, HTL is much more energy efficient. It is capable of utilising wet feedstock, thus eliminating the need for costly dewatering and drying steps (Yang *et al.*, 2017). The energy efficiency of HTL is further supported by lower operating temperatures and shorter residence times compared to pyrolysis (Zheng *et al.*, 2013).

The application of the HTL process as a direct treatment method of e-waste has not been studied much, as it is mostly used in the conversion of lignocellulose feedstocks to high-quality biocrude-oil. However, HTL of organic epoxy resin, which serves as a binder in most PCBs, has been shown to depolymerise to form valuable phenolic compounds, including phenol, o-cresol, and p-cresol (dos Passos *et al.*, 2020; Yin *et al.*, 2011). Similarly, in the hydrothermal treatment of several plastics commonly found in e-waste, including polycarbonate and high-impact polystyrene, decomposition to form the respective monomers has taken place (Zhao, Xia, *et al.*, 2019). This could indicate a disentanglement of inorganic materials such as metals and glass from the organics, similar to pyrolysis, allowing for the partitioning of e-waste metals into a metal-rich solid product.

Although some studies on the recovery of organic materials from e-waste through hydrothermal processing have been carried out, there is little information available related to the fate of the e-waste metals via hydrothermal processing. The recovery of metals during hydrothermal treatment of other feedstock has however been studied. Raikova *et al.* (2016) studied the recovery of contaminant metals in algae used to remediate acid mine drainage and found most metals partitioned to the solid product after hydrothermal treatment. Similar results were shown during the hydrothermal treatment of swine manure containing high heavy metal concentrations (Lu *et al.*, 2018). Furthermore, Huang & Yuan (2016) concluded a synergistic effect in the immobilisation of

contaminant metals present in sewage sludge after hydrothermal co-processing was applied with lignocellulosic biomass, indicating increased metal partitioning to the solid product, rather than it being in a more reactive state in the liquid or gaseous products. The extent of this effect depends on the metals present and subsequent speciation under hydrothermal conditions.

Lignocellulose is a primary compound found in the walls of plant cell and consists of a complex matrix of lignin polymers, carbohydrate biopolymers including cellulose and hemicellulose, and less common minerals, proteins, and extractives. The distribution of these constituents varies depending on the type of lignocellulosic biomass (Menon & Rao, 2012; Ponnusamy *et al.*, 2020). One such biomass is lignosulphonate biomass, obtained through the extraction of lignin through the sulphite pulping process. Currently, 90% of commercial lignin is available in the form of lignosulphonate (Abdelaziz *et al.*, 2019; Aro & Fatehi, 2017). HTL of lignosulphonate produce biochar rich in functional groups which could aid in immobilization of metals.

Consequently, HTL could be a potential option as a novel treatment method for e-waste, especially when co-processing with biomass that convert to biochar structures. Additional benefits of HTL include the following: minimal secondary pollutant production, reagent consumption can be limited to a solvent and biomass, and energy efficiency, as well as being similar to pyrolysis, which has been proven suitable in laboratory-scale e-waste treatment (Andooz *et al.*, 2022). Furthermore, PCBs form an estimated 3%-6% of all e-waste and are core components in most electrical and electronic equipment, together with high concentrations of precious metals, heavy metals, and other polymer fractions, thus serving as an ideal feedstock for experimental treatment via HTL pathways (Ghosh *et al.*, 2015; Vermeşan *et al.*, 2020). The potential disentanglement of non-organic components from organic fractions and the conversion of those organics to other valuable materials, along with the potential immobilisation of e-waste metals through co-processing with lignocellulosic biomass, could result in HTL becoming a promising option for the valorisation and end-stage treatment of e-waste.

1.3 Problem statement

The exponential increase in both demand and supply of electronic equipment, along with an overall decrease in the lifespan, has resulted in a rapid increase in e-waste generation. Inappropriate disposal systems result in the majority of e-waste being landfilled, causing air, soil, and water pollution (Asante *et al.*, 2019). This is not only limited to landfill sites. Many recycling and treatment facilities also result in pollution due to environmentally unfriendly end-processing methods. Most end-processing methods involve combinations of pyro-metallurgy and hydrometallurgy of mechanically pre-processed e-waste. However, many of these processes are not economically feasible without subsidy, and they produce secondary pollution through emissions and effluents.

Furthermore, economic sustainability is hindered by inadequate concentrations of organic pollutants and/or metals in the treatment leachate (Adeleke *et al.*, 2021).

It is therefore considered necessary to investigate novel treatment processes for end-processing that could potentially overcome the disadvantages of current technologies, and then subsequently lead to a more environmentally friendly and economically sustainable recovery process for e-waste. Zhan *et al.* (2020) identified significant gaps in the literature related to the applicability of hydrothermal processing for the treatment of solid waste, which includes e-waste. Consequently, HTL could provide a solution to the disadvantages of current technologies by means of treatment and recovery of both metals and organic materials in e-waste, through a more energy-efficient and environmentally friendly process.

1.4 Aim

The aim of this study is to determine the suitability of direct liquefaction as a treatment method for locally obtained PCB e-waste co-processed with lignosulphonate biomass for the recovery of metals and organic compounds.

1.5 Objectives

The objectives of this study are the following:

- To prepare and characterise the composition and properties of lignosulphonate biomass and locally obtained printed circuit board e-waste
- To determine the recovery efficiency of metals and the formation of organic compounds at various liquefaction temperatures through the characterisation of reactor products
- To determine the recovery efficiency of metals and the formation of organic compounds after HTL at various residence times through the characterisation of reactor products
- To determine the effect of various waste PCB loadings during HTL on the formation of organic compounds and the recovery efficiency of metals through the characterisation of reactor products.

1.6 Scope of study

This study will investigate the influence of HTL conditions while co-processing PCB e-waste with lignosulphonate biomass. The effect of the liquefaction temperature (250-330°C), residence time (20-80 min), and waste loading (0-100 wt.% of feed) on the recovery of metals and the formation of organic compounds will be determined. The joint effect of temperature and residence time will be expressed using suitable severity factor (SF) calculations. The formation of organics will be established by analysing the elemental composition, chemical composition, molecular weight distribution, energy content, and yields of the reactor products. Metal recovery will be established

through subsequent reactor product digestion, followed by a compositional analysis of the recovered elements.

1.7 Outline of dissertation

This dissertation comprises five chapters. Chapter 1 provides the background and motivation, along with the aim and objectives of this study. In Chapter 2, several key topics are discussed to provide the necessary understanding for discussions in the later chapters. Key topics include the following: the properties of both lignocellulosic biomass and e-waste, with emphasis on waste PCBs; the current technologies used for the treatment of e-waste; and an explanation of the HTL process, products, common feedstocks, and operating parameters. Also addressed is the current literature relating to the implementation of hydrothermal processes for the treatment and extraction of valuable metals and organic materials typically present in e-waste and other metal-containing feedstocks. Potential depolymerisation mechanisms for both PCBs and lignin are described. The use of a SF is discussed. Chemical speciation of metals is evaluated, as well as the use of HTL char as an adsorbent for metals such as those reported to be present in e-waste. Lastly, the mechanisms for sorption are also briefly discussed.

Chapter 3 comprises four main sections. The first is dedicated to the materials used during experiments. Furthermore, it describes the procurement and subsequent preparation of e-waste and lignosulphonate into a homogeneous mixture. Details of all relevant chemicals and gases used during experiments and analyses are given. The second section provides a brief explanation of experimental sets relating to the study objectives. The third section explains the experimental methods used in this study. The experimental setup is illustrated, along with the experimental procedures used. Product separation and recovery steps are examined, as well as the methods implemented for metal recovery. Lastly, the fourth section provides background to calculations used to determine product yields and the analytical analyses used to characterise product fractions and feedstocks. The SFs are also examined.

Chapter 4 describes results of analyses of feedstocks and product fractions as obtained through various experiments (as set out in the objectives of this study). Detailed discussions and interpretations of the obtained data, with the identification of trends and correlations, are given. Aspects covered include the characterisation of feedstocks; the influence of several operating parameters on the HTL product yields, including a combined SF analysis on the product yields; and assessment of the influence of operating parameters on the chemical properties and organic composition of reactor products. Lastly, the influence of operating parameters on metal distribution is reported.

Chapter 5 includes a section that summarises the results, followed by a discussion, which includes emphasis on key trends. An endeavour is made to provide a satisfactory conclusion to each of the proposed objectives and ultimately the overall aim of the study. Recommendations for future studies are made, after carefully evaluating the results and identifying subsequent gaps in the literature. Such future studies could be valuable toward obtaining further knowledge related to HTL of e-waste and the potential for large-scale industrialisation.

A full reference list is provided containing the relevant publications as cited in this dissertation. Appendix A provides additional experimental data from experiments. Appendix B provides further additional information. Appendix C provides the experimental error calculations and results for all analyses and yields.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a detailed review of e-waste and the application of several treatment and recovery methods for this problematic waste stream, along with an in-depth review of the HTL process and related mechanisms applicable to e-waste treatment. The ever-growing reliance on technology and the ongoing demand for advancements in all sectors of life has become a norm in modern society. However, these advancements continuously render countless electrical products redundant and significantly reduce their lifecycle (Islam *et al.*, 2020). Annual e-waste generation is currently estimated at about 54 million tonnes, with forecasts of close to 75 million tons by 2030 (Al-Salem *et al.*, 2022).

As a result, effective recycling and material recovery from e-waste has emerged as a crucial issue, leading many nations to develop a variety of electronic waste management methods that are compatible with their capacities (Dutta *et al.*, 2023). For example, South Africa mainly implements open dumping and incineration, with some efforts towards dismantling and sorting, whereas the United States implements material separation through chemical and mechanical means, along with standard landfilling and incineration (Ghosh *et al.*, 2016; Lee *et al.*, 2018). The nature of e-waste results in complex management systems. E-waste can consist of more than 100 hazardous and non-hazardous components, broadly categorised into ceramics, organic material, and inorganic material (Dutta *et al.*, 2023; Kaya, 2016). Section 2.2 addresses the global legislation, categorisation, and composition of e-waste, including PCBs, which are utilised as the feedstock in this study.

The inorganic materials in e-waste consist of various metals, resulting in a potential secondary source of base and precious metals (Otto *et al.*, 2018). Most treatment methods give priority to the recovery of these metals. Section 2.3 will elaborate on several of these treatment methods for waste PCBs. However, effective treatment methods should seek to minimise the environmental impact whilst retaining acceptable material recovery (Islam *et al.*, 2020). Therefore, studying new treatment methods to recover both valuable metals and recycle the organic fraction of e-waste, which consists of several types of plastic and glass fibres, should be a priority.

Direct liquefaction technology is a potential method to convert recyclable and non-recyclable plastics into various added-value products (Poravou *et al.*, 2022). Several studies have concluded the partitioning of metals in various feedstocks into a single product fraction where it is readily available for recovery (He *et al.*, 2021; Lu *et al.*, 2018, 2017; Raikova *et al.*, 2016). Section 2.4

presents a detailed review of the HTL process, including a detailed explanation of the process, common feedstocks, reaction products, mechanisms, as well as key operating parameters. Section 2.5 discusses the use of a SF to combine the effects of temperature and residence time on the product yields of the HTL process.

Section 2.6 addresses specific applications of hydrothermal processes as pertain to e-waste treatment, with emphasis on the formation of organic products. Section 2.7 expands on the inorganic products, by examining the reported disentanglement, partitioning, and recovery of metals generally present in e-waste and metal-containing feedstocks through hydrothermal pathways. Section 2.8 addresses metal sorption as a potential pathway for the previously mentioned disentanglement and partitioning of metals in e-waste and other feedstocks. The application of HTL-derived biochar as an adsorbent is considered. The chapter concludes with mention of five potential sorption mechanisms.

2.2 Electrical waste

2.2.1 Categorisation and legislation

The large-scale and complex issue of e-waste has resulted in many countries implementing initiatives, and incorporating a range of legislations, in the pursuit of harnessing this lucrative secondary resource whilst minimising the environmental health impacts. To limit the negative effects, more than 2000 provisions of legislation in more than 90 jurisdictions have been enacted (Ilankoon *et al.*, 2018; Thakur & Kumar, 2022). As a result, by 2019, approximately 71% of the global population across 78 countries was covered by at least some basic policies, regulations, or legislation (Forti *et al.*, 2020).

Many international organisations and initiatives have also emerged to provide effective categorisation, monitoring, and management solutions for e-waste. Examples of these include the European Commission WEEE-directive that implements a take-back approach for the six categories of appliances listed in Table 2-1. The Basel Convention (1989) was one of the first initiatives addressing the export of hazardous e-waste to less developed areas, with 172 nations agreeing to the Convention (Ilankoon *et al.*, 2018; Sthiannopkao & Wong, 2013). However, these initiatives are mainly applicable to developed nations, whereas most developing African countries still lack effective e-waste legislation and management. In most African nations, the growing informal sector is responsible for collecting and recycling most of the continent's e-waste. Currently, these governments have very minimal and ineffective supervision over this sector (Forti *et al.*, 2020; Patil & Ramakrishna, 2020). In 2019, only 13 of the 54 African countries had e-waste regulations, with unlawful practices including illegal dumping, acid leaching, and incineration still commonly conducted by the informal sector (Forti *et al.*, 2020).

Because the products that fall under the category of electrical and electronic equipment (EEE) are so varied, precise categorisation is essential, not only for statistical reasons but also for the implementation of practical waste management. As a result, EEE can be divided into 54 different categories, based on the end-of-life characteristics, average weight, equivalent material composition, and equipment function. Each category is considered homogeneous. This categorisation thus allows for raw material flow analysis (Forti *et al.*, 2018).

These 54 EEE categories can be further divided into six broad categories relating to the waste management properties of each. Due to a lack of current functional e-waste systems or schemes, it should be noted that WEEE containing accumulators, batteries, and electric vehicle components are not yet categorised (Forti *et al.*, 2020). The six categories, along with examples of typical household EEE in each category, are presented in Table 2-1.

Table 2-1: Categorisation of EEE adopted by the EU-WEEE directives (adapted from Forti *et al.*, 2018, 2020; Mihai *et al.*, 2019)

Number	Category	Example of EEE
1	Temperature exchange equipment	Heat pumps, air conditioners, freezers, and refrigerators.
2	Screens and monitors	Tablets, notebooks, laptops, monitors, and televisions.
3	Lamps	High-intensity discharge lamps, fluorescent lamps, and LED lamps.
4	Large equipment	Photovoltaic panels, copying equipment, large printing machines, electric stoves, dishwashing machines, dryers, and washing machines.
5	Small equipment	Control instruments, stereo systems, medical devices, microwaves, and ventilation equipment.
6	Information technology and telecommunication equipment	Telephones, personal computers, routers, and mobile phones.

These six categories conform to the current WEEE directives that were passed into law by the European Commission in 2012 (Ilankoon *et al.*, 2018). All components, assemblies, and consumables that make up the entire product or a portion thereof at the time of disposal are included in the description for each EEE category (Wath *et al.*, 2011). Consequently, valuable components such as PCBs will be distributed among the six categories. PCBs are an essential part of nearly all EEE—they provide mechanical support and connect components by means of conductive pathways (Kaya, 2016). Categories 4 and 5 typically contain low-grade PCBs, whereas Categories 2 and 6 contain medium- to high-grade PCBs (Hudson *et al.*, 2013). PCBs can be categorised according to the concentration of gold. Low-grade contains <100 ppm, medium-grade 100-400 ppm, and high-grade >400 ppm (Hagelüken, 2006). Thus, it is not only important to broadly categorise e-waste, it is also important to accurately determine the composition of valuable

components or assemblies within each category (PCBs, for example) in order to establish reliable and economically viable waste treatment solutions.

2.2.2 Characterisation of e-waste and PCBs

Although e-waste is a composite waste source consisting of many hazardous and non-hazardous materials, the base materials typically include ferrous metals, non-ferrous metals, polymer plastics, rubber, concrete, circuit boards, wood, glass, plywood, and ceramics (Betts, 2008). Plastics and glass constitute ~21 wt.% and ~5 wt.% of e-waste, respectively. Rubber, concrete, and ceramics each constitute ~14 wt.%. Ferrous metals such as steel and iron account for ~47 wt.%, whereas only 7 wt.% is attributed to copper. Other non-ferrous metals account for ~6 wt.% (Pant *et al.*, 2012; Zeng *et al.*, 2018). However, precise compositional analyses across such vast waste streams are difficult. This is because the metal content varies between the types of EEE and the ongoing evolution of the various materials used in EEE products (Chauhan *et al.*, 2018). The primary economic force behind e-waste recycling is the abundance of non-ferrous metals present therein. These include base metals such as cobalt, zinc, lead, copper, nickel, and aluminium. Precious and rare earth metals are also found, including palladium, platinum, silver, gold, and ruthenium. In total, e-waste consists of approximately 57 valuable elements (Kaya, 2016; Tesfaye *et al.*, 2017; Thakur & Kumar, 2022).

Additionally, organic materials such as glass fibres and certain polymer plastics can be considered valuable as secondary materials. For example, Rajagopal *et al.* (2017) produced sustainable composite panels using non-metallic waste present in waste PCBs. Furthermore, the CreaSolv process (developed by the Fraunhofer IVV Institute, Germany) encompasses the separation of brominated flame retardants (BFRs) from polymers in e-waste whereafter precipitated BFR-free polymers are further processed via extrusion into useful products (Freegard *et al.*, 2006; Sahajwalla & Gaikwad, 2018). High-impact polystyrene, polypropylene, polycarbonate (PC) blends, acrylonitrile-butadiene-styrene, and polystyrene have generally been found to be the most prevalent polymers in WEEE (Ma *et al.*, 2016). Glass fibres typically found in e-waste include metal oxides, for example, calcium oxide, sodium oxide, and alumina (Khan *et al.*, 2022).

However, e-waste is considered a hazardous waste material due to the presence of certain persistent constituents such as tetrabromobisphenol A (TBBPA), BFRs, polycyclic aromatic hydrocarbons, dioxins, polychlorinated biphenyls (PCBS), and a range of heavy metals, including lead and lithium (Liu *et al.*, 2023; Thakur & Kumar, 2022). A list of potentially hazardous organic materials and heavy metals is presented in Table 5-17 in Appendix B. Herein, the sources of ecological exposure to humans are presented, as well as the routes of exposure to the human system.

In recent years, waste PCBs have become more attractive to enterprises and researchers due to their high base and precious metal contents. The concentrations of precious metals such as gold, silver, and platinum in waste PCBs are significantly higher than in the respective mined ores (Kaya, 2016). Table 5-18 in Appendix B gives the metal concentrations in the various metal ores compared to the PCBs (Bizzo *et al.*, 2014). Thus, recycling is important from both an economic and environmental viewpoint.

The heterogeneous nature of waste PCBs leads to the necessity to characterise the PCB structure, the type, components, and chemical composition (Ghosh *et al.*, 2015). The aim of many studies has therefore been to determine the composition of waste PCBs. The metals, ceramics, and plastics typically account for 40%, 30%, and 30%, respectively (Ghosh *et al.*, 2015; Kaya, 2016, 2018; Sum, 1991; Tenorio *et al.*, 1997).

All PCBs generally have the same basic structure: an insulating laminate or substrate, a conductive coating internally or externally printed on the substrate, and the various electrical components attached to the laminate or substrate. These electrical components can vary; however, waste PCBs contain approximately 8% switches, 12% resistances, 23% empty PCB, and 33% semi-conductors (Tohka & Lehto, 2005).

All PCBs can be categorised as multi-layered, double-sided, or single-sided. Single-sided PCBs have the conductive coating etched onto only one side, whereas double-sided have the coating etched onto both sides. Certain double-sided PCBs have 0.2-mm holes through the substrate that connect the conductive layers. The conductive layers can be etched or printed with a thin foil of copper. The thickness is in the range 17.5-175 μm , with an overall PCB thickness of 0.2-7 mm (Kaya, 2016). The chemical composition varies significantly due to the wide range of applications and the subsequent types of PCBs; however, the composition can be divided into three categories: ceramics, metals, and organics (Sum, 1991). Figure 2-1 presents these categories with approximate weight fractions, as well as examples of materials and elements found in each category.

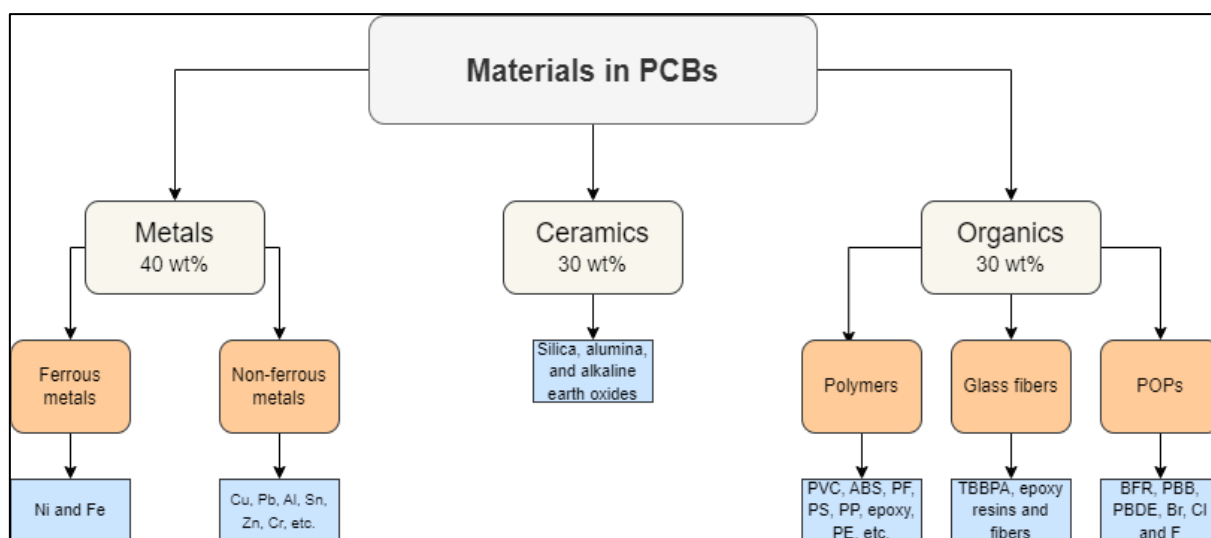


Figure 2-1: Composition and common materials found in waste PCBs (adapted from Chauhan *et al.*, 2018; Kaya, 2016)

The organic materials in PCBs mainly comprise plastic polymers, resins with reinforcing materials such as glass fibres or cellulose, and organic pollutants. Many of these pollutants can be attributed to fire retardants (FRs) used in PCBs. The plastics mainly comprise C-H-O polymers, nitrogen-containing polymers, and halogenated polymers. Ceramic materials can be found on various electrical components, such as slots and bridges on PCBs (Ghosh *et al.*, 2015). With regards to the metal composition, the copper conductive layer is most prevalent at ~5-30 wt.% of metals, followed by iron, aluminium, tin, nickel, and lead, all of which are present in the frames, soldering, and electrical components (Ghosh *et al.*, 2015; Kaya, 2016; Takanori *et al.*, 2009). Duan *et al.* (2011) compared the average compositions of metals, plastics, and ceramics in waste PCBs as reported in 11 studies, as is illustrated in Table 2-2.

Table 2-2: The composition of plastics, ceramics, and metals in waste PCBs as reported in several studies (adapted from Duan *et al.*, 2011; Kaya, 2016)

Category	Material	Composition	Category	Material	Composition
Metals	Cu	6.0-27.0%	Plastics	Polyethylene	9.9-16.0%
	Al	2.0-7.2%		Polystyrene	4.8%
	Fe	1.2-8.0%		Polypropylene	4.8%
	Sn	1.0-5.6%		Epoxy	4.8%
	Ni	0.3-5.4%		Polyvinyl chloride	2.4%
	Pb	1.0-4.2%		PTFE	2.4%
	Zn	0.2-2.2%		Nylon	0.9%
	Sb	0.1-0.4%	Ceramics	Silica	15.0-30.0%
	Au	80-2050 ppm		alumina	6.0-9.4%
	Ag	110-4500 ppm		Alkali-earth oxides	6.0%
	Pd	50-2200 ppm		Titanates-micas	3.0%
	Pt	4.6-30 ppm			
	Co	1-4000 ppm			
	Ti	1.0-4000 ppm			

Precious metals such as silver, gold, and palladium are used in plating and the contact joints of integrated circuits, whereas platinum is commonly used in sensors, relays, and switches. Several hazardous metals are also present, including chrome, lead, cadmium, zinc, antimony, and nickel (Sum, 1991).

PCB substrates can be manufactured from a wide range of materials, depending on the required function and on the origin of the PCB—the substrates can be categorised by these materials. Some of these materials include polytetrafluoroethylene (PTFE), more commonly known as Teflon, and polyimide substrates. PTFE is a desirable material due to its good strength; it is also lightweight, flexible, and flame-resistant; thus, it is used in high-frequency technology. These substrates function under high stress and temperatures, making them useful in military products. However, their cost is significantly higher than the basic materials used in polymer composite substrates (Ezema Ike-Eze *et al.*, 2023). Metal-based substrates are also advantageous because conductive materials increase the lifespan of PCBs. Lastly, polymer composite-reinforced substrates are the most common; they comprise the largest variety of substrates—for example, CEM1, CEM3, FR1, FR2, FR3, FR4, and FR5 (CEM, composite epoxy material; FR, fire retardant) (Macleod, 2002; Nassajfar *et al.*, 2021). The PCBs typically used in mobile phones, tablets, laptops, and personal computers can mainly be divided into two types, FR2 and FR4. FR4 PCBs are the most common due to their high dielectric strength, low cost, and good insulation; yet FR2 PCBs are commonly used in household appliances such as televisions and microwaves (Hall &

Williams, 2007). Typically, FR4 PCBs are green or blue, whereas FR2 PCBs are brown or yellow (Ezema Ike-Eze *et al.*, 2023; Ladou, 2006).

A conductive copper layer is coated on multiple layers of epoxy resin and reinforced with glass fibre to create FR4 PCBs, whereas FR2 PCBs consist of a copper layer coated on only one layer of glass fibre or cellulose reinforcement and a phenolic resin. Both PCB types have FRs added for safety and fire protection. To prevent oxidation, thin films of silver or tin are used (Hall & Williams, 2007). Resins are organic polymer plastics that can create environmental issues when incinerated or landfilled. Due to the thermosetting nature of resins, they cannot be remitted or reformed (Kaya, 2016). Difunctional epoxy resins such as bisphenol A, or multifunctional epoxy resins such as epoxy novolacs, based on creosol, phenol, cyanate esters, polyimides, and bismaleimide-triazine epoxy blends, are examples of common resins. A hardener is also used, to give the cross-linking necessary to create a thermoset plastic. Dicyanodiamide is a widely used hardener; other options include 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl sulphone (Hall & Williams, 2007).

As mentioned, many types of PCB substrates are commercially available; however, glass-fibre-reinforced epoxy resins, such as FR4, are the most common among waste PCBs. Epoxy is described as a thermosetting resin or matrix material that contains epoxide groups in the molecular structure. These epoxide groups, also recognised as ethoxyline or oxirane groups, form the characteristic functional group of epoxy polymers—they involve one oxygen and two carbon atoms in a ring structure (Yu *et al.*, 2009). Roughly 90% of the global production of epoxy resins is synthesised via the condensation reaction between epichlorohydrin and bisphenol A (BPA) in the presence of a base catalyst such as sodium hydroxide, to form oligomers of diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Saba *et al.*, 2016). Figure 2-2 illustrates the reaction between epichlorohydrin and BPA to form DGEBA epoxy resin in the presence of a base catalyst.

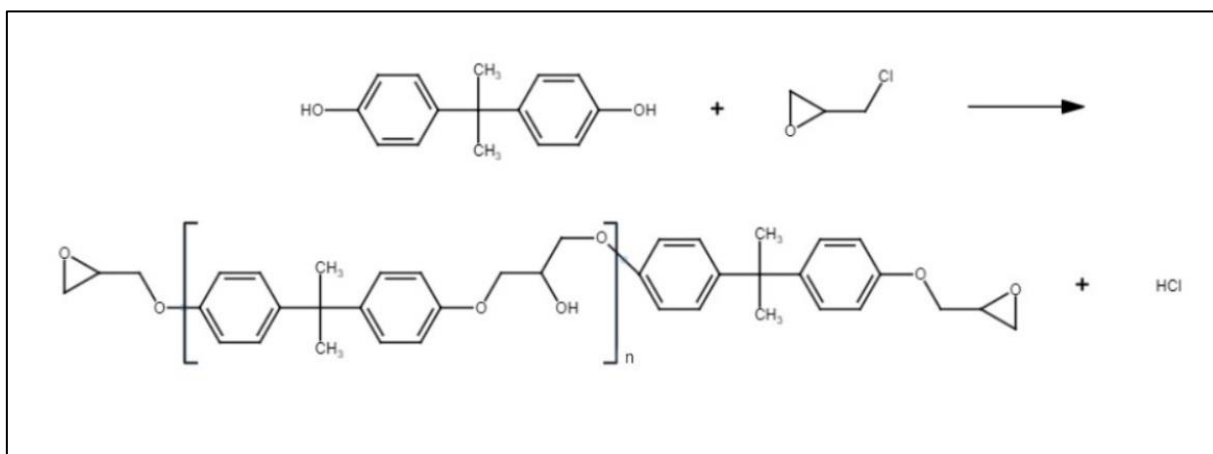


Figure 2-2: Condensation reaction of epichlorohydrin and BPA to form DGEBA epoxy resin

As shown in Figure 2-2, the condensation reaction results in terminal epoxide groups. These groups allow for separate reactions with nucleophilic compounds, such as the various hardeners,

curing agents, and co-reactants commercially available. Amine-containing hardeners are the most common) (Saba *et al.*, 2016). For example, the diamine molecules can react with the epoxide groups in a process known as curing wherein a rigid thermosetting polymer is produced (Zhang *et al.*, 2012). Typically, the degree of polymerisation of DGEBA epoxy resin varies between 1 and 20 (Rudin & Choi, 2013).

Furthermore, owing to the inherent combustibility and flammability of thermoset polymers, FRs are added for safety and fire protection. Epoxy resins can be fire retarded through additives or via a reactive FR (Weil & Levchik, 2004). Additive FRs do not bond to the polymer; these additives are only combined and uniformly dispersed within the polymer; however, they can easily leak through the thermoset matrix (Stapleton *et al.*, 2008). Reactive FRs bond to the polymers via a further polymerisation reaction, thus they do not easily leach from the epoxy matrix (Ezema Ike-Eze *et al.*, 2023). FR4 PCBs are fire retarded via the polymerisation reaction between difunctional DGEBA epoxy resin and TBBPA in the presence of a catalyst (Saba *et al.*, 2016), according to the reaction illustrated in Figure 2-3.

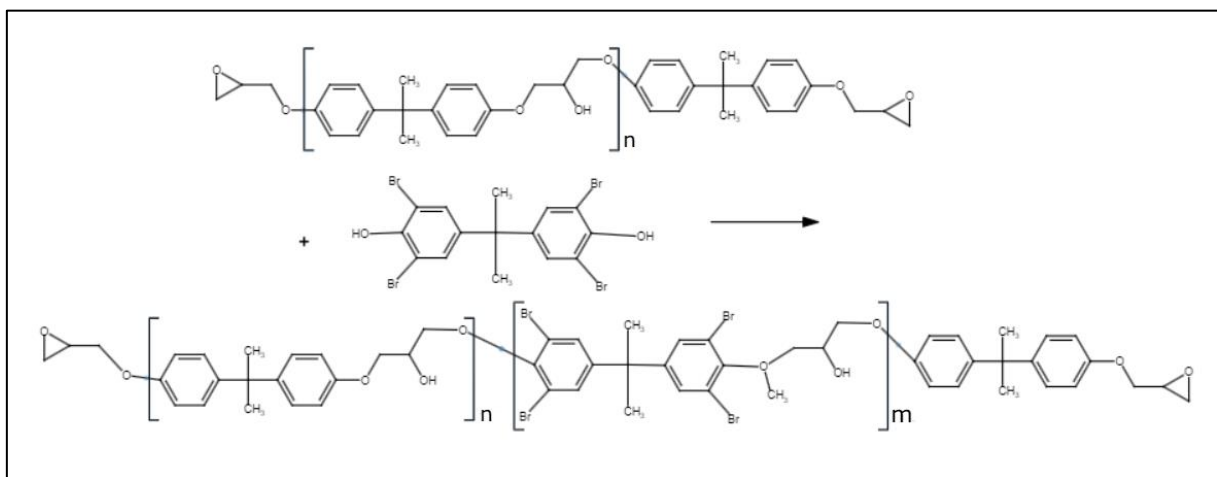


Figure 2-3: Polymerisation reaction between DGEBA epoxy resin and TBBPA to produce a fire retarded epoxy resin

BFRs such as TBBPA are organobromide components that inhibit the ignition of flammable polymer plastics. However, manufacturers are actively decreasing the usage of brominated FRs because they produce toxic brominated compounds when incinerated (Hall & Williams, 2007).

2.3 Recycling methods for waste PCBs

In the recovery of most metallic components from waste PCBs, most raw materials are recovered by dividing the process into three separate stages (D'Adamo *et al.*, 2019). First, a pre-treatment stage involves the disassembly of electronic components that could impact downstream extraction as well as easily removable reusable components. In some cases, compositional analysis is performed at this stage (Jianzhi *et al.*, 2004). Mechanical separation follows, wherein size

reduction and separation take place. The resulting powders can be separated based on the physical properties of the various materials present, such as weight, magnetism, conductivity, and thickness (Vermeşan *et al.*, 2020). Finally, the metallurgical processes follow, in which the metal powders are refined through bio-metallurgy, hydrometallurgy, pyrometallurgy, or a combination of these technologies (Ferella *et al.*, 2015). Such a recycling system prioritises the valuable metal fractions, with the non-metallic fractions typically not fully utilised. As a result, methods within this system are viable; however, there are many unsolved issues, such as non-metallic fraction recovery and pollutant or waste generation (Bizzo *et al.*, 2014).

2.3.1 Mechanical separation

Mechanical or physical separation is implemented in the second stage of the above-mentioned recycling system for waste PCBs, during which upgrading via the liberation of metals from non-metals takes place. Although generally regarded as the most efficient recycling route, it does present significant challenges due to the heterogeneity of waste PCBs (Hopewell *et al.*, 2009; Vermeşan *et al.*, 2020). Mechanical separation includes shredding, washing, and sieving, whereafter magnetic separation, electro-mechanical separation, or gravity separation can be applied (Vermeşan *et al.*, 2020). These processes require proportionally lower capital than other methods. Mechanical separation is less effective, however; as a result of inadequate metal separation, metal loss is between 10% and 35% (Kaya, 2016). Electro-mechanical separation, such as eddy currents, tribo-electrical separation, and corona electrostatic separation are proven technologies for separating metallic and non-metallic fractions (Jiang *et al.*, 2009). Low energy costs, no emissions, and simple processes are all factors that support the use of mechanical separation. Nonetheless, several challenges remain here, such as dust formation and metal loss (Xiang *et al.*, 2007). Due to the complex and diverse nature of waste PCBs, it becomes difficult to separate and utilise the non-metallic fractions. Recent advancements in polymer recovery technology could be useful in addressing this challenge (Moroni *et al.*, 2018).

2.3.2 Bio-metallurgy

The bio-metallurgical recovery of various metals has been implemented due to the capability of metal recovery from low- and high-grade sources, such as waste PCBs. Although this technology is relatively novel, it has been gaining popularity in recent years (Andrade *et al.*, 2022). This technology implements a series of acidophilic bacteria with sulphur- and iron-oxidising characteristics (Priya & Hait, 2020). Several studies have determined the viability of metal dissolution and mobilisation in waste PCBs via bacteria-assisted bio-leaching (Benzal *et al.*, 2020; Priya & Hait, 2020; Yang, Zhu, *et al.*, 2017). By selectively mobilising base and precious metals at low temperatures, by making use of microorganisms, bio-leaching holds great potential. It also leaves a clean non-metallic residue for processing. Additionally, using microorganisms to produce

weaker organic acids instead of manufacturing strong reagents for metal leaching offers two major advantages. Treatment and disposal of weaker organic acids has a reduced environmental impact than when conventional reagents are used for metal leaching. It is also much more economical than procuring large amounts of strong acids (Kaya, 2016). However, there are still drawbacks to this treatment of waste PCBs. Given that many toxic substances are present, the growth rate of bacteria is reduced, subsequently impeding the rate of reaction possible for large-scale bio-metallurgical waste PCB treatment (Ghosh *et al.*, 2015).

2.3.3 Hydrometallurgy

Hydrometallurgical processing of waste PCBs is centred on the recovery of metals. This method of extracting metals involves employing a range of strong reagents to mobilise and leach base and precious metals into metal-rich leachates for further processing. This can be achieved with inorganic acids, such as alkaline reagents, aqua regia, nitric acid, or sulphuric acid (Udayakumar *et al.*, 2022). Base metal recovery is a critical factor towards the overall economic feasibility of waste PCB leaching. Furthermore, increased base metal recovery results in a precious metal-rich residue, allowing for complete precious metal recovery with additional leaching. Subsequent refinement typically entails electrowinning, ion exchange, or cementation (Ashiq *et al.*, 2019). Process parameters can also be controlled relatively easily, for example, reagent choice and concentration, as well as leaching time, temperature, and agitation rate (Udayakumar *et al.*, 2022). Although this process poses less of an environmental hazard than pyrometallurgical routes, considerable amounts of sludge must be treated before disposal. Moreover, the organic materials present in waste PCBs influence, and limit, the leaching parameters. The kinetics of leaching are typically slow, thus posing a drawback for large-scale implementation (Kaya, 2016).

2.3.4 Pyrometallurgy

The pyrometallurgical option is the conventional route for waste PCB metal recovery, although this process requires high capital due to high energy requirements. Furthermore, a metal-rich residue is produced, thus additional hydrometallurgical or mechanical processes are required for high-purity metal recovery (Kaya & Šzeri, 2009). Pyrometallurgical processes include plasma arc furnace smelting, incineration, copper smelting, pyrolysis, and roasting at high temperatures (generally 500-1200°C), in the presence of certain gases, for the recovery of non-ferrous metals (Wan *et al.*, 2021). These processes are considered the economic route for e-waste recycling metal recovery overall. This is due to the acceptance of any e-waste form. Thus, WEEE scrap not separated in the initial dismantling stage can be used without sacrificing the metal recovery (Sum, 1991). The various flammable compounds and plastics also produce energy, thus decreasing the total energy required. However, large amounts of slag are produced from pyrometallurgical routes, with aluminium and iron typically migrating to this by-product, resulting in difficult recovery of these

metals (Ma, 2019). Additionally, the high operating temperatures result in the volatilisation of heavy metals such as lead and cadmium. The release of BFRs, furans, halogenated dioxins, and other persistent organic pollutants are of concern in these processes (Kaya, 2016). Therefore, additional emission control is required for an environmentally suitable process, further increasing the capital and operational costs (Udayakumar *et al.*, 2022).

2.4 HTL

Although many treatment methods exist, HTL presents a modern alternative for waste PCB recycling. HTL is a pyrometallurgical process, also known as hydrous pyrolysis (Jazrawi, 2014). Furthermore, HTL is a thermochemical process involving the dissolution of feedstock that is typically not soluble under atmospheric conditions. HTL can process wet feedstock, allowing for significant energy savings through the elimination of feedstock drying. Thus, lignocellulosic materials such as wood biomass or algae and waste-based feedstocks are suitable. Process conditions include pressures of 50-200 bar under moderate temperatures between 200 and 400°C for about 5-120 min, with the addition of an aqueous solvent (generally water), as a hydrogen source (Alper *et al.*, 2020; Ponnusamy *et al.*, 2020). Water boils at 100°C, hence maintaining the operating pressure above the vapour pressure will hold water in a liquid state—also known as subcritical conditions. These conditions influence the properties of water; however, the most significant changes occur when approaching the critical point (374°C and 221 bar for water). When this critical point is exceeded, a supercritical state is achieved. As the operating temperature increases above 100°C, the hydrogen bonds of water begin to break, releasing H⁺ and OH⁻ ions, with a concomitant decrease in viscosity and dielectric constant, resulting in a usable solvent and considerably impacting the HTL reactions (Laredo *et al.*, 2023; Seward & Driesner, 2004).

Depolymerisation reactions can be facilitated via mechanisms such as aromatisation, deoxygenation, dehydration, hydrolysis, and fragmentation; repolymerisation reactions are also possible. The resulting products include gaseous emissions, an aqueous phase, biocrude-oil, and biochar or residue, depending on the carbon content (Toor *et al.*, 2011). The biocrude-oil is generally an energy-dense product, which can be extracted from the processed mixture using various organic solvents, such as acetone or dichloromethane. The extraction solvent plays an important role in the final quality of crude oil and the overall economy of the HTL process (Ratha *et al.*, 2022). Both HTL yields and product quality can be controlled by various process parameters, the most influential being temperature, pressure, residence time, feed type, feed loading, solvent-to-feed ratio, and catalyst (Kumar, 2022). Although HTL is technically viable without the use of a catalyst, much research has been done on the use of catalysts under subcritical conditions (Biller & Ross, 2011; Jindal & Jha, 2016a; Nazari *et al.*, 2015; Shakya *et al.*, 2015).

2.4.1 HTL feedstocks

2.4.1.1 Lignocellulosic biomass and lignosulphonate

Lignocellulose is a primary compound found in the walls of plant cell and it stands as a renewable, carbon-neutral compound readily available for the production of chemicals and fuel. A complex matrix of lignin polymers and carbohydrate biopolymers such as hemicellulose and cellulose, as well as less prominent minerals, proteins, and extractives form lignocellulosic biomass. Furthermore, the distribution of these constituents varies, depending on the type of lignocellulosic biomass (Kumar *et al.*, 2020; Menon & Rao, 2012). For example, cellulose is the most prominent biopolymer in woody biomass, while lignin is the second most abundant polymer (~15%-40% of wood). HTL solid and biocrude yields after the processing of wood biomass vary between 17% and 68%; however, commercial application is challenged by low conversion and biocrude yields (Dimitriadis & Bezergianni, 2017). Lignin is a largely underutilised material, with only 2% used to produce value-added products, although it currently forms the largest renewable resource of aromatic compounds globally. Lignin serves as a defensive barrier in cell walls; its concentration and distribution vary between plant species (Aro & Fatehi, 2017; Lange *et al.*, 2013).

Lignin is biosynthesised via a phenylpropanoid reaction pathway in which the three main monomers of lignin undergo oxidative polymerisation. These three monomers or monolignols are sinapyl, coniferyl, and *p*-coumaryl alcohol, as illustrated in Figure 2-4.

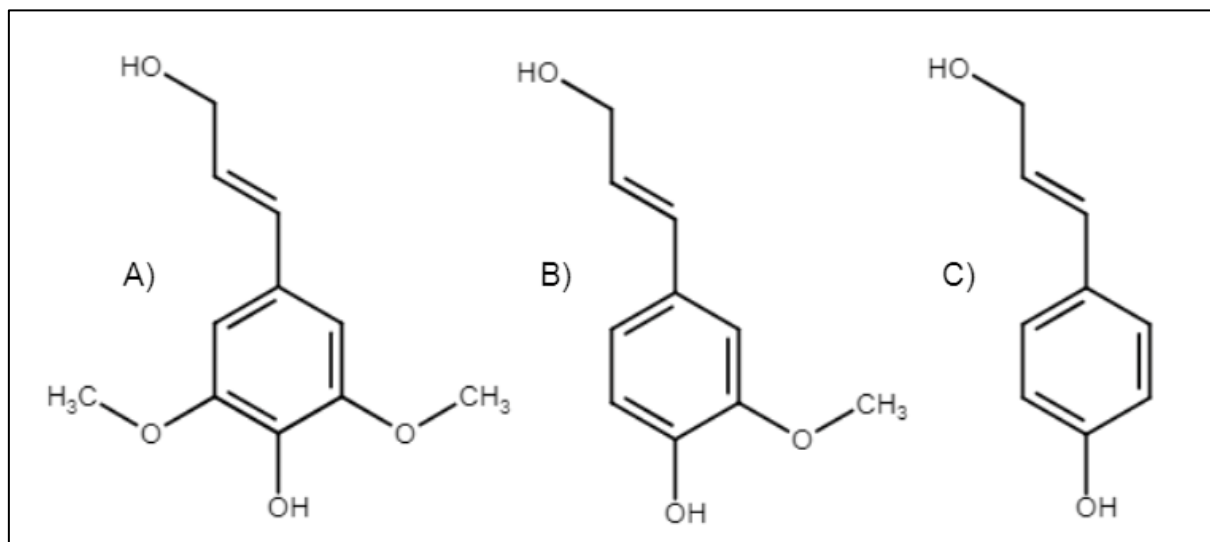


Figure 2-4: Molecular structure of the three main monolignols present in lignin: A) sinapyl alcohol, B) coniferyl alcohol and C) *p*-coumaryl alcohol (adapted from Kumar *et al.*, 2020)

These monomers undergo radical polymerisation to form carbon-to-carbon and ether bonds, after which the monolignols are incorporated into lignin as syringyl, guaiacyl, and *p*-hydroxyphenyl units. The composition of these units varies between plant species due to differences in bonding tendency (Kumar *et al.*, 2020; Del Río *et al.*, 2020). Furthermore, lignin polymers contain various

functional groups, such as carboxyl, carbonyl, methoxy, and hydroxyl groups, that bond to aliphatic or aromatic moieties, all to various extents and with various distributions (Kai *et al.*, 2016). As a result, lignin is a cross-linked biopolymer without ordered repeat units, thus its composition exhibits wide variations. An example of the full lignin structure is illustrated in Figure 5-23 in Appendix B.

Lignin must undergo separation processes, such as sulphite pulping or kraft pulping, to be effectively liberated from wood. Kraft lignin is obtained with the aid of Na₂S or NaOH. Currently, 90% of commercially available lignin is in the form of liginosulphonate and can be obtained from the sulphite pulping process. Liginosulphonate is produced by implementing sulphurous acid or sulphite salts at different pH levels (Abdelaziz *et al.*, 2019; Aro & Fatehi, 2017). The structure and properties of liginosulphonate can vary depending on the type of sulphite salt used. Bases such as calcium and sodium are most commonly used; ammonium or magnesium can also be used (Elumalai & Pan, 2011). Figure 2-5 shows the partial chemical structure of liginosulphonate as liberated when using sodium sulphite salts (Megiatto *et al.*, 2016).

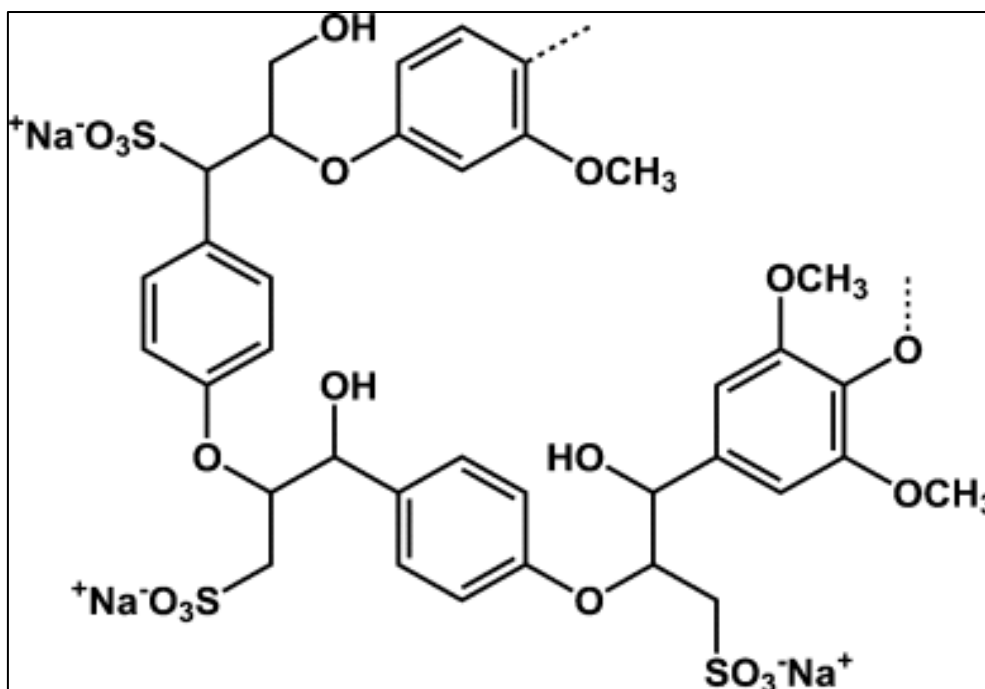


Figure 2-5: The partial chemical structure of sodium lignosulphonate produced via the sodium sulphite pulping process (reused from Megiatto *et al.* (2016) with permission from Elsevier, obtained through RightsLink)

Lignosulphonates contain large amounts of sulphur due to the introduction of sulphonic groups during pulping. These groups retain their deprotonated status in an aqueous medium, thus lignosulphonates are anionically charged and soluble in water at a neutral pH (Aro & Fatehi, 2017).

2.4.1.2 Waste materials

Several types of waste materials have been studied as feedstocks for HTL, including municipal, food-processing, and agricultural waste. Waste plastics and sewage sludge have been established

as potential HTL feedstocks to produce biocrude-oil (Suzuki *et al.*, 1988; Williams & Slaney, 2007; Zhai *et al.*, 2014). The yield of biocrude-oil from HTL of sewage sludge has reached 15%. It has a complex composition of hydrocarbons, alcohols, esters, and phenolic compounds, as well as a range of nitrogen-containing products such as amines, indoles, and amides (Zhai *et al.*, 2014). Various waste plastics have been studied, including polyethylene terephthalate, polyvinyl chloride, polystyrene, polypropylene, and polyethylene. Depending on the selection of plastics, the biocrude-oil yield ranges between 2% and 95%, with emissions containing butane, propane, propane, ethane, methane, and alkene products. Biocrude-oil from mixed plastic feedstocks contain large amounts of aromatic compounds (Williams & Slaney, 2007).

HTL of solid waste and swine manure also produces biocrude-oil (heating value 36 MJ/kg) (Xiu *et al.*, 2010). Agricultural residues have been converted to biocrude-oil, delivering yields of 20%-36%. The calorific value of this biocrude is ~30 MJ/kg, and its composition is ~70% carbon, 7% hydrogen, and 1% nitrogen (Dimitriadis & Bezergianni, 2017; Minowa *et al.*, 1998).

2.4.1.3 Microalgae

Microalgae has attracted much attention in recent years due to its potential as a renewable energy source. Compared to other biomass sources such as wood, algae boasts a high yield per hectare and fast growth rates, furthermore, it does not compete for viable agricultural land. Nonetheless, the high moisture content of algae requires significant drying due to the high heat of vaporisation of water, thus algae treatment is too energy-intensive for most thermochemical processes (Dimitriadis & Bezergianni, 2017). HTL is therefore an ideal refining method as it can process wet feedstock.

The products of HTL processing of algae are typically biocrude-oil, gas, an aqueous phase with water-soluble products, and solid residue (Biller & Ross, 2011). Consequently, many studies have been conducted on the HTL processing of various strains of microalgae to produce yields of biocrude-oil in the range 16%-64% with heating values 28-37 MJ/kg (Chen *et al.*, 2012; Jin *et al.*, 2013, 2014; Vardon *et al.*, 2011). The contents of biocrude-oil derived from microalgae generally include hydrocarbons, aldehydes, ketones, and unsaturated fatty acids (Dimitriadis & Bezergianni, 2017; Shuping *et al.*, 2010).

2.4.2 HTL products

2.4.2.1 Biocrude-oil

Historically, biocrude-oil has been the only desirable product derived from HTL of biomass, and the focus of the majority of studies has been on optimising the quality and yields of this product fraction. HTL-derived biocrude-oil is typically a water-immiscible, viscous, dark brown, and energy-dense liquid (Cao *et al.*, 2017). HTL oil yields for lignocellulosic biomass are in the range 10%-60%; yields of close to 80% have been achieved (Dimitriadis & Bezergianni, 2017). HTL oil is

similar to conventional crude oil, with roughly 70%-95% of the energy content of petroleum-based oil. However, biocrude-oil is unstable and corrosive due to the high oxygen and acid content, thus upgrading is required through hydrotreatment in which the oxygen, nitrogen, and sulphur are removed, resulting in a renewable diesel product (Cao *et al.*, 2017; Yang *et al.*, 2022).

The chemical and physical properties of HTL biocrude-oil are heavily dependent on the feedstock and operating parameters. Hence, the composition is complex, with a wide range of molecular weights. Gas chromatography (GC) can be applied to partially characterise bio-oil, however, certain heavy constituents cannot be extracted into the GC column, thus presenting a challenge for accurate compositional analysis (Anouti *et al.*, 2016; Cao *et al.*, 2017). HTL bio-oil generally contains >100 compounds, which can be divided into several categories. Gollakota *et al.* (2018) have elaborated on the main product types detected in biocrude-oil produced via HTL. These include the following: monoaromatics (phenol, styrene, toluene, benzene, etc.), fatty acids (oleic acid, myristic acid, palmitic acid, hexadecenoic acid, etc.), alkanes and alkenes (hexadec-ane/-ene, pentadec-ane/-ene, cycloalkane, etc.), polyaromatic compounds (indene, naphthalene, pyrene, etc.), nitrogen compounds (indoles, amides, amines, nitriles, etc.), and other oxygenated compounds (ketones, alcohols, aldehydes, furans, etc.).

2.4.2.2 Biochar and residue

The HTL solid product can be divided into two main categories: biochar and residue. Biochar is defined as a carbon-rich solid produced via the thermochemical degradation of biomass in the absence of oxygen—the carbon content is >65%. Residue is similarly produced; however, it does not contain sufficient carbon to be classified as biochar. It can be obtained via HTL processing of low-carbon feedstocks (Wijitkosum & Jiwnok, 2019).

The HTL residue composition is heavily dependent on the feedstock type. Plastic waste feedstock tends to produce residue that has a heterogeneous composition of metals, paper, polymers, and ceramics (Ciuffi *et al.*, 2021). Pedersen & Conti (2017) studied the hydrothermal processing of several high-density polymers, concluding a residue yield of 0-80%. Plastics such as PC, polylactic acid and polymethyl methacrylate produced no residues.

Biochar yields can range from 2% to 70%; this wide range justified by the considerable effect of operating conditions such as temperature, residence time, feedstock, and catalyst (Ponnusamy *et al.*, 2020; Tekin *et al.*, 2012). HTL biochar has an irregular solid surface structure, with pores of varying shapes and sizes. Pore size, total volume, and surface area are important physical properties of biochar. Studies indicate that HTL biochar, regardless of feedstock, has a total volume and surface area that is typically less than activated carbon and biochar derived from pyrolysis. The pore volume of HTL biochar varies between 0.058 and 0.082 cm³g⁻¹, whereas the surface area ranges from 1.56 to 17 cm²g⁻¹. The average pore size is 18-36 nm, thus biochar can

be classified as a mesoporous material (Kumar & Pant, 2015; Leng, Yuan, Huang, Wang, *et al.*, 2015; Liu & Zhang, 2009; Ponnusamy *et al.*, 2020). Biochar contains a variety of polar groups. Moreover, HTL biochar consists of more oxygen-containing functional groups than pyrolysis biochar. These functional groups include carbonyl, carboxyl, lactone, hydroxyl, and phenol (Liu & Zhang, 2011; Ponnusamy *et al.*, 2020). Furthermore, biochar can hold volatile organic matter, necessary for adsorption. As a result, HTL biochars are better suited for metal, dye, and pollutant adsorption than pyrolysis biochars, despite having a lower surface area (Leng *et al.*, 2015; Liu & Zhang, 2009, 2011; Ponnusamy *et al.*, 2020).

2.4.2.3 Aqueous phase

The HTL aqueous phase product offers an unutilised energy and nutrient resource. However, it is generally considered a waste stream bottlenecking the technical and economic upscaling prospects of HTL processes (Watson *et al.*, 2020). A large fraction of HTL products is in the form of a water-miscible aqueous phase. Depending on the feedstock and operating conditions, aqueous yields range between 20% and 50%. Roughly 10%-50% carbon and 50%-70% nitrogen migrate to the aqueous phase during HTL (Biller *et al.*, 2016; Cao *et al.*, 2017). After HTL, small polar organic products are more commonly found in the aqueous phase rather than in the biocrude-oil (Caprariis *et al.*, 2017). Lignocellulosic biomass typically yields aqueous phases containing mainly phenolics, alcohols, and organic acids (mostly as glycolic acid). Inorganic elements such as sulphur, silicon, and sodium are also present (Panisko *et al.*, 2015). With regards to sodium lignosulphonate (as used in this study), Marais *et al.* (2019) found that the main phenolic products recovered in the HTL aqueous phase include catechol, *p*-cresol, guaiacol, and vanillin. This adds potential value to this waste stream because phenolic compounds are commonly used for industrial purposes, and in the fragrance and pharmaceutical industries. Furthermore, the conversion of phenolic compounds to Benzene, toluene, ethylbenzene, and xylene materials may also increase the value of the HTL aqueous phase (Ponnusamy *et al.*, 2020). Utilising plastic waste as HTL feedstock results in a variety of products and aqueous phase yields, depending on the type of plastic. For example, dos Passos *et al.* (2020) reported 47.6%-62.5% yields of the aqueous phase when epoxy resin was used as feedstock. Furthermore, significant amounts of phenol were detected in the aqueous phase.

2.4.2.4 Gas

Gaseous emissions are another by-product of HTL. These generally pose a challenge to upscaling due to potentially harmful emissions (depending on the feedstock). Biomass feedstock typically yields 5%-10% of the original organic compounds. The main gas component is CO₂, with CH₄, CO, and H₂ also present (Cao *et al.*, 2016; Magdeldin *et al.*, 2017). Moreover, the HTL of different waste plastics has varying effects on the associated gas products. For example, Williams & Slaney

(2007) conducted HTL experiments and found the range of gas yields to be 2%-38%. Furthermore, a mixture of waste plastics produced significant amounts of light hydrocarbons, such as butane, propane, ethane, and methane.

2.4.3 HTL reaction mechanisms

The chemistry and reaction mechanisms of HTL are not yet fully understood. The abundance of chemical reactions and a wide range of products presents a challenge to confirming accurate mechanisms and kinetic models (Jindal & Jha, 2016b). Studies to date have focused on the different degradation pathways of lignin, cellulose, and hemicellulose present in lignocellulose (Xu & Li, 2021). Yin *et al.* (2011) studied the hydrothermal decomposition of BFR epoxy resin and presented probable decomposition pathways for FR4 brominated epoxy resin (BER) present in waste PCBs.

2.4.3.1 Reaction mechanism for biomass and lignin

The overall mechanism for HTL can generally be described by five steps. First, polymers depolymerise into fragments or monomers, which further decompose to form intermediate compounds. Hereafter, concurrent reactions occur: intermediate compound gasification, gas phase equilibrium reactions, and polymerisation into solids and oils (Ghavami *et al.*, 2021).

These steps can be applied to describe the reaction mechanisms related to the HTL of lignin. First, the complex lignin structure is depolymerised into various smaller fragments by hydrolysis and cleavage of the ether and carbon-carbon bonds (Xu & Li, 2021). These lignin fragments can be further decomposed into lighter demethoxylated compounds via complex, concurrent reactions, including hydrolysis, deoxygenation, dehydrogenation, dehydration, decarboxylation, and dealkylation. Hereafter, more complex intermediate chemicals such as alcohols, aldehydes, ketones, esters, phenolics, acids, and furans can be formed (Ghavami *et al.*, 2021; Rudra & Jayathilake, 2022; Xu & Li, 2021). Figure 2-6 illustrates a possible route for the depolymerisation of a lignin molecule into lignin fragments, whereafter smaller compounds are formed via the hydrolysis of methoxy groups. Although not illustrated, the other decomposition reactions occur concurrently with the demethoxylation reaction in Figure 2-6 (Liu *et al.*, 2006; Toor *et al.*, 2011).

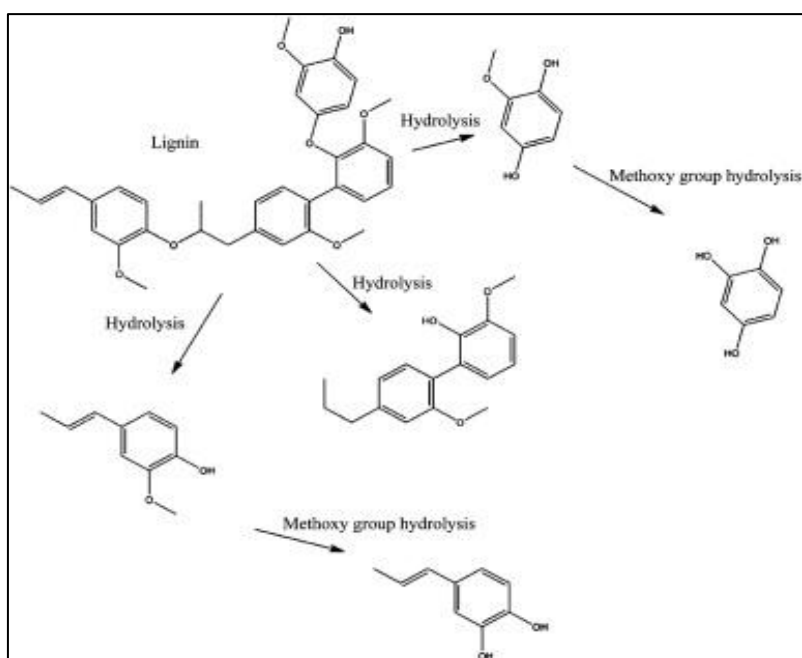


Figure 2-6: Basic reaction scheme for the decomposition of lignin through hydrolysis (reused from Toor *et al.* (2011) with permission from Elsevier, obtained through RightsLink)

After the decomposition into lighter intermediates commences, gas formation is initiated by reactions such as decarboxylation and steam methane reforming. Water-gas shift and methanation are the main equilibrium reactions during gas formation. Repolymerisation of intermediate chemicals produces char and biocrude-oil. Temperature is the main operating parameter, dictating the preferred production of bio-oil or biochar. Further gasification of biochar can take place (Ghavami *et al.*, 2021).

2.4.3.2 Reaction mechanism for PCB epoxy resin

Yin *et al.* (2011) have presented two possible reaction mechanisms for the decomposition of BER during HTL processing of waste PCBs: thermal decomposition and hydrolysis. According to Luda *et al.* (2002), BER will begin to decompose at 295°C, with a maximum decomposition rate at 297°C, in an inert environment. Typically, the thermal decomposition of polymers is dominated by free radical reactions (Barontini *et al.*, 2004). When the energy provided by the system is greater than the bond dissociation energy of the polymer, bonds will break and produce free radicals, as described by the bond-energy theory. The initial free radical formation leads to a propagation phase wherein more free radicals are formed as the initial free radical reacts with stable molecules, thus the polymer is gradually decomposed (Luda *et al.*, 2002; Yin *et al.*, 2011). Figure 2-7 illustrates a potential thermal decomposition pathway for BER as a two-step mechanism.

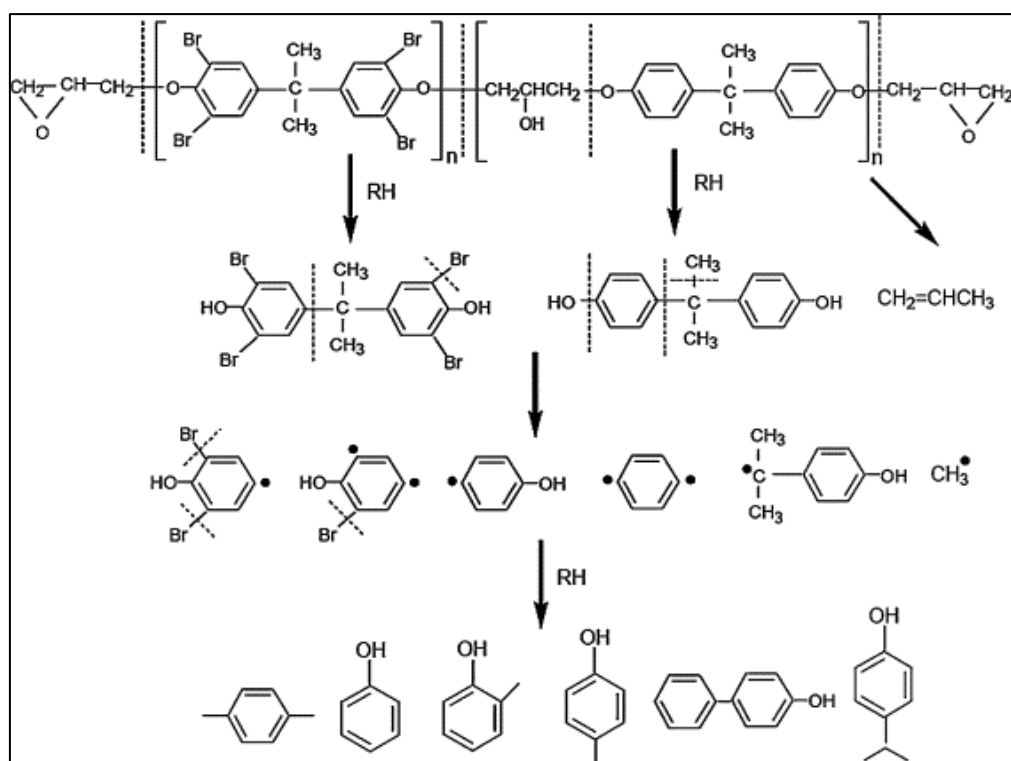


Figure 2-7: Thermal decomposition of BER at high temperatures (reused from Yin *et al.* (2011) with permission from Elsevier, obtained through RightsLink)

The first step involves the cleavage of weak bonds between monomeric units. The formation of BPA and TBBPA from this first step has been confirmed (Luda *et al.*, 2002). As more energy is applied to the system, higher energy bond cleavage becomes prominent; carbon-carbon, C₆H₅-O, and C₆H₅-Br bonds are cleaved. This allows the formation of smaller compounds such as *p*-xylene, *p*-cresol, *o*-cresol, phenol, phenyl phenol, *p*-isopropyl phenol, etc. (Yin *et al.*, 2011).

Hydrolysis is another potential decomposition pathway due to the hydroxide and hydronium ions obtained by adding water as a solvent. First, water leads to cleavage of the ether bonds in the epoxy resin monomeric units, resulting in the formation of BPA and other oligomers. Hereafter, the BPA decomposes to form *p*-isopropyl phenol and phenol (Yin *et al.*, 2011). The reaction mechanism for the hydrolysis of BER is illustrated in Figure 2-8.

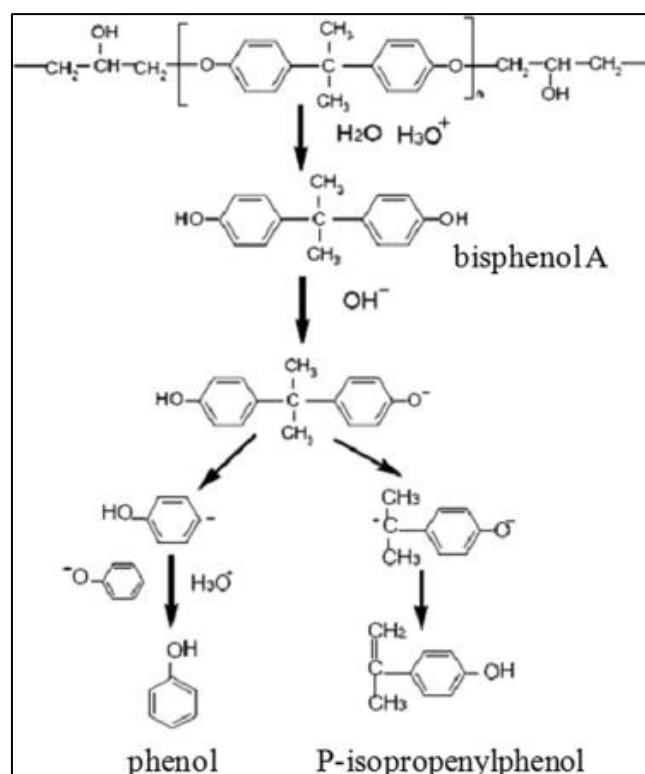


Figure 2-8: Hydrolysis of BER (reused from Yin *et al.* (2011) with permission from Elsevier, obtained through RightsLink)

2.4.4 HTL operating parameters

HTL of lignocellulose biomass and waste is a complicated process, wherein various operating parameters can have significant effects on product distribution, properties, and composition. Important parameters include temperature, residence time, solid-liquid ratio, pressure, and the heating rate (Dimitriadis & Bezergianni, 2017).

2.4.4.1 Temperature

Temperature is the most important operating parameter in HTL—it can influence yields, product composition, and the energy values of products. It is a well-established consensus that temperature has a synergistic effect on bio-oil yields due to enhanced fragmentation (Akhtar & Amin, 2011; Xu & Li, 2021). When the operating temperature provides sufficient energy to overcome the activation energies of bonds, comprehensive depolymerisation occurs. Subsequently, higher temperatures increase the free radical concentration as well as the tendency for fragments to repolymerise (Akhtar & Amin, 2011). Numerous HTL experiments have been conducted to determine the effect of temperature during HTL of various feedstocks. Generally, an increase in temperature increases the yield of bio-oil, however, this yield will reach a maximum, whereafter yields begin to decrease with further temperature increases. As a result, higher HTL temperatures are not viable for bio-oil production and energy efficiency. Intermediate temperature ranges have proven optimal for bio-oil yields (Xu & Li, 2021).

Furthermore, temperature dictates the competition between reactions such as hydrolysis, depolymerisation, and repolymerisation during HTL. Reaction temperatures within the subcritical range for water result in ionic reactions such as dehydration and hydrolysis to be favoured, with these increases resulting in ongoing bond cleavage and feedstock decomposition into lighter molecules. Moreover, condensation of these lighter molecules improves bio-oil yield (Xu & Li, 2021). When the reaction temperature approaches, and exceeds, the critical temperature of water, repolymerisation into residue or char becomes dominant, as well as the decomposition into gaseous products, thus reducing bio-oil yields (Islam *et al.*, 2018).

Besides the influence on yields, temperature can dictate the composition of products. For example, higher temperatures lead to a high carbon content of bio-oils due to the removal of oxygen; consequently, the heating values are significantly improved (Cao *et al.*, 2017).

2.4.4.2 Residence time

Residence time can be considered the second most influential process parameter. It is usually defined as the time duration wherein HTL is maintained at the desired temperature, excluding time for heating and cooling. Time has a direct impact on the yield distribution of HTL products (Cao *et al.*, 2017). In general, shorter residence times allow for the decomposition of feedstocks, with an increase in time allowing for increased bio-oil yields; however, longer residence times lead to the formation of gas, as well as intermediate products forming char or residue, therefore decreasing biocrude-oil yields (Xu & Li, 2021). Once the feedstock reaches the saturation point, increases in residence times result in higher probabilities for secondary reactions to form gas and solid products. Thus, increased residence times will lead to oil yields reaching a maximum, whereas gas and char or residue yields continuously increase until saturation is achieved (Akhtar & Amin, 2011). The upper limit to bio-oil yields at long residence times can be explained by the cracking of liquid product into intermediates, as well as the condensation, crystallisation, and polymerisation into char or residue (Xu & Etcheverry, 2008).

Residence time has a significant effect on the composition of HTL products. For example, Karagöz *et al.* (2004) observed differences in decomposition products between short and long residence times at 180°C and 250°C. Furthermore, the effect of residence time on complex reactions is heavily dependent on the reaction temperature—both parameters dictate the extent of HTL (Dimitriadis & Bezergianni, 2017).

2.4.4.3 Liquid-to-solid ratio

Water is an important variable in the HTL of feedstocks. It has various implications, such as acting as a hydrogen source, inhibiting secondary intermediate reactions, protecting free radicals, and the dispersion of feedstocks. Consequently, many studies have investigated the effects of the liquid

solvent-to-solid feed ratio during HTL (Cao *et al.*, 2017). Higher liquid-to-solid ratios enhance the dissolution of fragments, thereby reducing the prevalence of secondary reactions, thus decreasing gas and solid formation, while promoting biocrude-oil formation. Conversely, low liquid-to-solid ratios result in decreased dissolution of fragmented compounds, then the interactions between water and feedstock molecules become less prominent, thus promoting solid formation (Akhtar & Amin, 2011). However, increasing the liquid-to-solid ratio has an upper limit, whereafter there is a significant decrease in the biocrude-oil yield due to the self-condensation of bio-oil compounds to form solids (Cao *et al.*, 2017). Energy efficiency is also impacted at higher liquid-to-solvent ratios as more water requires heating (Dimitriadis & Bezergianni, 2017).

2.4.4.4 Pressure

Reaction pressure can be an influential process parameter under certain conditions. Generally, pressure is self-generated, it is mainly related to the reaction temperature and solvent, however, the initial pressure in batch reactors can be controlled via the input of an inert gas, such as nitrogen, before heating (Basar *et al.*, 2021). High pressures can be beneficial to the overall energy requirements for HTL because energy loss through phase transitions is avoided by the holding of water in liquid state until the critical point is reached, whereafter it becomes uneconomical due to high temperature requirements (Cao *et al.*, 2017). Maintaining pressure above the critical pressure of a solvent increases medium density, providing better penetration and feedstock decomposition. At supercritical conditions, the influence of pressure on the properties of a solvent and HTL reactions is significantly reduced (Durak & Aysu, 2016). For example, Qian *et al.* (2017) studied the effect of HTL pressure on sewage sludge at 250-400 bar and concluded that once the critical point of 221 bar was reached the pressure had an insignificant effect on the yield of biocrude-oil.

2.4.4.5 Heating rate

The heating rate is another variable affecting the HTL process. Higher heating rates support the fragmentation of feedstocks and inhibit the formation of residue or char, although secondary reactions that result in higher gas yields become more dominant at extreme heating rates due to near instantaneous decomposition and bond cleavage of macromolecules. Conversely, slower heating rates promote polymerisation reactions, leading to the formation of char (Akhtar & Amin, 2011). Heating rates have little influence on product distribution in HTL due to the dispersion and dissolution stability of fragmented molecules in high-pressure water, therefore yields of biocrude-oil are insensitive to changes at already high heating rates. However, improved bio-oil yields have been observed when increasing from low to high heating rates (Cao *et al.*, 2017; Xu & Li, 2021).

2.5 Severity factor

The combined effect of residence time and temperature on complex kinetic systems as present during the HTL of biomass can be quantitatively estimated by combining these operating parameters into a single variable, known as the kinetic SF. This allows for the direct transfer of laboratory-scale results to large-scale processes, as well as assisting in optimisation (Iroba *et al.*, 2014). The use of this SF is backed by the overlapping effect of residence time and temperature, as both parameters can be independently varied to achieve the same experimental outcome, assuming that kinetics follow a first-order dependence on concentration and the rate constant dependence on if temperature is of the Arrhenius model behaviour (Overend *et al.*, 1987; Prestigiacomo *et al.*, 2022). If the process can be assumed hydrolytic and follows an overall first-order conversion, the reaction ordinate can be expressed as follows (Iroba *et al.*, 2014):

$$R_o = t \times e^{\left[\frac{T_r - T_b}{E_A}\right]} \quad (1)$$

where R_o is the reaction ordinate, t is the residence time, T_r is the hydrolysis temperature, T_b is the base reference temperature (generally taken as 100°C), and E_A is the activation energy, where a conventional value of 14.75 can be used under the above-mentioned assumptions. Thus, the SF can be estimated by Equation 2 (Iroba *et al.*, 2014):

$$SF = \log_{10}(R_o) \quad (2)$$

The SF factor therefore allows for a comprehensive comparison of yield data by pairing time and temperature. However, the reaction ordinate is not universally valid, thus the SF can be exclusively viewed as a means of weighing time at a set reaction temperature via an arbitrary rate process—acting only as a device to combine these two parameters into a single variable (Lloyd & Wyman, 2005; Overend *et al.*, 1987).

2.6 Hydrothermal treatment of non-metallic PCB fractions

HTL treatment methods for non-metallic fractions in e-waste offer promising technology, however, they have received little attention. Considering the beneficial chemical and physical properties of water under sub- or super-critical conditions during hydrothermal processing, the latter could be a suitable method for recycling non-metallic waste PCB fractions. Evaluation of the hydrothermal treatment of non-metallic waste PCB fractions has been considered in a few studies (Yin *et al.*, 2011; Zhao, Xia, *et al.*, 2019).

Yin *et al.* (2011) studied both sub- and super-critical HTL of waste PCBs through investigating the effects of additives, residence times, and reaction temperatures on product distribution, and debromination, in a 5.7-ml batch reactor. Results indicated BER decomposition >80%. At >300°C

for 30 min, mainly phenol was produced when alkaline additives were present. At 300°C, debromination was incomplete; compounds such as 2,6-bromophenol and 2-bromophenol were detected. At higher temperatures, debromination was complete, and the subsequent phenolic content was even higher. Yin *et al.* (2011) concluded that low-temperature hydrolysis and high-temperature thermal decomposition reactions were the probable reaction mechanisms, as seen in Figure 2-8 and Figure 2-7, respectively.

Yildirim *et al.* (2015) concluded similar results during the hydrothermal treatment of waste PCBs in a 500-ml batch reactor. Approximately 94% of BER was decomposed at 400°C with a water solvent and NaOH additives present. Bio-oil products were composed of 62.5 wt.% phenol, with some additional phenolic compounds present. Furthermore, the bromine content mainly migrated to the aqueous phase, with almost no bromine detected in the bio-oil product. Similarly, Soler *et al.* (2017) investigated the debromination of waste PCBs under subcritical HTL conditions and observed that 18-64 wt.% of bromine migrated to the aqueous phase. Okajima *et al.* (2002) also observed 90% BER decomposition at 350-380°C, when using water as solvent at sub- and supercritical states. Monocyclic phenolic compounds such as *p*-isopropyl phenol and phenol were detected. These results are similar to the findings of Xing & Zhang (2013), wherein waste PCBs were depolymerised under sub- and supercritical HTL conditions, with liquid products containing no bromine, with approximately 59% phenol and 22% 4-(1-methyl ethyl)-phenol. Furthermore, a 97.8% debromination rate was achieved at 400°C and 120 min.

From these studies, it is evident that phenolic compounds are common organic products obtained from HTL of waste PCB non-metallics. These phenolic compounds have shown desirable bioactive properties, such as antiproliferative, anticancer, antiviral, anti-inflammatory, antimicrobial, and antioxidant activities, resulting in much interest from key industries. These properties offer many health benefits, thus pharmaceutical, cosmetic, and food industries utilise these compounds. Applications in the packaging and textile industries have also been explored (Albuquerque *et al.*, 2021).

2.7 Metal recovery through hydrothermal treatment

HTL presents an effective method for the removal of hazardous substances from solid waste. It is capable of separating halogens from halogen-containing polymers, as illustrated by the debromination of BER and waste PCBs (Okajima *et al.*, 2002; Xing & Zhang, 2013; Yildirim *et al.*, 2015; Yin *et al.*, 2011). Although rarely the focus of study, HTL has also been proven to extract various metals from high-metal-content solid waste, such as waste PCBs, manure, sewage, and biomass (Zhan *et al.*, 2020).

Xing & Zhang (2013) evaluated the metal recovery from waste PCBs during sub- and supercritical HTL treatment, along with the debromination capacity. After treatment at 400°C for 120 min, ~98 wt.% Cu could be separated from the solid residue product with the aid of a high-speed crusher. The solid residue product was not homogenous, therefore the fractions obtained from crushing could be divided into three categories: large metals (>2 mm), small metals (0.15-2mm), and nonmetals (<0.15 mm). Cu reached a purity of 97% and 93% in the large and small metal fractions, respectively, whereas Pb, Sn, Zn, and Ag were most common among the small metal fractions.

Matsumoto & Oshima (2014) studied the supercritical HTL of waste PCBs under both oxidative and nonoxidative conditions. At 400°C and 250 bar, without an oxidant, >99% of Au and Cu was recovered as stable solids. Under oxidative conditions, solid state Au recovery remained unchanged; conversely, 90% of Cu was recovered in the form of Cu oxides. Furthermore, the presence of Cu enhanced the decomposition of organics in waste PCBs. Similarly, Li & Xu (2015) studied the supercritical treatment of heterogeneous waste memory modules, which is a form of waste PCB, for the decomposition of BER and recovery of Cu. After treatment, the Cu could easily be recovered from other inorganics (such as glass fibres) due to lower interfacial bonds of the solid residue product, thus achieving a Cu recovery rate of 99.89%.

As there are only a few studies addressing metal recovery through HTL of waste PCBs, the metal recovery capabilities from other metal-containing feedstocks were considered. Lu *et al.* (2017) studied the recovery of heavy metals and alkaline-earth metals after HTL of human faeces. Characterisation of the products revealed that most of the Zn (94%), Fe (72%), Al (88%), Mg (81%), and Ca (89%) migrated to the solid residue, whereas most of the Na (73%) and K (89%) was found in the aqueous phase. As a result of the alkaline nature of the aqueous phase, Na and K could easily be dissolved, whereas Zn, Fe, Al, Mg, and Ca formed metal salts, thus precipitating to the solid residue. Lu *et al.* (2018) studied the heavy metal migration during HTL of swine manure for the production of bio-oil. More than 70% of metals migrated to the solid residue. The metals included Cd (85%), Pb (79%), As (75%), Cu (74%), and Zn (80%). The accumulation in the solid residue could be attributed to salt-forming participation reactions. On the other hand, the remaining metal distribution to the bio-oil and aqueous phase was dependent on the metal speciation.

Similarly, He *et al.* (2021) evaluated the transition and recovery of heavy metals during HTL of *Sedum plumbizincicola*. Heavy metals were mainly found in the solid residue and aqueous phase, with <10% migrating to the bio-oil. Furthermore, As was the only heavy metal accumulating in the aqueous phase. Increased residence times at low temperatures lead to improved immobilisation of Mn, Fe, As, Cr, Pb, Zn, and Cd. Increasing the temperature facilitated the transition of all metals, excluding As, to the solid residue. However, at temperatures >330°C, the metal content in the solid

residue was reduced, with ~30% of metals found in the liquid products, possibly due to the degradation of the metal-organic bonds at high temperatures.

2.8 Metal sorption

2.8.1 Chemical speciation of metals

HTL has proven to be an effective means of metal recovery from a wide range of metal-containing feedstocks. Due to the low reaction temperatures, most metals tend to remain in a stable solid state, and they can be recovered in the solid residue product. However, fractions of metals can migrate to the liquid products as they are transitioned to a more reactive state or through the formation of water-soluble metal compounds during HTL. This transition can be facilitated by various processes, such as ionisation, complexation, or solubility changes under HTL conditions (He *et al.*, 2021). Hence, the risks of the presence of heavy metals in liquid products must be minimised by immobilising as many metals in the solid residue as possible (Huang & Yuan, 2016). Therefore, it is necessary to categorise the speciation of metals. The speciation of metals can be determined through the European community bureau of reference (BCR) sequential extraction method, which aims to extract and categorise the various metal speciations into four groups (Huang & Yuan, 2016).

First, the exchangeable fraction (F1) is described by the metals that are loosely bound to the surface of the feedstock and can be easily exchanged. These include metals that dissolve into free ions during HTL, as well as complexed soluble metal ligands. Second, the reducible fraction (F2) describes metals that are bound to easily reducible agents, such as sulphides, iron, or manganese oxides. Third, the oxidisable fraction (F3), refers to metals bound to easily oxidisable agents, including complexes between organic materials and metals (He *et al.*, 2021). Lastly, the residual fraction (F4) represents the remaining solid residue containing stable metals tightly bound in the biochar that are unlikely to be released (Huang & Yuan, 2016).

From the BCR categorisations, it is evident that, during HTL, metal ions can dissolve as soluble ions and form complexes with organic ligands. In addition, metal ions can adsorb onto solid particles generated during HTL through various mechanisms. Fractions of metal ions undergo oxidation, resulting in the formation of metal oxide species that can precipitate or remain suspended. Furthermore, metals can be complexed with organic matter derived from the feedstock, hence impacting their distribution.

It should be noted that the BCR method only provides a general framework for the various speciations present during HTL—the complex nature of HTL results in potential overlap between the four groups. For example, organically bound metals incorporated into the biochar matrix could

exhibit characteristics of both the oxidisable fraction as well as the residual fraction. These organic-metal compounds can nonetheless be considered immobilised as they remain in the biochar.

2.8.2 Biochar adsorption

The migration of metals to the liquid products can be inhibited through the presence of biochars during HTL of high-metal content feedstocks. Several mechanisms have been proposed for the sorption of metals via biochars; however, the prevalence of each mechanism is subject to the physiochemical properties of biochars. These include surface area, porosity, surface charge, pH, functional groups, and mineral content (Li *et al.*, 2017).

Pore size and surface area in biochars are very important factors for metal sorption. In general, pores develop when biomass is converted to biochars; sizes can range from nano-pores (<0.9 nm) to micro-pores (<2 nm), then to meso-pores (2-50 nm) and macro-pores (>50 nm). Larger pore sizes constitute larger surface areas. Pores can act as a physical obstruction to metal sorption, as large sorbates cannot be entrapped in pores smaller than the sorbates themselves, regardless of polarity or charge. Typically, biochars derived from lignin-rich biomass sources form a macro-porous structure (Ahmedna *et al.*, 2004; Li *et al.*, 2017; Ponnusamy *et al.*, 2020). Studies have shown that higher operating temperatures give larger pore structures and subsequently larger surface areas; however, this is not universal, as extreme temperatures can begin to cause the degradation of pore structures, thus reducing the surface area (Li *et al.*, 2017).

The pH of biochars can also be a defining factor of sorption capacity. Biochar pH is dependent on feedstock and temperature, with increasing operating temperatures correlating to a higher pH (Li *et al.*, 2017). Higher pH is explained by the higher ash content of biochars at high temperatures, as well as the removal of acidic functional groups such as carboxyl groups. Basic functional groups are more prominent in biochars produced at higher temperatures (Al-Wabel *et al.*, 2013). Surface charge is also an important variable and is dictated by the solution pH. For example, if the solution pH is higher than the zero-charge point (solution pH where the biochar surface charge is zero), the biochar will be negatively charged and attach to metal cations such as Hg(II), Pb(II), and Cd(II). Conversely, if the solution pH is lower than the zero-charge point, metal anions will bind to the biochar. High temperatures can reduce negatively charged functional groups, resulting in a less negative overall surface charge (Li *et al.*, 2017).

Biochar functional groups determine the prevalence of sorption mechanisms such as complexation (Li *et al.*, 2017). For example, numerous functional groups are present in lignin structures, for example, hydroxyl, amino, methoxy, carbonyl, and carboxyl groups. Therefore lignin can serve as an effective adsorbent for heavy metal ions, such as Zn(II), Cd(II), Cu(II), Ag(I), and Pb(II), with hydroxyl groups having a higher affinity for these ions than carboxyl groups (Guo *et al.*, 2008; Li, Yang, *et al.*, 2022). Studies suggest that increasing temperature reduces the abundance of these

functional groups, possibly due to increased carbonisation (Li *et al.*, 2017). Lastly, biochar sorption can be influenced by the availability of mineral elements such as P, Mg, Ca, and K. The mechanisms relating to minerals are mainly precipitation and cation exchange (Cao *et al.*, 2009). Biochar yield can be influenced by operating parameters such as temperature and residence time. Therefore, the mineral concentration can be increased by decreasing the biochar yield.

Although pyrolysis-derived biochars have an increased surface area, the high temperatures increase the ash content, along with the loss of volatile compounds. Consequently, the functional groups with metal sorption abilities are reduced, thus inhibiting biochar sorption potential (Guo & Rockstraw, 2007; Ponnusamy *et al.*, 2020). However, HTL-derived biochars are prepared at lower temperatures, hence the functional groups are retained and lead to better metal sorption capacity (Liu & Zhang, 2011). Liu *et al.* (2010) compared the Cu sorption of HTL and pyrolysis biochars derived from pinewood and concluded that HTL biochar sorption was mainly achieved through ion exchange, whereas pyrolysis biochar sorption was achieved through physical sorption due to a higher surface area. HTL biochars increased the total oxygenated functional groups, while pyrolysis biochars decreased these functional groups. Thus, HTL biochar was found to have a higher sorption capacity for Cu, despite it having a lower surface area than pyrolysis biochars.

2.8.3 Mechanisms for metal sorption

Five governing mechanisms of metal sorption by biochars from an aqueous mixture have been proposed. These include precipitation, electrostatic attraction, chemical reduction, cation exchange, and complexation (Li & Xu, 2015). Figure 2-9 illustrates these five mechanisms.

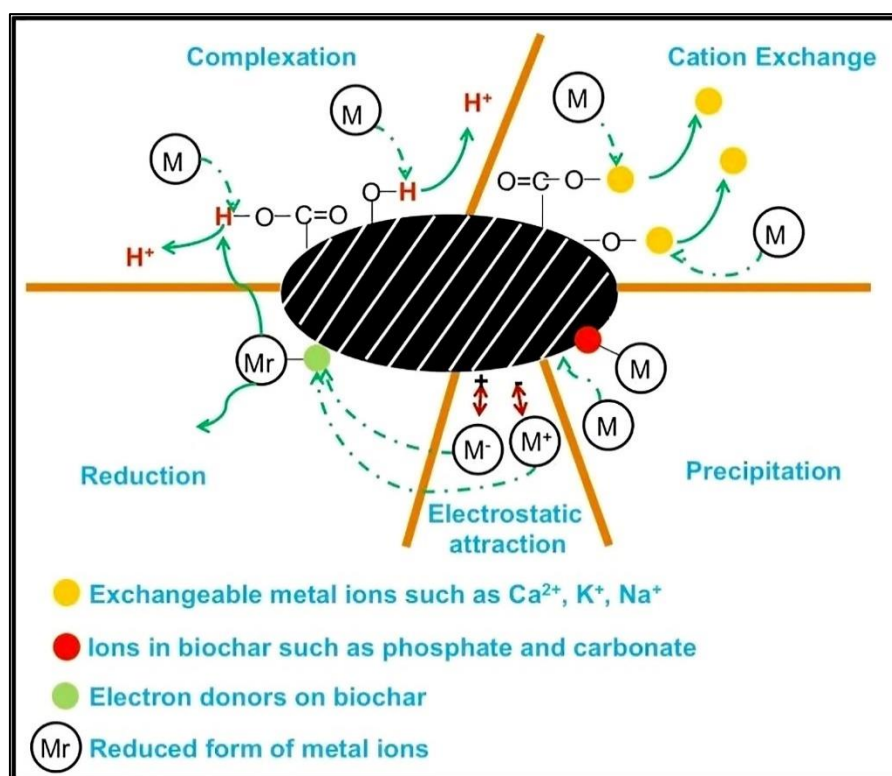


Figure 2-9: Biochar adsorption mechanisms of metals (reused from Li *et al.* (2017) with permission from Elsevier, obtained through RightsLink)

The extent of each mechanism is heavily dependent on the targeted metal to be adsorbed. For example, the main mechanism responsible for the sorption and reduction of Cr is electrostatic attraction and complexation, whereas adsorption of Cu(II) and Pb(II) in biochar derived from peat biomass is through complexation and cation exchange of carboxyl groups (Qin *et al.*, 2006; Zhou, Liu, *et al.*, 2016). Furthermore, the characteristics of the biochar adsorbent also dictate the prevalence of certain sorption mechanisms. Zhao *et al.* (2019) compared the sorption capacities of various types of biomass, including wood, sewage sludge, corn, and agricultural waste. A further comparison of pyrolysis biochars derived from wood, corn and sewage sludge was made, wherein complexation and cation exchange via Ca, K, and Mg are the main sorption mechanisms for Pb(II), Cu(II), Cd(II), and Cr(II).

2.9 Conclusion

In conclusion, the HTL of waste PCBs for metal and organic recovery has received limited attention in the literature to date—other types of feedstocks, such as lignocellulosic biomass, microalgae and plastic wastes appear to dominate this field of research (Jin *et al.*, 2020). Hence, there is a need for further studies on the HTL of waste PCBs and e-waste. Gaps in the available literature include the optimisation of process parameters, and a comprehensive study of the product composition and distribution (Mathanker *et al.*, 2021). Available literature on the co-liquefaction of waste PCBs and e-waste with biomass for metal adsorption is also limited—most studies only

explore the adsorption capabilities of individual biochars in multiple-metal solutions (Zhao *et al.*, 2019).

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter describes the materials and methods used in this study. Section 3.2 addresses the procurement of materials, including the chemicals and gasses used for experiments and analyses, and the preparation of raw materials to usable feedstocks. Section 3.3 describes the experimental sets and analyses performed. In Section 3.4, the experimental setup and methods used for HTL experiments are presented. The methods for digestion of samples are also described. Lastly, Section 3.5 gives detailed explanations of the analytical methods used in this study.

3.2 Materials

3.2.1 Raw materials

Two primary raw materials were used: waste PCBs and sodium lignosulphonate. The waste PCBs were locally sourced from a collection of discarded computers, collected in Potchefstroom and Klerksdorp, South Africa. The PCBs underwent disassembly, which included the removal of components such as motherboards and memory circuits. Figure 3-1 illustrates the end-products from the disassembly and pre-processing of waste PCBs into a suitable HTL feedstock.

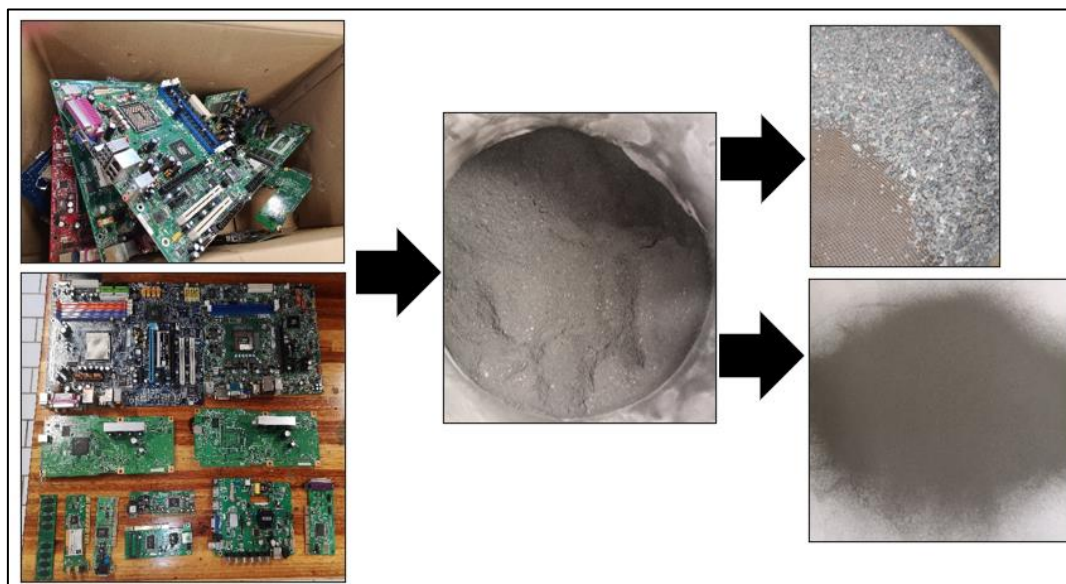


Figure 3-1: Pre-processing steps for waste PCB feedstock (left) with milled sample (middle), smeared metals (top right) and sieved sample (bottom right)

Pre-processing entailed the milling of whole PCBs to particle sizes <2.36 mm. Milling was carried out by the SGS Vaal River Chemical Lab, Orkney, South Africa. Milled samples were

heterogeneous due to the smearing tendencies of certain metals in PCBs. Van Yken *et al.* (2021) concluded that a reduced particle size increases the likelihood of a homogeneous waste PCB sample, as well as exposing more metals to the effect of chemical treatment. Therefore, further sieving was conducted to obtain suitable samples for HTL experiments. This was accomplished by manually sieving the milled samples to obtain particle sizes <177 µm. In addition to waste PCBs, sodium lignosulphonate (a by-product of the sulphite pulping process) was obtained from SAPPI, South Africa. The inclusion of this biomass was motivated by the potential immobilisation of metals during co-HTL with metal-containing feedstocks (Huang & Yuan, 2016). To ensure that representative subsamples were taken from both feedstocks; the cone-and-quartering method was used, in accordance with the ASTM D6323-19 standard. Subsequently, both feedstocks were stored in airtight containers to prevent contamination or moisture absorption.

3.2.2 Chemicals and gases

Various chemicals and gasses were required. Table 3-1 lists the materials (as used for the HTL experiments, product recovery, and digestion), their purities and the names of suppliers, and their specific applications here.

Table 3-1: Materials used during HTL and product recovery

Material	Supplier	Purity (%)	Application
Deionised water	North-West University	100	Solvent for HTL
Nitrogen	Afrox	99.9	HTL reaction atmosphere
Acetone	Sigma-Aldrich	99.9	Organic solvent for bio-oil extraction
Hydrochloric acid	ACE Chemicals	37	Digestion of metals
Nitric acid	ACE Chemicals	55	Digestion of metals

Various other chemicals were used during the preparation of products for compositional analyses. These materials, including their purity and names of suppliers, and their application in various analyses, are listed in Table 3-2.

Table 3-2: Materials used during product preparation for compositional analyses

Material	Supplier	Purity (%)	Application
Dichloromethane	ACE Chemicals	>99.8	Bio-oil dissolving agent for GC-MS and FTIR analyses
Potassium bromide	Sigma-Aldrich	>99.0	Blank sample for FTIR analysis
Gallic acid	PhytoLab	>98.0	Internal standard for total phenolic determination
Dimethylsulphoxide	Honeywell Riedel-de Haën	>99.7	GPC mobile phase for bio-oil analysis
Lithium bromide	Sigma-Aldrich	>99.0	GPC mobile phase for bio-oil analysis

3.3 Experimental sets

In this study, there are three experimental sets corresponding to the objectives presented in Section 1.5. The first experimental set is the characterisation of sodium lignosulphonate and the processed PCB sample. Table 3-3 presents the compositional analyses that were performed for feedstock characterisation.

Table 3-3: Compositional analyses for the characterisation of feedstocks

Sodium lignosulphonate	Waste PCBs
Elemental	Elemental
Proximate	Proximate
FTIR	FTIR
ICP-OES	ICP-OES
	XRF

In the second experimental set, the influence of operating temperature and residence time on the HTL products, as well as the repeatability and confidence levels for experiments, is determined. The effect of these two variables was determined using 250, 275, 300, and 330°C as operating temperatures. The residence time was varied: 20, 40, 60, and 80 min. For these experiments, a 43% volume loading and a 1:1 PCB to lignosulphonate loading were used. The solid and solvent mass loadings were selected as 44 wt.% and 56 wt.%, respectively. The HTL experiment with the optimal conditions for bio-oil yield was repeated four times to establish the repeatability of the experiments.

The third experimental set seeks to determine the influence of waste PCB loading on the HTL products. The effect of waste loading was determined by varying the PCB mass loading of the total solid input, resulting in a PCB loading of 0, 10, 30, 50, 70, 90, and 100 wt.%, while maintaining a constant total solid mass loading. The solvent mass loading was kept constant and the operating conditions for optimum bio-oil yield from experimental set two were selected. Table 3-4 provides

the analyses used to characterise HTL products from experimental sets two and three. Section 3.5 expands on the results, including the methods and instruments used for the analyses conducted in this study.

Table 3-4: Analyses of HTL products

Bio-oils	Residues	Aqueous phases
ICP-OES	ICP-OES	ICP-OES
Elemental	Elemental	Total phenols
FTIR	FTIR	
HHV	Proximate	
GC-MS		
GPC		

3.4 Experimental methods

3.4.1 HTL

3.4.1.1 Experimental setup

The HTL experiments were conducted within a batch SS316 autoclave with maximum operational parameters of 450°C and 150 bar. The autoclave comprises a casing equipped with a detachable sleeve designed to hold the feedstocks during experiments. The reactor sleeve measured 50 mm in diameter and 120 mm in height, and had a capacity of ~180 ml. The reactor casing (wall thickness 20 mm) incorporates an internal copper seal. The casing could be secured to the top section of the vessel through the fastening of eight upward-protruding bolts. The reactor vessel and instruments are shown in Figure 3-2.

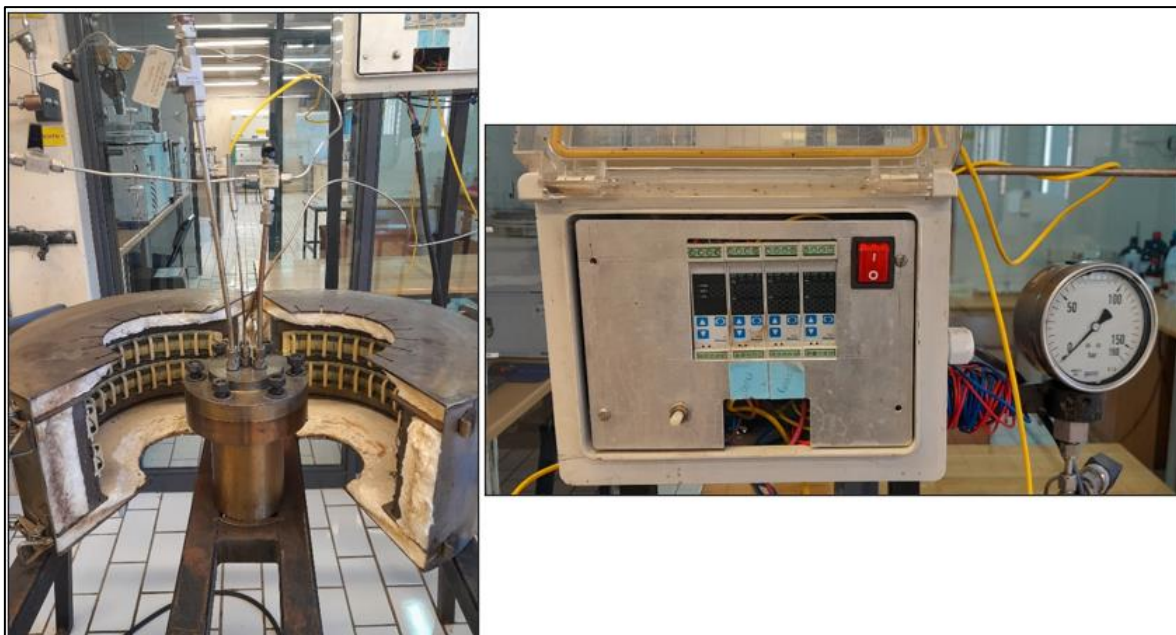


Figure 3-2: HTL reactor vessel (left), temperature indicator and controller, and pressure gauge (right)

The upper section of the reactor was equipped with an emergency pressure relief valve that activates at 160 bar to prevent structural damage by depressurising the reactor. Heating was achieved through the use of a removable heating mantle. In terms of instrumentation, both a pressure gauge and a temperature indicator and controller (TIC) were connected to the reactor. A schematic of the entire reactor setup is presented in Figure 3-3.

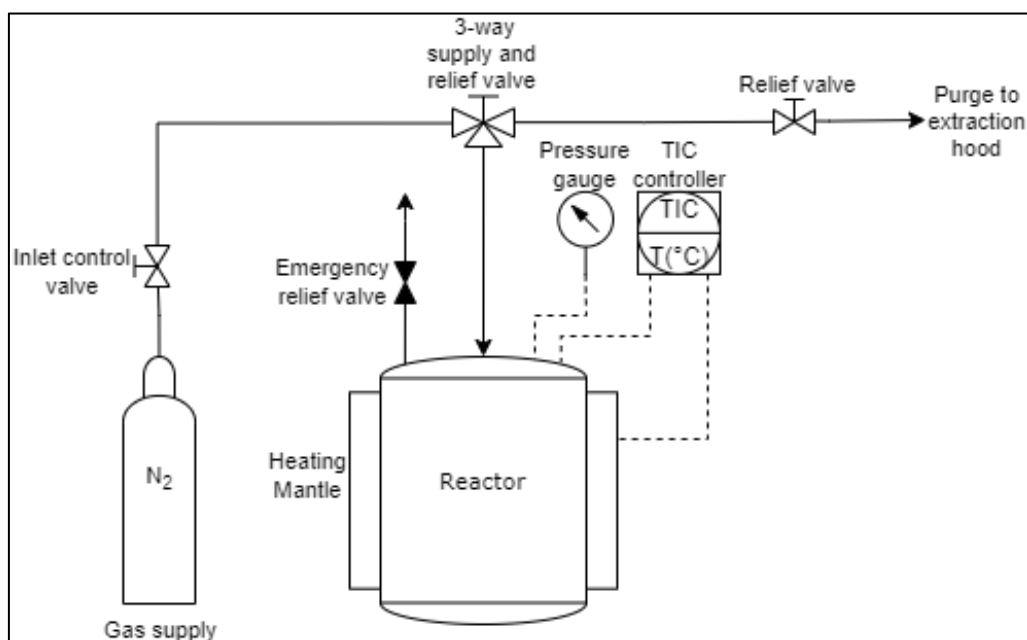


Figure 3-3: Schematic of reactor setup

Both the reactor and heating mantle were equipped with Wika type-K thermocouples, connected to the TIC, enabling simultaneous monitoring and control of the reactor and mantle temperatures. The

nitrogen supply and pressure relief system were managed via a Swagelok SS-41GXS2 three-way valve. Purging of the vessel was carried out through gas lines extended to an extraction hood.

3.4.1.2 Reactor preparation

Due to the extreme operating conditions of the HTL experiments, the reactor was inspected prior to all experiments. The copper seal, casing bolts, and valves were visually and manually checked for any damage. To prevent cross-contamination, the reactor sleeve was treated for 5 min with a cleaning solution containing dilute hydrofluoric acid, nitric acid, and sulphuric acid. Hereafter, hot water and soap were used to wash the sleeve, whereafter it was dried at 105°C for 10 min prior to the loading.

3.4.1.3 Sleeve loading

Sleeve loading steps were consistently maintained to minimise variations in feedstock input. First, the waste PCB and lignosulphonate samples were blended before being transferred to the reactor sleeve. A total solid input of 30 g was selected for this purpose. Subsequently, ~30 g deionised water was added to the sleeve, followed by mixing (using a glass stirrer) to create a uniform slurry. Any residual material on the glass stirrer was carefully washed into the sleeve with additional deionised water, ensuring that the total liquid input remained within the specified limit of 39.6 g. The liquid and solid loading equates to 56.9 and 43.1 wt.%, respectively. These loading parameters were determined through several experiment iterations to achieve conditions that generated enough HTL products for subsequent analyses, whilst also ensuring that the reactor pressure remained above the vapour pressure of water (maintaining subcritical conditions) for the selected temperatures, without surpassing the maximum design pressure.

3.4.1.4 Experimental procedure

The loaded sleeve was placed inside the reactor casing. The upper section was then secured to the casing, ensuring the thermocouple reached the feedstock mixture inside the sleeve. Bolts were systematically fastened with a torque wrench to a maximum of 110 Nm. Hereafter, the reactor was pressurised to 50 bar using nitrogen gas. A water–soap mixture was sprayed on all valves and fittings, and around the copper seal. The setup was then observed for 10 min to detect any potential leaks. If no leaks were detected, the water–soap mixture was removed using high-pressure air. Next, the nitrogen and air were gradually purged from the sealed reactor. To remove oxygen from the reactor, the purging procedure was carried out three times. Subsequently, the heating mantle was secured around the reactor and the desired mantle temperature setpoint was selected. The temperature and pressure of the reactor were monitored and recorded at 5-min intervals to establish comprehensive temperature and pressure profiles for each HTL experiment.

The temperature profiles are illustrated in Figure 5-1 to Figure 5-5 and the pressure profiles are illustrated in Figure 5-6 to Figure 5-10 (all taken up in Appendix A). These profiles provided a basis for assessing the consistency of operating parameters for each experiment. The mantle temperature was adjusted to control the reactor temperature for the desired residence time once the selected operating temperature was achieved. The reactor temperature was maintained within 2°C of the setpoint. After the desired residence time was reached, the heating mantle was opened, and the reactor was allowed to cool to 30°C. The gas product was gradually vented, whereafter the reactor was opened to enable the removal of the sleeve for product separation and recovery.

3.4.1.5 Product separation and recovery

After HTL, the reactor sleeve was removed and weighed. Some of the aqueous phase escaped the sleeve during HTL. The product was therefore collected from the reactor casing and top section with a paper towel and weighed accordingly. A Büchner funnel vacuum filtration setup was used to collect most of the aqueous phase, whereafter the Büchner flask in the filtration setup was replaced. The solid residue was washed with 300 ml acetone solvent to recover the bio-oil product. After washing, the solid residue, along with the filter paper, was dried at 60°C overnight. The mass of solid residue was determined. The product was then stored in sealable plastic bags.

The bio-oil product was recovered after removal of the acetone solvent by vacuum distillation, using a Buchi R-100 rotary evaporator. However, small fractions of the aqueous phase tended to remain with the bio-oil product. Thus, the remaining aqueous phase was decanted from the bio-oil product after chilling the heterogeneous mixture at -18°C for 7 min. Chilling increased the viscosity of the bio-oil product, allowing for easier decanting of the remaining aqueous phase. The remaining bio-oil was transferred to a sealable glass storage vessel. The bio-oil was dried overnight at 60°C, and weighed accordingly, before storage in a refrigerator. The gas products from the HTL experiments could not be collected.

3.4.2 Metal recovery

The metal distribution in the HTL products was of particular importance in the present study. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the concentrations of various metals in the product fractions. However, ICP-OES is only applicable to aqueous solutions, thus necessitating the digestion of PCB feedstock, bio-oil, and residue samples, to enable the determination of their metal contents. Samples were prepared according to the US EPA solid waste 846 Test Method 3051a for microwave-assisted acid digestion of sediments, sludges, soils, and oils. This method is effective for dissolving various metals, including Cu, Fe, Al, Pb, Ag, Cd, Zn, etc. (Das & Ting, 2017). Digestion was performed in an Anton Paar Multiwave PRO microwave digestion system, as illustrated in Figure 3-4.



Figure 3-4: Microwave digester (left), lip-sealed digestion vessel (middle), and digested sample (right)

To prevent contamination, the digestion vessels were cleaned in a similar manner to the reactor sleeve. In the case of solid samples, 0.5-g samples were manually transferred to the vessels. It was rather difficult to transfer bio-oil sample to the bottom of the digestion vessels, thus 0.25-g bio-oil samples were first dissolved in 20 ml acetone and then transferred to the vessels. Removal of the acetone, by evaporation, was achieved by drying the vessels plus content overnight at 60°C. The test method prescribed the use of 12 ml aqua regia (3 parts hydrochloric acid and 1 part nitric acid) as a digestion agent. PTFE-coated magnetic stirrers were placed inside each loaded vessel before fastening the vessels to the rotor inside the microwave digester. Digestion was performed for 1 h at 175°C. Thereafter, the samples were filtered through a 0.45-μm syringe filter and solutions for analysis were made up to 50 ml with deionised water. Analyses were then carried out by ICP-OES.

3.5 Analytical methods

3.5.1 Product yields

The total masses of residues and bio-oils were determined by measuring the dry-weight products following their separation. The mass of the aqueous phases was derived from the product mass after the initial Büchner vacuum filtration, along with the amount decanted and evaporated from the bio-oil post-drying. Consequently, the mass of the gaseous products was determined through the conservation of mass, as outlined in Equation 3:

$$Mass_g = Mass_f - Mass_{AP} - Mass_{BO} - Mass_R \quad (3)$$

where $Mass_g$ is the mass of the gas product; $Mass_f$ is the total mass of feedstock, including the mass of water; $Mass_{AP}$ is the mass of the aqueous phase; $Mass_{BO}$ the mass of the bio-oil; and $Mass_R$ the mass of the residue. Hence, the product yields can be expressed by Equation 4:

$$Product\ yield\ (m\%) = \frac{Mass_p}{Mass_f} \times 100 \quad (4)$$

Here, $Mass_p$ denotes the mass of the bio-oil, aqueous phase, gas, or residue product.

3.5.2 Severity analysis

As described in Section 2.5, the SFs are a representational variable that combines the effects of temperature and residence time into a single factor, which can then be used to compare HTL product yields. The calculated SF values for the second experimental set are presented in Table 3-5.

Table 3-5: Combined severity factors for temperatures and residence times used in this study

Temperature (°C)	Residence time (min)	Severity factor
250	20	5.72
	40	6.02
	60	6.19
	80	6.32
275	20	6.45
	40	6.75
	60	6.93
	80	7.06
300	20	7.19
	40	7.49
	60	7.67
	80	7.79
330	20	8.07
	40	8.37
	60	8.55
	80	8.68

3.5.3 Compositional analyses

3.5.3.1 Elemental analysis

Elemental analysis involves the determination of the mass fraction for hydrogen, carbon, and nitrogen in both organic and inorganic samples. This is achieved through combustion in an

environment of pure oxygen, with helium serving as an inert purging and carrier gas. Analyses were performed on feedstocks, bio-oils, and residues using a CE-440 elemental analyser (Exeter Analytical Inc.). From the elemental mass fractions, the H/C, N/C, and O/C ratios were calculated, using the relevant atomic weights. The SANS 17247:2006 standard operating procedure was followed.

3.5.3.2 Proximate analysis

The proximate analysis provides a compositional distribution of moisture, volatiles, fixed carbon, and ash content in a sample. The moisture content was calculated as the mass loss after drying a 0.5-g sample in a ceramic crucible at 105°C for 12 h. After moisture loss, the volatile content was determined as the mass loss from heating the sample at 900°C for 7 min in a Carbolite Gero VMF 1000 furnace. The ash content was determined as the remaining mass after heating the sample at 815°C for 12 h in a Carbolite Gero AAF 1100 furnace. Mass loss during this step represents the fixed carbon content of the sample. Moisture, fixed carbon, and ash content were determined according to the NREL/TP-510-42622 and SANS 131:1997 / ISO1171:1997 standard methods. The volatile content was according to the SANS 50:1998 / ISO562:1998 standard methods.

3.5.3.3 HHV analysis

The higher heating value (HHV) provides the energy generated when a sample is fully oxidised. The HHV values of several bio-oils were determined using an IKA KV600 digital chiller and an IK C5003 bomb calorimeter. However, HHV analysis could not be performed on all bio-oils due to the required sample mass to be oxidised and the limited mass of most bio-oil samples available. Thus, various correlations were compared using the compositional data obtained from elemental analyses to determine a correlation with the smallest average absolute error to the values obtained from the bomb calorimeter (Demirbas *et al.*, 2018; Mateus *et al.*, 2021). Equation 5 has the lowest average absolute error and was used to estimate the HHV of all bio-oils (Bychkov *et al.*, 2017):

$$HHV (MJ.kg^{-1}) = 0.00355C^2 - 0.232C - 2.230H + 0.0512CH + 0.131N + 20.6 \quad (5)$$

where C , H , and N are the mass % values of carbon, hydrogen, and nitrogen determined by elemental analysis.

3.5.3.4 Total phenolic content analysis

The quantification of the total phenolic content in the aqueous phase samples was carried out following the method outlined by Vernon *et al.* (1999), using the Folin–Ciocalteu reagent, with gallic acid serving as the standard reference. A Shimadzu UVmini-240 UV-VIS spectrophotometer was used to measure the absorbance at 765 nm. The phenolic content is reported in grams per litre

(g/l) as phenols and calculated in terms of gallic acid equivalents. Figure 5-24 in Appendix B shows the calibration curve using gallic acid as a standard compound.

3.5.3.5 GC-MS analysis

A semi-quantitative analysis of the bio-oils was conducted using gas chromatography-mass spectrometry (GC-MS), in a method used to determine the presence of chemical compounds in the bio-oils. The concentration of a chemical substance within a sample, expressed as an area%, can be determined by examining the area under the corresponding peak in the chromatograph. Compounds identified with a certainty of $\geq 80\%$ were quantified and categorised into different chemical groups, with their relative proportions normalised to 100%.

The GC process involves the vaporisation of a sample into a gaseous phase, followed by separation into various compounds using a capillary column and an inert carrier gas. The interaction of the different compounds and the stationary phase of the column, influenced by factors such as polarity and boiling point, dictates the time it takes for each compound to elute from the column. This elution time is specific to each compound—it is referred to as the retention time. By means of GC, hundreds of compounds can be separated. The compounds are then directed into a mass spectrometer where they are identified based on their mass-to-charge ratio (m/z). Analyses were conducted using an Agilent Technologies 7890 GC instrument, coupled with a 5975C inert detector. A capillary column (Agilent J&W VF-5ht Ultimet) with a length of 30 m and diameter of 25 μm , with a film thickness 0.2 μm , was used. Helium was used as the carrier gas. For analysis, bio-oil substances were dissolved in dichloromethane.

3.5.3.6 GPC analysis

Gel permeation chromatography (GPC) is a size-exclusion technique used to characterise the molecular masses of samples that have a complex range of molecules and subsequent molecular masses, such as bio-oil samples. A PerkinElmer Flexar HPLC with a refractive detector was used. The instrument was equipped with two 7.5-mm Agilent Technologies Polargel-L 300 columns. The GPC columns separated molecules by physical size—the larger molecules move faster through the column than smaller molecules. The operating temperature of the columns was 55°C. Bio-oil samples were dissolved in a mobile phase consisting of 1 part dimethylsulphoxide to 9 parts water (vol/vol) and lithium bromide.

According to the literature, in the case of complex samples the molecular weights are represented as a distribution rather than discrete values. GPC molecular weights are typically expressed in several ways. The most commonly used representation is the number average molecular weight (M_n), which is determined by considering the mole fraction distribution of different molecules within a sample. Another common method for characterising the molecular weight of a sample involves

the weight average molecular weight (M_w), which is calculated based on the weight fraction distribution of all molecules present. The ratio of these two averages can be used to determine the polydispersity index (PDI). This index provides valuable insights into the range of molecular masses present in a sample. Higher PDI values indicate a broader distribution of molecular weights.

3.5.3.7 FTIR analysis

Fourier-transform infrared (FTIR) spectroscopy was used for qualitative analysis, to identify the organic functional groups present in the feedstock, bio-oil, and residue samples. Here, a sample is subjected to an infrared (IR) beam containing a range of wavelengths. Some of these wavelengths are absorbed by atoms within the sample, while the remaining unabsorbed wavelengths pass through to a detector and produce a signal. The Fourier transform process then translates these signals into a spectrum covering 400 cm^{-1} to 4000 cm^{-1} . The distinctive functional groups within the sample can be discerned by examining the peaks at various wavelengths. All notations, wavenumbers, and functional group assignments used in the analysis of FTIR spectrums are described in Table 5-20 in Appendix B. A Shimadzu- IR Affinity-1 FTIR instrument was used. For solid samples, potassium bromide was used for blank preparation prior to analysis. Dichloromethane was used to transfer an arbitrary mass of bio-oil to the FTIR container. This allowed the bio-oil to form a thin film that could be penetrated by the IR beam.

3.5.3.8 ICP-OES analysis

ICP-OES can accurately determine the concentration of elements in aqueous samples. All feedstocks and HTL products were analysed by ICP-OES to determine the metal concentrations. An Agilent Technologies 725-ES ICP-OES instrument was used. However, due to the absence of a laser or spark ablation system, all solid and oil samples required digestion prior to analysis, as is described in Section 3.4.2.

The operation of ICP-OES relies on the capacity of atoms and ions to absorb energy, causing electrons to transition to higher energy states. During the analysis process, an energy source is provided by argon plasma at temperatures $>9000^\circ\text{C}$. As electrons move from higher to lower energy levels, they emit light at specific wavelengths. The latter vary, depending on the type of element or ion, and on the energy level transitions involved. Consequently, the amount of light emitted is directly related to the number of ions or atoms undergoing these energy state transitions. Thus, the correlation between element concentration and light intensity, as proposed by the Beer–Lambert law, allows for the accurate determination of elemental concentration in a sample. Table 5-19, in Appendix B, lists the mineral and metal elements for which concentrations were determined in this study, as well as the instrumental and calculated detection limits for each element in product samples.

3.5.3.9 XRF analysis

X-ray fluorescence (XRF) analysis was used to identify various metals within the waste PCB feedstock. XRF analysis achieves this by assessing the sample's chemistry through the measurement of characteristic fluorescent X-rays emitted by each element upon excitation from a primary X-ray source. Analyses were carried out using a Thermo Scientific ARL ADVANT'X IntelliPower XRF sequential spectrometer. The analytical services were provided by XRD Analytical and Consulting and UIS Analytical Services (Gauteng), South Africa.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the findings of this study and a detailed discussion thereof. Section 4.2 addresses the characterisation of both the lignosulphonate and waste PCB feedstocks through compositional analysis. Section 4.3 examines the influence of temperature, residence time, and waste loading on the yields of HTL products. The SF analysis is introduced, to assess the combined impact of temperature and residence time on product yields. In Section 4.4, the influence of the residence time, temperature, and waste loading on the chemical properties of HTL products are considered through structural and compositional analyses. Section 4.5 provides insight into the impact of temperature, residence time, and waste loading on the organic composition of HTL products. Finally, in Section 4.6, the influences of temperature, residence time, and waste loading on the mineral and metal elemental distributions in HTL products are discussed. Detailed experimental data is included in the chapter, with further experimental data presented in Appendix A. All calculations related to the experimental errors are detailed in Appendix C.

4.2 Characterisation of waste PCBs and lignosulphonate

Both feedstocks used for HTL experiments were in a fine and homogeneous powder form; sieved waste PCBs was light brown in colour and lignosulphonate was grey. The milled-only waste PCBs were a heterogeneous mixture containing smeared metals and larger ceramic fragments.

4.2.1 Elemental composition

Elemental analysis of milled waste and sieved waste PCBs and lignosulphonate was conducted in triplicates. Results are presented in Table 4-1.

Table 4-1: Elemental analysis of lignosulphonate, sieved waste PCB, and milled waste PCB feedstock

Feedstock	C (wt.%)	H (wt.%)	N (wt.%)	R (wt.%)
Milled waste PCBs	21.07 ± 7.51	1.71 ± 1.46	0.56 ± 0.04	76.40 ± 8.14
Sieved waste PCBs	17.56 ± 0.48	1.46 ± 0.05	0.44 ± 0.28	80.54 ± 0.25
Lignosulphonate	32.76 ± 0.80	3.63 ± 0.06	0.19 ± 0.05	63.42 ± 0.81

The polymeric nature of sodium lignosulphonate justified the significant carbon fraction observed. There were also notable concentrations of oxygen, sulphur, and sodium in the lignosulphonate. The relatively low hydrogen and nitrogen content, coupled with the higher carbon content of lignosulphonate, aligned with typical distributions reported in the literature (Huang *et al.*, 2022; Mei *et al.*, 2020; Zhou *et al.*, 2016). Regarding the elemental distribution in milled waste PCBs, the

heterogeneous nature of these materials resulted in less reliable data due to significant experimental errors. Waste PCBs contained large amounts of carbon, likely attributed to the glass-fibre-reinforced BER used in PCB substrate manufacturing. This notable carbon fraction highlights the importance of recovering organic materials from waste PCBs, beyond focusing solely on the valuable metal fraction. The large remaining fraction was a consequence of the high concentrations of metals (metal analysis data are given in Table 4-3) and ceramics present. Zhang *et al.* (2010) reported similar carbon, nitrogen, and hydrogen fractions for PCB wastes.

4.2.2 Proximate composition

Proximate analysis was conducted in triplicates for both milled and sieved waste PCBs, and lignosulphonate. The results are presented in Table 4-2.

Table 4-2: Proximate analysis of lignosulphonate, sieved waste PCB, and milled waste PCB feedstock

Feedstock	Moisture (wt.%)	Volatiles (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
Milled waste PCBs	1.08 ± 0.05	20.88 ± 1.76	-0.37 ± 3.31	78.41 ± 4.75
Sieved waste PCBs	1.12 ± 0.01	22.84 ± 0.77	0.97 ± 0.59	75.07 ± 0.38
Lignosulphonate	3.84 ± 0.05	53.91 ± 1.76	16.91 ± 1.31	25.33 ± 4.75

The lignosulphonate contained small amounts of moisture. This may be due to the protonation of negatively charged lignosulphonate molecules when exposed to atmospheric moisture (water is released into samples). However, this effect can be minimised by storing the lignosulphonate sample in an airtight container (Özkan & Çokça, 2023). A significant fraction of volatile content was present in lignosulphonate, suggesting the potential presence of reactive components. The ash content of the lignosulphonate was >20 wt.%. This may lead to higher pH levels during HTL and consequently affect the metal adsorption properties of the resulting biochar. Huang *et al.* (2022) reported similar results for the proximate analysis of sodium lignosulphonate.

In the waste PCBs, a notable fraction of volatile content was observed. This may be attributed to the release of volatile organic compounds (VOCs) during the heating of BER (Guo *et al.*, 2012). The very low fixed carbon fraction suggests that most of the epoxy resin is removed during continuous heating at elevated temperatures. However, it should be noted that the reported mass fraction of fixed carbon may be lower than the actual amount due to the potential interference from the oxidation of metals at high temperatures. This is supported by the negative mass fraction reported for milled waste PCBs, having proportionally more metals than sieved waste PCBs due to smeared metals present. Lastly, the high ash content in waste PCBs could be attributed to their high concentrations of metals and ceramics. Bizzo *et al.* (2014) have reported similar results for the proximate analysis of waste PCBs.

4.2.3 FTIR analysis

As observed in the elemental analysis results, the sieved PCB feedstock contained a large amount of carbon, likely attributed to the presence of BER. Therefore, FTIR analysis was used to identify the various organic functional groups (Figure 4-1). Here, peaks of the FTIR spectrum are labelled from one through ten, with corresponding wavelengths, descriptions, and notations detailed in Table 5-20 in Appendix B.

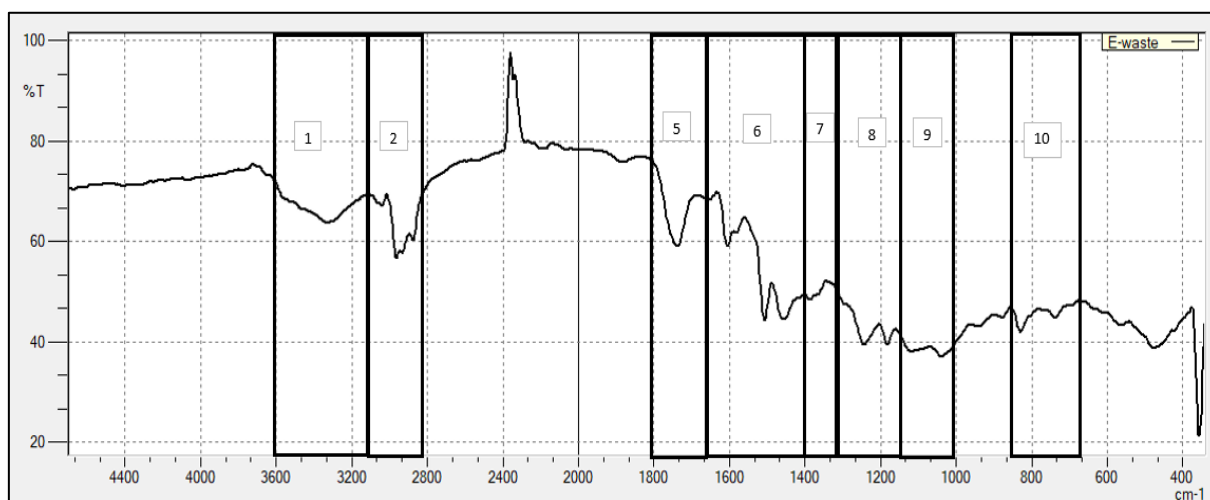


Figure 4-1: FTIR spectrum of sieved waste PCB feedstock

Figure 4-1 shows several peaks. The first peak spanning 3600-3100 cm⁻¹, denoted as 1, indicates the presence of -OH stretch groups, likely corresponding to the hydroxyl groups on the epoxy carbon chain. It could also suggest the presence of Si-OH groups on the surface of the glass fibres (Hu *et al.*, 2018). Notation 2 comprised one small peak around 3050 cm⁻¹ and a larger peak spanning 2850-3000 cm⁻¹, representing the sp² and sp³ C-H stretching vibrations, respectively. The peak indicated by notation 5 corresponds to the C=O stretching vibration, potentially resulting from the ester bonds of the curing agent that bond to the terminal epoxide groups of the epoxy resin (Shin *et al.*, 2019). Notation 6 revealed three distinct peaks associated with the aromatic ring structures of the epoxy resin. The smaller peak in notation 7 represents sp³ C-H bend vibrations. The two peaks designated by notation 8 represent the C-O stretching vibrations, while the bands in notation 9 represent the characteristic C-O-C bonds within the epoxy resin (Hu *et al.*, 2018). Finally, the minor peak in notation 10 at roughly 830 cm⁻¹ corresponds to sp² C-H aromatic vibrations.

In Figure 5-17 in Appendix A, a comparison is made between the spectra of waste PCB and pure epoxy resin. These spectra are very similar. The peaks from the waste PCBs are less prominent due to the presence of metals and ceramics, which dilute the concentration of epoxy resin in the feedstock. Thus, FTIR analysis confirmed that BER constitutes the majority of the organic materials in the waste PCB feedstock.

Lignosulphonate has a complex polymeric structure; hence various functional groups are present. The FTIR spectrum of lignosulphonate feedstock is shown in Figure 4-2.

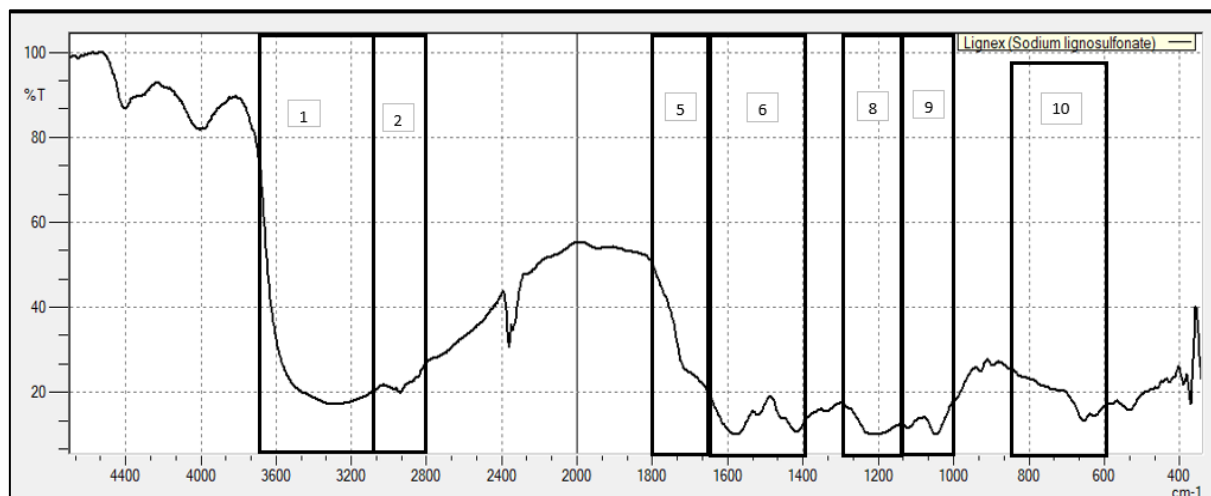


Figure 4-2: FTIR spectrum of lignosulphonate feedstock

The broad band denoted as 1 represents the -OH stretch groups, mainly associated with the phenolic hydroxyl groups. The smaller band in notation 2 is attributed to the C-H vibrations in methylene and methyl side chains. The minor peak indicated by notation 5 corresponds to C=O stretch groups of aromatic acids. The three peaks identified by notation 6 are characteristic of the aromatic ring structures. The band in notation 8 arises from phenolic C-O group vibrations. The peak designated by notation 9 is characteristic of C-O vibrations from syringyl and guaiacyl monomeric units within the lignin structure. Lastly, the peak in notation 10 can be attributed to sp^2 C-H aromatic vibrations (Daud *et al.*, 2021). Thus, the FTIR spectrum confirmed the complex structure of lignosulphonate.

4.2.4 Metal composition

The elemental mineral and metal composition of sieved waste PCBs was assessed by first digesting three samples of the feedstock and subsequently analysing the digestate using ICP-OES. Lignosulphonate is soluble in water at neutral pH. Three samples were dissolved and analysed. The results are presented in Table 4-3.

Table 4-3: ICP-OES concentrations of metals in sieved waste PCB and lignosulphonate feedstock

Element	Sieved waste PCBs (mg/g)	Confidence level ($\pm$) (mg/g)	Lignosulphonate (mg/g)	Confidence level ($\pm$) (mg/g)
Ca	55.18	5.23	0.35	0.09
K	0.38	0.02	2.68	0.22
Mg	2.62	0.10	0.55	0.13
Na	0.95	0.06	139.43	10.83
S	2.24	0.14	200.02	16.15
P	1.10	0.05	0.36	0.07
Al	61.42	3.23	0.01	3.15E-03
Ag	0.62	0.07	ND	0.00
Au	0.31	0.04	3.54E-04	8.14E-04
Cu	83.31	1.57	0.01	0.01
Fe	62.33	2.84	0.02	0.01
Ni	5.08	0.40	2.12E-03	1.50E-03
Pb	4.86	0.37	6.54E-05	1.80E-04
Sb	0.57	0.06	1.39E-03	1.30E-03
Sn	42.20	1.55	ND	0.00
Ti	2.84	0.31	4.49E-04	1.37E-04
Zn	6.45	0.46	8.22E-04	3.07E-03

*ND: Not detected

Sulphur and sodium were the predominant mineral elements in the lignosulphonate. Trace amounts of aluminium, copper, and iron were noted. The elevated sulphur concentration resulted from the introduction of sulphonic groups during the pulping process, whereas the high sodium content was attributed to the use of sodium as the salt in the pulping process (Aro & Fatehi, 2017).

In the waste PCBs, a diverse array of minerals and metals was observed. The presence of calcium and magnesium may be due to the alkali-earth oxides commonly used in ceramics found in PCBs. In terms of metal composition, copper was the most abundant (it is used in the conductive layers). Iron, tin, and lead were also abundant materials (they are typically used in the soldering and PCB frames). Aluminium was another significant metal due to its favourable thermal conductivity and mechanical stability, making it suitable for various applications in PCBs (batteries, heat sinks, and LEDs). A moderate concentration of titanium was noted, potentially originating from PCB fasteners (although it is not commonly used in PCB assemblies). Nickel and zinc were also present (likely used in the surface finishing and plating to prevent oxidation). Finally, small amounts of gold and silver (typically used as contact materials) were present (Kaya, 2016).

Although ICP-OES analysis is a reliable method for determining major and trace elements in various samples, it is nonetheless essential to validate the accuracy of mineral and metal

distributions by comparing the ICP-OES results of waste PCB samples with results from another common metal analysis technique, such as XRF analysis. Data of such a comparison are presented in Table 5-16 in Appendix A. The results demonstrated striking similarities in the concentrations of most minerals and metals. The calcium and magnesium concentrations were lower in the ICP-OES analysis. This may be attributed to these elements being in alkali-earth oxide form, therefore the digestion in aqua regia may not fully overcome all strong ionic bonds of these oxides. Similarly, the aluminium was also lower in the ICP-OES analysis, potentially due to aluminium typically forming a protective oxide layer on the surface. Nonetheless, the confidence levels associated with ICP-OES analysis of waste PCBs underscored the repeatability and reliability of the digestion and analysis procedures.

4.3 Effect of operating parameters on product yields

The aqueous phases, residues, bio-oils, and gas products of all the HTL experiments were measured and the yields were calculated in terms of mass fractions, as depicted in Section 3.5.1. Figure 4-3 shows the product yields (together with experimental data and errors) obtained from HTL experiments conducted at various residence times ranging from 20 to 80 min and operating temperatures from 250 to 330°C.

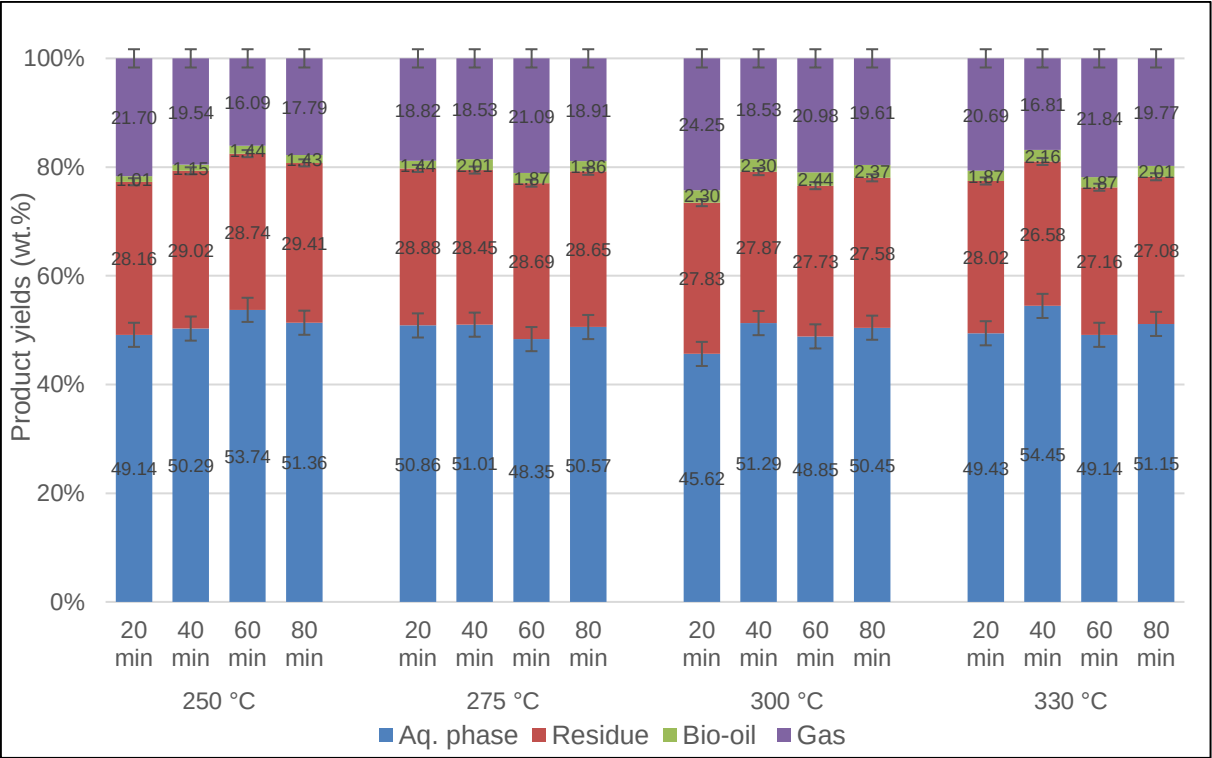


Figure 4-3: Aqueous phase, residue, bio-oil, and gas yields for HTL experiments with varying temperatures (250°C-330°C) and residence times (20-80 min)

The experimental errors for the aqueous phase and gas product were 2.22 wt.% and 1.68 wt.%, respectively. The residue exhibited an experimental error of 0.65 wt.% and the bio-oil a minimal

experimental error of 0.23 wt.%. Table 5-1 in Appendix A provides all the yield data for experiments carried out at different operating temperatures and residence times.

The predominant product fraction obtained for all HTL experiments was the aqueous phase. Although the latter typically consists of water and small polar organic products, it can be inferred (based on mass conservation) that various reactions in water as solvent, including hydrolysis, occur during HTL, as all aqueous phase yields were below the input mass fraction of water (59.60 wt.%). The aqueous phase yields here were similar to yields obtained by dos Passos *et al.* (2020) during the HTL of epoxy resin. Additionally, a notable quantity of gas was produced. This can be expected because both waste PCBs and lignosulphonate contain significant amounts of volatile content, as confirmed by the proximate analysis. Consequently, the formation of lighter VOCs through feedstock decomposition into light intermediates increased the gas yields. Gas production was favoured by the cracking of bio-oils and gasification of residues. These gas yields were consistent with those documented in the literature for the HTL of single or mixed waste plastics (Williams & Slaney, 2007). The solid residue also constituted a substantial fraction of the product yields.

Two polymer-containing feedstocks were used during HTL, hence the yields of the solid product could be influenced by numerous reactions, including the repolymerisation of intermediates, and cracking and condensation of the bio-oils, leading to the formation of biochar structures in the residue, as well as gasification of the residues. Moreover, the potential adsorption of metals by these structures could have an impact on the residue yield. Lastly, the bio-oil yields were very low (the highest was 2.44 wt.%). Generally, solid formation through repolymerisation of reactive intermediates is favoured in the absence of hydrogen donors or when free radicals are in excess, with no hydrogen present for stabilisation, leading to the association with each other to afford heavy compounds. Therefore, the low bio-oil yield could result from a preference for biochar formation from the lignin, particularly as the two polymer-containing feedstocks produce an abundance of free radicals (Gollakota *et al.*, 2018). Alternatively, the use of lignin-rich biomass (such as sodium lignosulphonate) tends to favour solid formation, due to the difficulty of degrading the complex and the branched structure of lignin; it consequently remains as a residue, thus reducing the bio-oil yield (Nizamuddin *et al.*, 2017).

It was difficult to conclude any trends from data in Figure 4-3 alone, thus the SFs were calculated (as described in Section 2.5) in efforts to obtain insight into the combined effect of residence time and temperature on the gas, bio-oil, and residue yields. In the discussion of the effect of temperature, data from both a short (20 min) and a long (80 min) residence time are presented, while the data from a low (250°C) and a high (330°C) temperature are provided to discuss the

effect of residence time. Data from intermediary residence times and temperatures are presented in Figure 5-11 to Figure 5-14 in Appendix A.

4.3.1 Reaction temperature

The SF values were calculated for all operating temperatures at 20 min and then plotted alongside the corresponding product yields. Figure 4-4 show the relationship between residue, gas, and bio-oil yields as they vary with temperatures.

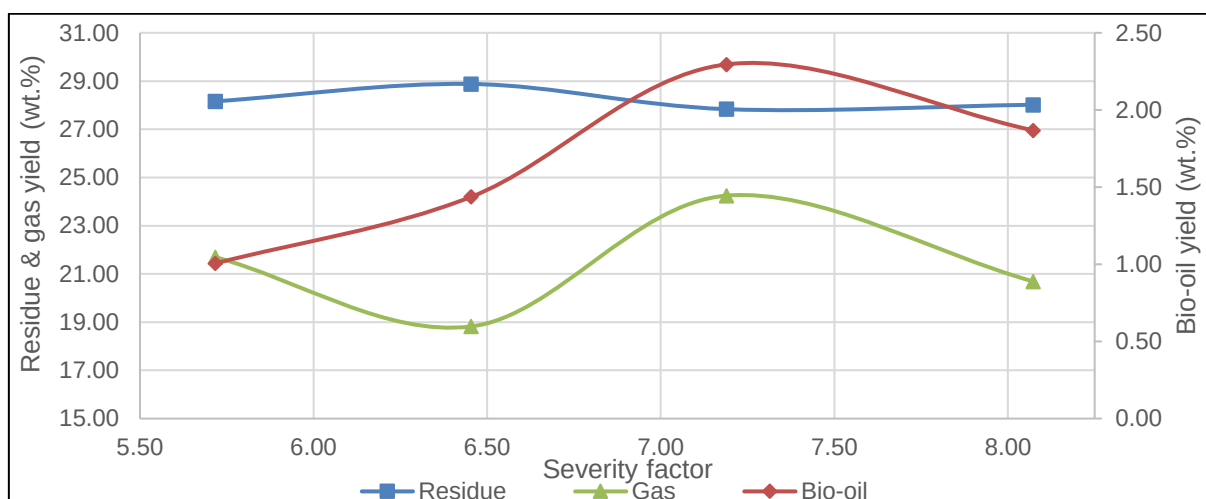


Figure 4-4: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 20 min at 250, 275, 300, and 330°C

An initial low bio-oil yield was noted, probably due to the inadequate decomposition of the lignin and epoxy resin polymers at low temperatures and short residence times. The thermal cracking of lignin typically occurs at $\sim 280^{\circ}\text{C}$, meaning that at lower operating temperatures the reaction rate is too slow for a residence time of 20 min, resulting in most of the lignin remaining in a solubilised state within the aqueous phase (Ghavami *et al.*, 2021). Similarly, the epoxy resin also decomposes slowly at temperatures $< 295^{\circ}\text{C}$, as insufficient energy is provided for thorough bond cleavage (Yin *et al.*, 2011).

As observed, the bio-oil yield increased with increasing temperatures as more energy becomes available for decomposition. However, a turning point was reached at 300°C , after which the yield decreased at 330°C . This aligns with reports in the literature, where bio-oil yields typically increase with temperature due to the formation of more light intermediate compounds through the decomposition of the polymer fragments via various reactions such as hydrolysis, decarboxylation, and dealkylation, followed by the recombination of these lighter compounds into bio-oils. However, at higher temperatures, cracking of the bio-oils to lighter gases may occur, as well as the formation of solid products from heavier compounds, thus explaining the slight increase in solid yield at 330°C (Ghavami *et al.*, 2021; Xu & Li, 2021). At 300°C , a slight decrease in the solid residue was observed, possibly due to more substantial feedstock depolymerisation and increased bio-oil

formation, although, overall, at a short residence time, the solid residue yields were not significantly affected.

In contrast, temperature variations had an influence on the gas products at a short residence time. The increase in gas yield at 300°C could be attributed to the increased decomposition of the epoxy resin and lignin, as their respective degradation temperatures were surpassed. This would lead to the formation of more VOCs and contribute to the slight decrease in residue yield. The decrease in the gas yield at 330°C suggests that condensation and repolymerisation favoured heavier compounds; conversion was to solid products rather than to light gaseous compounds. The slight increase in residue and decrease in gas product at 275°C might also be related to this phenomenon. The effect of temperature on the trends for both residue and gas yields at a longer residence time differed from trends observed at a shorter residence time, as illustrated in Figure 4-5.

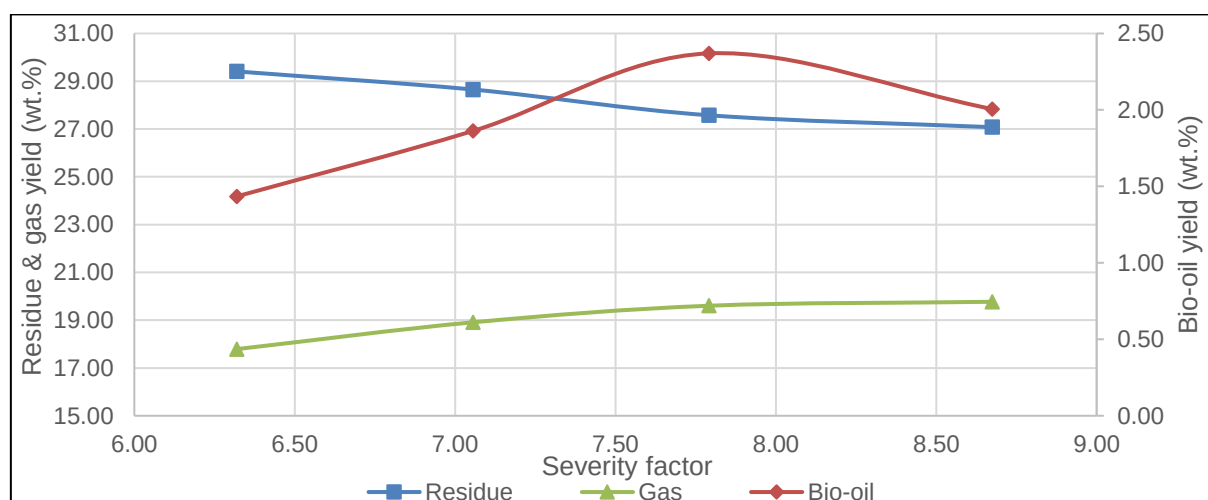


Figure 4-5: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 80 min at 250, 275, 300, and 330°C

A comparison between the results of bio-oil yields at both the short and long residence times revealed a consistent trend. Initially, a low bio-oil yield was observed at 250°C, then, as the temperature increased, more intermediate compounds formed through feedstock decomposition; they subsequently recombined into bio-oil. A turning point in the bio-oil yield was again reached at 300°C, with higher temperatures leading to the bio-oil cracking. Consequently, an intermediate temperature, in this case 300°C, is preferred for bio-oil production. This decrease in the bio-oil yield could also explain the slight stabilisation of the residue yield at 330°C as heavier compounds form from the cracked fragments of bio-oil.

Nevertheless, the residue decreased as the temperature was increased, in contrast to the increase in gas yields. This suggests that at a longer residence time, higher temperatures allow for better decomposition of lignin and epoxy resin. However, under these more severe conditions, the

gasification of the heavier molecules in the residue becomes more prominent, with their subsequent conversion into lighter compounds—thus increasing the gas production. Furthermore, at high temperatures, the initial defragmentation step of feedstocks directly produces gaseous products, which could also support the consistent increase in gas yield and decrease in residue yield (Mazaheri *et al.*, 2010). These results align with trends observed during the liquefaction of paper wastes at various temperatures (Nizamuddin *et al.*, 2017).

4.3.2 Residence time

Where temperature is widely recognised as the primary influencing process parameter pertaining to product yields, residence time also has a direct influence on the distribution of yields. Figure 4-6 provides an overview of yield trends across various residence times at a relatively low temperature.

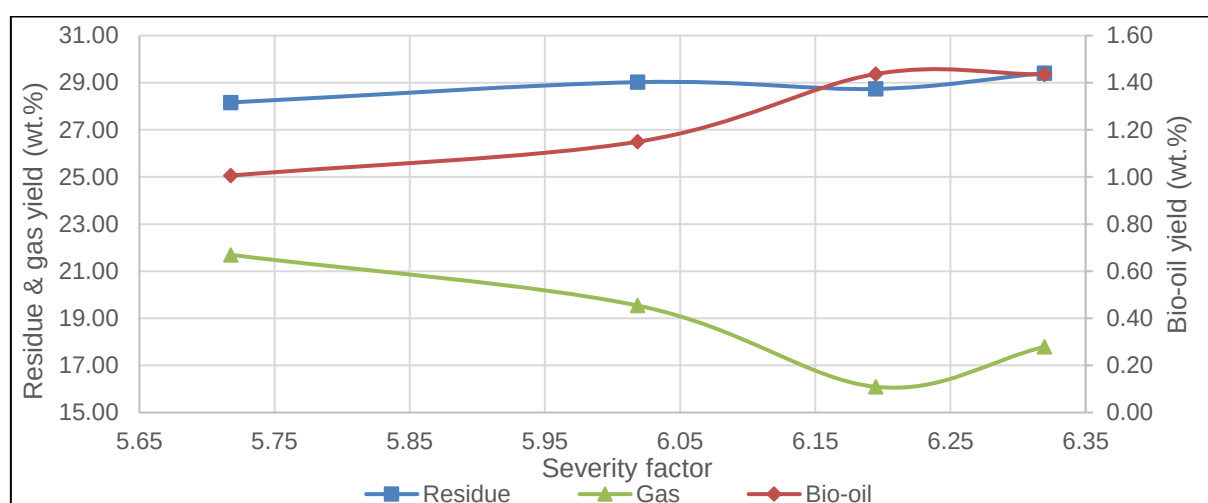


Figure 4-6: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 250°C at 20, 40, 60, and 80 min

The overall bio-oil yield for all residence times remained notably lower at 250°C due to a sluggish reaction rate. Despite this slow reaction rate, the bio-oil yield gradually increased with extended residence time, reaching stability at 60 min. This stabilisation occurs as the balance between intermediate recombination and bio-oil cracking reaches equilibrium. Consequently, at these levels of severity, a significant decline in bio-oil yield due to cracking, and subsequent repolymerisation and condensation reactions, was not observed. However, this decline could potentially be mitigated by the slight increases seen in both gas and residue yields. These increases may arise from the limited cleavage of lignin and epoxy resin molecules at the lower temperature, within the initial 20, 40, and 60 min, whereas the 80 min residence time allows for more substantial cracking of the weakest bonds in the feedstocks, then resulting in increased gas yield and the formation of intermediates that repolymerise into heavier molecules, thus contributing to the higher residue yield. This occurs without significant bio-oil cracking.

There was a slight increase in residue yield with increasing residence times, indicating that the formation of heavier compounds is favoured. This was supported by the overall decrease in gas formation at 20, 40, and 60 min, as fewer light compounds were formed, and gasification of the residues became less prominent with increasing residence times. The trends of slightly increasing bio-oil and residue yields with extended residence time at low temperatures align with findings commonly reported in the literature (Xu & Li, 2021).

As previously discussed, at low temperatures the energy input to the system is insufficient for effective feedstock decomposition. However, residence time variations at higher temperatures yielded distinct trends in all product fractions, as illustrated in Figure 4-7.

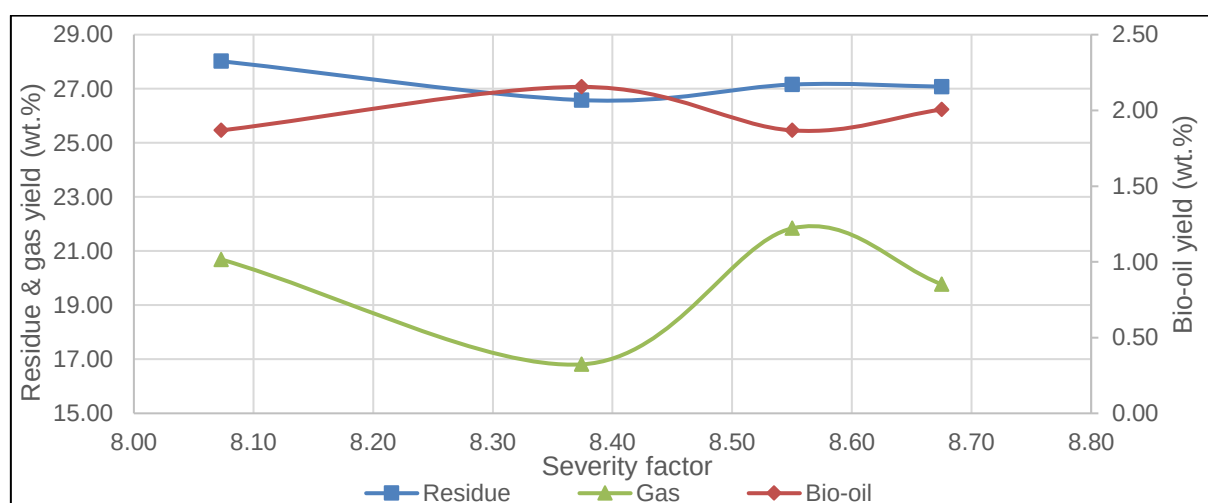


Figure 4-7: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at SFs calculated for 330°C at 20, 40, 60, and 80 min

At 330°C, the bio-oil yield trends deviated from those at lower temperatures. Initially, the bio-oil yield increased and then began to decline at 40 min, indicating the onset of cracking. The slight increase observed at 80 min was unexpected—it did not conform to the anticipated trend of increased cracking severity at higher residence times. Instead, it suggests that intermediate compounds may recombine to form more bio-oil during this time frame. While this could be considered an outlier, it aligns with observations made by Run Dong *et al.* (2013). They noted similar fluctuations in both the gas and liquid products with changes in residence times at 325°C during liquefaction of rice straw, mirroring the trend seen in Figure 4-7. These fluctuations were attributed to a dynamic equilibrium between the liquid and gas phases at high temperatures, driven by decomposition and repolymerisation reactions, which also justifies the fluctuating gas yield. An inverse correlation was also evident between residue and bio-oil yield with increasing residence time, likely due to these same cracking and repolymerisation reactions.

Given that temperature carries greater influence than residence time, and that the optimal temperature for bio-oil production was determined to be 300°C, the optimum residence time was

derived from the yield curve for various residence times at 300°C, as depicted in Figure 5-14 in Appendix A. The bio-oil yield remained relatively constant with increasing time, giving the same bio-oil yield at residence times of both 60 and 80 min. Consequently, 80 min was selected as the optimum residence time as it yielded a slightly higher residue yield, thus offering the potential added benefit of metal adsorption through the formation of heavier compounds in the residue.

4.3.3 Waste loading

The influence of feedstock loading on product yields was also investigated. As described in Section 3.3, the combined total solid loading of lignosulphonate and waste PCBs remained constant, whereas the mass loading of waste PCBs was in the range 0%-100 wt.% of the input. In these experiments, the optimal reaction conditions of 300°C and 80 min were used. Figure 4-8 presents a visual representation of the product yield distributions.

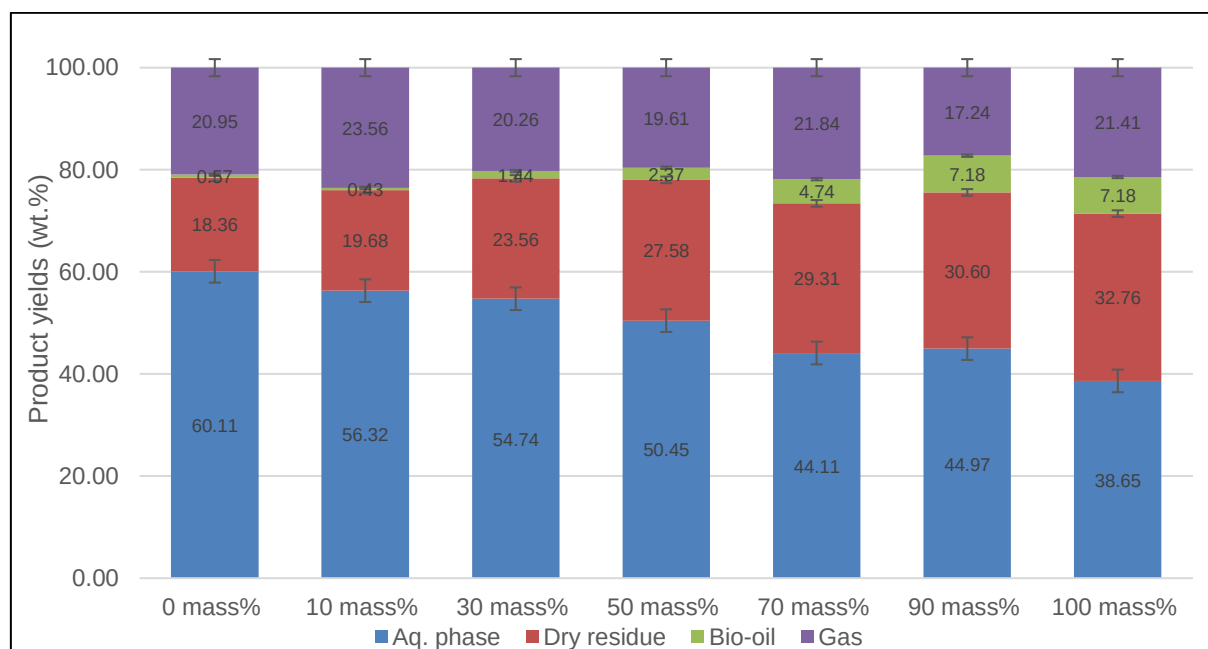


Figure 4-8: Aqueous phase, residue, bio-oil, and gas yields for HTL experiments with waste PCB mass loadings of 0 to 100 wt.%

Under these conditions, no clear trend in the gas yields was evident. This suggests that both lignosulphonate and epoxy resin produce comparable amounts of volatile products during HTL, irrespective of the loading. In terms of the aqueous phase, there was a reduction with increasing waste loading. This reduction is primarily attributed to the dissolution of lignosulphonate in the water, leading to an increased aqueous phase yield.

Regarding the bio-oil, there was a clear trend of increasing bio-oil yield with increasing waste loading. At these operating conditions, complex lignin molecules can undergo cleavage to form intermediate compounds that appear to favour the formation of heavier solid molecules and light gaseous products over the production of bio-oil. This accounts for the lower bio-oil yield at lower

waste loading. Conversely, epoxy resin decomposes and forms bio-oil more prominently. This could be due to the epoxy resin's simpler structure, making it more susceptible to reactions such as hydrolysis and cracking. Another contributing factor may be solid formation being favoured in an environment with an abundance of free radicals. Subsequently, through the decrease in lignosulphonate loading, the concentration of free radicals in the reaction mixture also decreased, thus the bio-oil formation increased (Gollakota *et al.*, 2018). In this case, it would be expected that the solid product decreases due to the reduction of free radicals with increasing waste loading, however, the opposite is observed. This is mainly due to the waste PCBs consisting of large fractions of inorganic compounds, thus producing a low-carbon residue of metals and ceramics as most of the epoxy resin is converted to bio-oil.

Furthermore, at 0 wt.% waste loading approximately 19 wt.% of carbon-rich biochar was produced, which could be desirable for metal adsorption. Conversely, the residue yield obtained from a 100 wt.% PCB loading was approximately 24% lower than the input PCBs. This reduction signified a significant step towards the valorisation of e-waste and confirms the decomposition of the organic material. The concentration of metals in the low-carbon residue is another crucial factor, as discussed in Section 4.6 later.

4.4 Effects of operating parameters on the chemical properties of products

The effects of temperature, residence time, and waste loading on the chemical properties of HTL products are now addressed. Determinations were carried out from elemental analysis and HHV calculations, as well as proximate analysis and GPC analysis. To examine the effects of temperature and time, representative conditions of 40 min and 300°C were selected. Additional data from other conditions are provided in Appendix A and referred to as required.

4.4.1 Reaction temperature

4.4.1.1 Elemental composition

Temperature exerts a notable influence on the quality of HTL products. Table 4-4 presents the distributions of carbon, hydrogen, nitrogen, and the remaining fractions of the bio-oils and residues obtained at 40 min for all selected temperatures.

Table 4-4: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C

Product	Operating parameters		C (wt.%) (±1.45)	H (wt.%) (±0.45)	N (wt.%) (±0.25)	R (wt.%) (±2.12)
	Residence time (min)	Temperature (°C)				
Bio-oils	40	250	57.35	5.66	0.52	36.47
		275	65.60	6.80	0.88	26.73
		300	68.44	6.89	0.90	23.76
		330	71.73	7.03	0.78	20.46
Product	Operating parameters		C (wt.%) (±0.86)	H (wt.%) (±0.05)	N (wt.%) (±0.03)	R (wt.%) (±0.90)
Residue	40	250	22.19	1.80	1.07	74.94
		275	22.31	1.73	0.32	75.65
		300	20.47	1.40	0.24	77.89
		330	18.57	1.21	0.51	79.71

A substantial portion of carbon is directed towards the bio-oils. Elevating the reaction temperature resulted in a consistent increase in the carbon content due to the removal of oxygen through deoxygenation reactions, such as decarboxylation or decarbonylation. This increase in carbon content could be attributed to the relatively high oxygen content of bio-oils, with oxygen constituting a significant part of the remaining fraction (Cao *et al.*, 2017). The decline in the remaining fraction with increasing temperature was also justified. Yin *et al.* (2011) observed increased debromination rates of epoxy resin at high temperatures, which could contribute to the decreasing remaining fraction of the bio-oils.

Figure 5-15 in Appendix A presents the van Krevelen plot for bio-oils, revealing a clear decrease in the O/C ratio with increasing temperature. Furthermore, the H/C ratio indicated an overall decrease with increasing temperature as well, suggesting a greater presence of aromatic compounds in the bio-oils due to the decrease in aliphatic compounds. Thus the decrease in H/C indicated the presence of more aromatic compounds in the bio-oils due to aliphatic compounds containing a higher H/C ratio (Wadrzyk *et al.*, 2019).

The residues contained a notable amount of carbon, attributed to both the unreacted epoxy resin and the heavy organic molecules converted to the solid product, since unreacted lignin will be dissolved in the aqueous phase. The carbon content decreased with increasing temperature. This may be due to enhanced decomposition of epoxy resin at higher temperatures, corresponding to the increase in carbon content of the bio-oils. The cracking rate of the bio-oils and repolymerisation rate of intermediates into carbonaceous heavy molecules were lower than the decomposition rate of epoxy resin at this residence time, thus explaining the continuous decrease of carbon in the residue.

However, at 80 min the carbon content initially decreased then increased at 330°C as more heavy organic molecules were produced and converted to the residue, then heavy molecule formation overtook the decomposition of epoxy resin (see Table 5-3 in Appendix A). Cracking of bio-oils could also be a contributing factor. Thus, higher temperatures resulted in secondary reactions that could have an influence on the residue composition. Simultaneously, the remaining content of the residues followed the inverse trend of carbon, as it comprises unreactive components (ceramics and metals) and thus dependent on the changes in carbon content. The nitrogen content of the residue and bio-oils could be attributed to the nitrogen-containing cross-linking agents used in the epoxy resin, as well as proteins within the lignin molecules of lignosulphonate. The nitrogen trend of the bio-oils was the inverse of the nitrogen trend observed for the residues, indicating that nitrogen exchange is affected by temperature. As the temperature increases, more nitrogen is directed to the bio-oil until 330°C, whereafter it decreases, and the nitrogen content in the residue then increases, likely due to cracking of nitrogen-containing molecules in the bio-oils.

4.4.1.2 Energy content

Although energy content is not an important factor when the recovery of materials is desired, the energy content of bio-oils should be determined in an effort to assess its applicability as a potential crude-oil energy source. To this end, use was made of Equation 5 here to estimate the HHV using results from the elemental analysis, as shown in Table 4-5 (Bychkov *et al.*, 2017).

Table 4-5: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C

Operating parameters		HHV (MJ/kg) (± 1.49)
Residence time (min)	Temperature (°C)	
40	250	23.04
	275	28.44
	300	30.25
	330	32.47

The estimated HHV increased with increasing temperatures. This increase in HHV is correlated to the deoxygenation process and subsequent increase in carbon and hydrogen contents of bio-oils at higher temperatures. As illustrated in Table 5-4 in Appendix A, this trend remained consistent across all the residence times considered in this study. The HHV of bio-oils falls within the range 21.86-33.45 MJ/kg. Generally, the HHV of bio-oils falls within the range 28-37 MJ/kg, depending on the composition; including hydrocarbons, ketones, fatty acids, and aldehydes (Dimitriadis & Bezergianni, 2017). Thus, at $\geq 275^\circ\text{C}$, bio-oils derived from waste PCBs and lignosulphonate are within this general range; however, at 250°C , the high oxygen content significantly reduces the HHV.

4.4.1.3 Proximate composition

Table 4-6 shows the proximate analysis of residues as a function of temperature changes at 40 min. The impact of temperature at other residence times is shown in Table 5-5 in Appendix A.

Table 4-6: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C

Operating parameters		Moisture (wt.%) (±0.45)	Volatile (wt.%) (±2.00)	Fixed carbon (wt.%) (±2.94)	Ash (wt.%) (±2.01)
Residence time (min)	Temperature (°C)				
40	250	3.90	25.81	4.78	65.51
	275	4.57	23.08	4.02	68.33
	300	4.51	20.66	4.25	70.58
	330	3.80	19.03	3.32	73.84

The proximate analysis offers valuable insights into the behaviour of the residues during combustion. No prominent trend in the moisture content of residues was observed, indicating that it is primarily water bound within the residue matrix, rather than surface moisture, affected by hydration or chemisorption. However, at 20 min, the moisture content increased slightly with temperature, while at 80 min it decreased slightly. This could support the case of hydration and chemisorption to an extent, based on functional group changes in the residue molecules. The fixed carbon content remained relatively stable across temperature variations. The large experimental error is due to the oxidation of metals in the residue at high temperatures.

The volatile content decreased with increasing temperature at all residence times, indicating that higher temperatures favour the decomposition of the VOCs in the feedstocks. The decrease observed in the carbon content of the residue at higher temperatures is thus related to the decomposition of the VOCs. The increase in ash content at higher temperatures resulted from the reduction of the volatile organic content, leading to the prominence of inorganic ash, including ceramics and metals.

4.4.1.4 Molecular weight and PDI

GPC analysis enabled the determination of the molecular weight and distribution of bio-oils, shedding light on the effect of temperature on the bio-oil properties. Table 4-7 presents the Mw, Mn, and PDI values for bio-oils obtained at all temperatures for 40 min.

Table 4-7: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C

Operating parameters		Mw (g/mol) (±77.58)	Mn (g/mol) (±2.87)	PDI (±0.54)
Residence time (min)	Temperature (°C)			
40	250	1395.26	256.22	5.46
	275	1402.87	195.95	7.67
	300	1150.30	146.19	7.86
	330	645.76	115.70	5.58

The Mw and Mn of the bio-oils obtained at low temperatures were relatively high. They are comparable to the original feedstock molecules (Kaharn *et al.*, 2022). This trend was similar to that for the bio-oils derived at 250°C, considering the Mw (2468 g/mol), Mn (945 g/mol), and PDI (2.60) of the lignosulphonate. GPC analysis could not be performed on the waste PCBs, nevertheless, research by Hou *et al.* (2023) suggests that the Mw for BPA-derived epoxy resin can vary between 300 to 50,000 g/mol. Chow *et al.* (2016) determined the Mw for BPA-derived epoxy resin to be 2454 g/mol. Consequently, it could be inferred that successful depolymerisation of both epoxy resin and lignin polymers occur during HTL.

Table 4-7 revealed a clear trend, where both the Mw and Mn consistently decreased with increasing temperatures. This behaviour remained consistent across various residence times, as demonstrated in Table 5-6 in Appendix A. Temperature strongly influenced the decomposition rate of bio-oil molecules into smaller compounds. Although the molecular size of the bio-oils decreased, elemental analysis results showed that the carbon content increased with temperature. This apparent contradiction can be explained by the decomposition reactions. While the molecular weight of individual molecules decreased due to depolymerisation, cracking, and deoxygenation, the carbon content still increased because the original carbon from the larger molecules was still contained within the smaller compounds constituting the bio-oils. This suggests that the majority of constituents from large organic bio-oil molecules do not transition into gaseous products after cracking, depolymerisation, and deoxygenation.

The PDI distribution exhibited a broad range of molecular weight distributions for the bio-oils, with a consistent trend at all residence times. First, a lower PDI was observed at 250°C, whereafter an increase was observed at 275°C as the large bio-oil compounds decomposed to form lighter molecules, with a large amount of comparatively heavy molecules remaining, thus creating a wider range. At 330°C, the PDI then decreases as most of the molecules decomposed further to much smaller base molecules with similar molecular weights.

4.4.2 Residence time

4.4.2.1 Elemental composition

Table 4-8 presents the effect of residence time on the elemental composition of bio-oils and residues at 300°C.

Table 4-8: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min

Product	Operating parameters		C (wt.%) (±1.45)	H (wt.%) (±0.45)	N (wt.%) (±0.25)	R (wt.%) (±2.12)
	Temperature (°C)	Residence time (min)				
Bio-oils	300	20	67.15	6.75	0.85	25.25
		40	68.44	6.89	0.90	23.76
		60	68.83	7.00	0.91	23.32
		80	69.38	6.82	0.88	22.91
Residue	300	20	20.38	1.45	0.21	77.96
		40	20.47	1.40	0.24	77.89
		60	22.09	1.44	0.21	76.25
		80	20.56	1.32	0.16	77.96

In the context of bio-oils, an increase in carbon content became evident with increasing residence time, although it was less pronounced compared to the impact of temperature variations. This trend was consistent across different time intervals at all temperatures considered here. See Table 5-3 in Appendix A. Upon studying the van Krevelen plot (Figure 5-15 in Appendix A), the O/C ratios showed a significant decrease with increasing residence time at 250°C; however, at a temperature of $\geq 275^\circ\text{C}$, this decrease became less prominent. Consequently, following the law of mass action, it can be inferred that at lower temperatures the deoxygenation reactions occurred at a faster rate, due to the higher oxygen concentration in the bio-oils. Conversely, at higher temperatures, this rate decreased as the oxygen concentration decreased. This also justified the similar, yet inverse, trend seen in the carbon content. Regarding the H/C ratio, at 250°C there was a decrease with longer residence times; however, at $\geq 275^\circ\text{C}$, no clear trends were observed, indicating that residence time does not have a significant impact on the aliphatic and aromatic composition of bio-oils at elevated temperatures.

Changes in residence time did not affect the carbon, hydrogen, and remaining content of the residues as noticeably as temperature changes. Table 5-3 in Appendix A shows that the prolonged residence times at 250°C had a negligible influence on the elemental composition of the residues. This is likely due to inadequate energy input into the system, resulting in a slow reaction rate of the desired decomposition reactions for the feedstocks, as well as for the secondary cracking and

decomposition reactions. However, at higher temperatures, the carbon content exhibited fluctuating carbon content with increasing residence times. This may result from the dynamic equilibrium between decomposition and secondary repolymerisation reactions, as observed in the product yields (Run Dong *et al.*, 2013). For example, at a high temperature (330°C), a decrease in carbon was noted at 20-40 min as the decomposition of the epoxy resin occurs. From 40 min, and longer, the carbon content increased due to repolymerisation reactions. This explanation is consistent with the similar trend observed for the yield of residue in Figure 4-7. It could therefore be concluded that residence time has a variable effect on the carbon, hydrogen, and remaining content, whereas temperature is the predominant process parameter.

The nitrogen content for both residues and bio-oils was not significantly affected by changes in residence time, suggesting that temperature is also the primary factor in the formation and cracking of nitrogen-containing compounds. This could indicate that the rate of these reactions is incompatible with the time range—it is likely too fast when the amounts of nitrogen available in the system are too low for changes to be observed.

4.4.2.2 Energy content

Table 4-9 shows the effect of residence time on the heating values of the bio-oils at 300°C. Data for other temperatures are presented in Table 5-4 in Appendix A.

Table 4-9: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min

Operating parameters		HHV (MJ/kg) (± 1.49)
Temperature (°C)	Residence time (min)	
300	20	29.30
	40	30.25
	60	30.62
	80	30.74

The heating values followed a similar trend to that seen for the less pronounced increase in the carbon content in the bio-oils with extended residence times. The highest HHV was observed at 80 min for all temperatures, in correlation with the higher carbon and hydrogen trends observed (as in Table 4-8).

4.4.2.3 Proximate composition

Table 4-10 gives the proximate analysis results for residues as a function of changes in residence time at 300°C. The effect of residence time at other temperatures is illustrated in Table 5-5 in Appendix A.

Table 4-10: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min

Operating parameters		Moisture (wt.%) (±0.45)	Volatile (wt.%) (±2.00)	Fixed carbon (wt.%) (±2.94)	Ash (wt.%) (±2.01)
Temperature (°C)	Residence time (min)				
300	20	3.95	22.88	3.74	69.43
	40	4.51	20.66	4.25	70.58
	60	4.27	20.86	3.95	70.93
	80	4.07	21.82	3.65	70.45

Table 4-10 and Table 5-5 reveal small fluctuations in the moisture contents with changes in residence times at all temperatures. This suggested that the moisture is predominantly bound within the residue matrix. A similar observation was made for the moisture fluctuations with increasing temperature; there was an increase in moisture at 250°C and a decrease at 330°C with increasing time. Therefore, surface moisture could be influenced by functional groups that are more prominent at lower temperatures and less prominent at higher temperatures. The fixed carbon content remained relatively stable—no significant changes were observed.

An overall decrease in volatile content with increasing residence time was noted. The rate of decrease was more pronounced at 250 and 275°C, after which this rate decreased for 300 and 330°C. This suggested that more VOCs are present in the feedstock at lower temperatures and that extended residence times allowed for a slower decomposition rate to release these compounds. Conversely, more energy at higher temperatures increased the decomposition rate, therefore the volatile content trend was less obvious (most of the volatile content is released before 20 min). The ash content is mainly dependent on the volatile content; hence, the observed trend appears to be inverted.

4.4.2.4 Molecular weight and PDI

The Mw, Mn, and PDI values for bio-oils obtained for all the selected residence times at 300°C are presented in Table 4-11.

Table 4-11: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min

Operating parameters		Mw (g/mol) (±77.58)	Mn (g/mol) (±2.87)	PDI (±0.54)
Temperature (°C)	Residence time (min)			
300	20	1134.55	153.39	7.40
	40	1150.30	146.19	7.86
	60	873.02	126.39	6.90
	80	976.90	134.27	7.27

The residence time had a noticeable impact on the molecular weight and distribution of the bio-oils. However, as with the elemental and proximate analyses results, temperature is a more influential parameter than residence time. This was confirmed after examining the entire temperature range investigated.

As is evident from Table 5-6 in Appendix A, at both 250 and 275°C the residence time did not have a prominent effect on the molecular weights since these low temperatures did not facilitate substantial depolymerisation of the bio-oils. However, decomposition was still observed, as the Mw and Mn values were still significantly lower than those of the two feedstocks. The PDI remained fairly constant, except at 275°C and 20 min, where it was slightly lower compared to the longer residence times at this particular temperature. This reason was the Mn decreasing faster than the Mw at the longer residence times. A possible explanation for this is the loss of low-weight molecules from the bio-oil at 275°C for 40, 60, and 80 min. At 300°C, the Mw, Mn, and PDI values remained constant until the 60 min mark, after which depolymerisation became evident, as the PDI decreased at 60 min. At 80 min, the PDI increased slightly, indicating repolymerisation into heavier molecules. Repolymerisation did not occur at 330°C because the molecular weights decreased as depolymerisation occurred with prolonged residence times. The PDI also decreased because molecules decomposed to similar weight ranges.

4.4.3 Waste loading

4.4.3.1 Elemental composition

Table 4-12 presents the elemental distributions of the bio-oils and residues, where the mass loading of waste PCBs varied between 0 and 100 wt.%. Here, 300°C and 80 min were selected as the process parameters.

Table 4-12: Elemental analysis of bio-oils and residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

Product	PCB loading (wt.%)	C (wt.%) (±1.45)	H (wt.%) (±0.45)	N (wt.%) (±0.25)	R (wt.%) (±2.12)
Bio-oil	0	59.09	6.81	0.66	34.10
	10	60.63	6.71	0.77	31.89
	30	61.13	6.69	1.15	31.03
	50	69.38	6.82	0.88	22.91
	70	69.42	6.79	1.24	22.55
	90	67.50	6.70	1.54	24.26
	100	68.19	6.65	1.48	23.69
Product	PCB loading (wt.%)	C (wt.%) (±0.86)	H (wt.%) (±0.05)	N (wt.%) (±0.03)	R (wt.%) (±0.90)
Residue	0	48.92	2.48	0.27	48.34
	10	34.70	1.98	0.17	63.15
	30	27.28	1.60	0.22	70.90
	50	20.56	1.32	0.16	77.96
	70	12.05	0.88	0.13	86.94
	90	5.80	0.50	0.03	93.68
	100	4.83	0.52	0.00	94.67

The waste loading had a significant impact on the bio-oil composition. Initially, the carbon content increased with waste loading up to 50 wt.%, whereafter the carbon content remained within the confidence level. This trend could be explained by the lignosulphonate causing an abundance of free radicals, which favours the formation of heavy organic solids, rather than recombining into organic molecules in the bio-oils (Gollakota *et al.*, 2018). Given the very low yields of bio-oils at lower waste loading (as depicted in Figure 4-8), the consistency in the carbon content from 50 to 100 wt.% could be attributed to only very small amounts of lignosulphonate carbon migrating into the bio-oils, with waste PCBs contributing most significantly to the carbon.

Considering the van Krevelen plot for bio-oils produced at various waste loadings (Figure 5-16 in Appendix A), significant changes became evident in both the O/C and H/C ratios. The decline in O/C with increasing waste loading suggested that the waste PCBs contained less oxygen than lignosulphonate does. Similarly, the H/C ratios decreased significantly with increasing waste loading. This may be attributed to lignosulphonate producing a mixture of aliphatic and aromatic compounds, whereas an epoxy resin mainly recombines into aromatic compounds; aromatic compounds generally have a lower H/C ratio (Wadzyk *et al.*, 2019).

Waste loading had a significant effect on the elemental distributions of the residues. According to data in Table 4-12, the carbon content of residues decreased significantly with increasing waste loading. At 0 wt.% loading (only lignosulphonate), the residue contained the highest carbon content. Conversely, at 100 wt.% loading (only waste PCBs), the residue displayed the lowest

carbon content. This indicated that lignosulphonate predominantly formed heavy organic molecules that converted into the residues, while waste PCBs underwent significant depolymerisation to form intermediates that tended to recombine into bio-oils or light gaseous products. This trend is advantageous as lignosulphonate is used to produce biochar structures, with the potential for metal adsorption. When only waste PCBs were used, the majority of the carbon migrated to the bio-oil and gas products, consequently producing a residue composed of mainly inorganics such as metals and ceramics, as evidenced by the residual content at 100 wt.% loading. This observation aligns with the significant loss of carbon content when comparing the residue to the waste PCB feedstock (see Table 4-1), subsequently indicating another desirable trend where the organic fraction was removed.

4.4.3.2 Energy content

Table 4-13 gives the heating values of the bio-oils produced at all waste PCB loadings.

Table 4-13: HHV of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

PCB loading (wt.%)	HHV (MJ/kg) (± 1.49)
0	24.79
10	25.55
30	25.86
50	30.74
70	30.75
90	29.53
100	29.87

The trend for bio-oil heating values is similar to the trend for bio-oil carbon content because the HHV is mainly dependent on the carbon and hydrogen contents of the bio-oils. At loadings >50 wt.%, the HHV exhibited minimal changes. These values were, nonetheless, notably higher than those obtained at loadings <50 wt.%. Notably, at a 100 wt.% PCB loading, the bio-oil HHV surpassed the typical energy values reported for bio-oils derived from woody biomass in catalytic HTL (Nagappan *et al.*, 2021).

4.4.3.3 Proximate composition

The proximate composition of residues, for the mass loadings of waste PCBs between 0 and 100 wt.%, is presented in Table 4-14.

Table 4-14: Proximate analysis of residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

PCB loading (wt.%)	Moisture (wt.%) (±0.45)	Volatile (wt.%) (±2.00)	Fixed carbon (wt.%) (±2.94)	Ash (wt.%) (±2.01)
0	10.53	37.68	28.18	23.62
10	5.43	32.16	22.33	40.08
30	4.57	24.68	11.52	59.23
50	4.07	21.82	3.65	70.45
70	1.51	16.01	-3.57	86.05
90	0.45	9.81	-5.56	95.30
100	0.34	8.53	-4.19	95.32

A noticeable decrease in the moisture content was observed with increasing waste loading. This is likely due to waste PCBs forming low-carbon residues (as previously confirmed). Consequently, these residues would not contain the components that are necessary for water to adhere to the solid, such as surface functional groups or porous structures. Conversely, lignosulphonate produced carbon-rich residues, leading to an increase in moisture content.

Similarly, the volatile content also decreased with increasing waste loading. Upon comparing a 0 wt.% waste loading to pure lignosulphonate (Table 4-2), it was clear that there was a significant increase in fixed carbon, while the volatile content decreased. This is advantageous for applications involving metal adsorption because more heavy organic functional groups are present in the residue. Conversely, when comparing the volatile content at a 100 wt.% waste loading to the PCB feedstocks, a notable decrease in volatiles was observed. This decrease was primarily attributed to the epoxy resin decomposing to form gas or bio-oil products, rendering the residues less hazardous as a result of VOC emissions. Furthermore, most of the carbon contained in the PCBs makes up the volatile content, thus the decrease in fixed carbon is justified. Interestingly, the negative values at 70, 90, and 100 wt.% waste loading could be attributed to the oxidation of metals at high temperatures, thus confirming significant concentrations of metals.

4.4.3.4 Molecular weight and PDI

The Mw, Mn, and PDI values for bio-oils obtained for all waste loadings are presented in Table 4-15.

Table 4-15: GPC analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

PCB loading (wt.%)	Mw (g/mol) (± 77.58)	Mn (g/mol) (± 2.87)	PDI (± 0.54)
0	370.85	108.63	3.41
10	505.25	105.55	4.78
30	1070.19	135.89	7.88
50	976.90	134.27	7.27
70	937.82	147.71	6.35
90	1261.28	168.11	7.50
100	1108.63	514.09	2.17

An analysis of the Mw and Mn values revealed that HTL experiments with high waste PCB loadings produced much higher molecular weights and distributions. Considering the H/C ratios, it follows that bio-oils at higher waste loadings produce more stable aromatic compounds with high molecular weights, whereas lignosulphonate produces a mixture of aliphatic and aromatic compounds, subsequently, they have lower molecular weights. Thus, mixing these feedstocks produced a wide range of molecules and justified the high PDI at 30, 50, 70, and 90 wt.%. Furthermore, these PDI values were higher than values for the lignosulphonate feedstock (2.60 g/mol), although the Mw and Mn were significantly lower. This confirmed that depolymerisation occurred and only intermediates recombined into a wide range of lighter bio-oil molecules.

4.5 Effect of operating parameters on the organic compounds in products

As mentioned earlier (Section 4.4), both the bio-oil and residue contain significant amounts of carbon. The effect of temperature, residence time, and waste loading on the organic composition of the HTL products is now addressed. The total phenolic content of the aqueous phases is given. FTIR analysis provides insight into the functional groups present in the bio-oils and residues. GC-MS analysis provides semi-quantitative findings pertaining to the compound distribution in the bio-oils. Additional data from determinations at other conditions are provided in Appendix A (referred to when applicable).

4.5.1 Reaction temperature

4.5.1.1 Water-soluble phenolic compounds

Table 4-16 presents the total phenolic contents of the aqueous phases obtained from HTL experiments at an intermediate residence time of 40 min for all selected temperatures. Data for other residence times are presented in Table 5-9 in Appendix A.

Table 4-16: Total phenol analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 40 min for 250, 275, 300, and 330°C

Operating parameters		g/l as phenol (± 0.11)
Residence time (min)	Temperature (°C)	
40	250	12.89
	275	6.43
	300	7.00
	330	5.45

The phenolic content of the aqueous phase was high. This arises from the decomposition of the epoxy resin and lignin to yield small polar phenolic compounds. These phenolics can occur in various forms, the most common being phenol, vanillin, *p*-cresol, and catechol (Marais *et al.*, 2019). The total phenolic content was significantly higher than at elevated temperatures than at lower temperatures (at 250°C, for example). Since lignosulphonate dissolves in water, and the reaction severity might be too mild for adequate decomposition, there could be a higher phenolic content due to the phenolic groups within the lignin molecules. Alternatively, it could indicate the formation of some polar phenolic intermediates from both feedstocks, however, less energy is available for the subsequent recombination and conversion into other product fractions.

From the data in Table 4-16 and Table 5-9, a consistent trend emerged across all residence times; the phenolic content decreased with increasing temperature. The decrease in phenolic content serves as the explanation for both the decomposition of lignosulphonate and for the recombination and conversion of polar phenolic intermediates with increasing temperature. The phenolic compounds may either recombine into aromatic compounds present in the bio-oils or transform into heavier compounds that contribute to the solid product. Basar *et al.* (2023) have reported similar findings for aqueous phases obtained from the HTL of mixed sludge cake.

4.5.1.2 Functional groups of bio-oils and residues

FTIR analysis provides valuable insight into the functional groups present in the bio-oils and residues. The findings are based on qualitative trends, however, the intensity of the peaks may provide some indication of the concentration of a functional group, although this relationship is not strictly linear. Figure 4-9 shows the FTIR spectra of the bio-oils obtained at all temperatures for a long residence time (80 min). The spectra of bio-oils derived at all temperatures at a short residence time (20 min) are presented in Figure 5-17 in Appendix A.

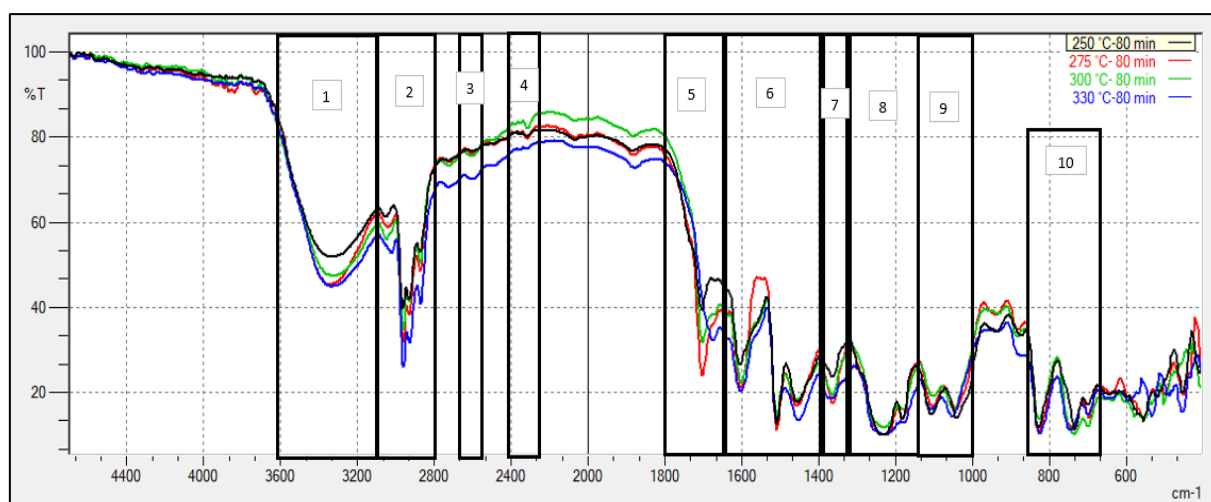


Figure 4-9: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 80 min for 250, 275, 300, and 330°C

The FTIR spectra serve as a valuable tool for the identification of functional groups within the bio-oils, while GC-MS analysis allows for a semi-quantitative assessment of the compounds containing these groups. The spectra obtained at 80 min closely resembled those acquired at 20 min, suggesting a consistent range of functional groups present in bio-oils. However, certain concentrations of compounds exhibited more variability with temperature at 20 min compared to at 80 min. Discussion of this variation will be included with the discussion of the subsequent GC-MS findings.

The bands and notations depicted in Figure 4-9 are further detailed in Table 5-20 in Appendix B. The first peak, designated as 1, corresponds to the -OH stretching vibration commonly found in phenolic compounds as hydroxyl groups. While these peak intensities remained relatively consistent across various temperatures, the peak for 250°C was slightly less intense, indicating a lower concentration of phenolic compounds in this bio-oil. In the spectra obtained for a residence time of 20 min (Figure 5-17 in Appendix A), significant difference in peak intensities was seen; the -OH group became more intense as temperature increased. This could be attributed to the decomposition of feedstocks and recombination into phenolic compounds being favoured at higher temperatures. This trend is also supported by the decrease in aqueous phase phenolic content with increasing temperature (Table 4-16) since part of these phenolics migrate to the bio-oil. Notation 2 comprised a small and large peak representing the sp^2 and sp^3 C-H symmetrical stretching vibrations, respectively. Their peak intensities were similar, irrespective of temperature, with the sp^2 C-H typically associated with aromatic rings or double-bonded carbon, whereas the sp^3 C-H were typically part of tetrahedrally coordinated single bonds, such as sections of saturated fatty acids or aliphatic ethers. Therefore, these peaks correspond to a variety of molecules in the bio-oils.

The small peak, designated by notation 3, signified the presence of sulphur-containing groups in the bio-oils. The small peak in notation 4 was indicative of nitrile groups, confirming the presence of nitrogen compounds in the bio-oils and it corresponded to the nitrogen content observed in the elemental analysis of the bio-oils. Notation 5 indicates the C=O groups and presents variations in peak intensities with increasing temperature at both 20 and 80 min. The presence of the C=O group may suggest a range of compounds, including carboxylic acids, ketones, esters, and aldehydes. More intense peaks are observed at 250 and 275°C, suggesting that some of these compounds are removed from the bio-oils at higher temperatures.

Furthermore, the three distinct peaks designated by notation 6 indicated the aromatic rings. No large deviations in peak intensity were observed with increasing temperature at both 20 and 80 min, suggesting that the bio-oils are mainly composed of aromatic structures, therefore corresponding to the low H/C ratios of the bio-oils. The sp^3 C-H asymmetrical bend vibrations, indicated by the peak in notation 7, are another indication of aliphatic compounds in the bio-oils (although there are several molecules that may possess this functional group). Notation 8 indicates the C-O peaks characteristic of the hydroxyl group in phenolic compounds. The C-O aromatic and aliphatic ether bonds are indicated by the peaks in notation 9. Lastly, notation 10 again indicates the aromatic rings through the sp^2 C-H bend groups.

To conclude, FTIR analysis confirmed that a wide range of molecules are present in the bio-oils, with the majority being aromatics, however, a notable fraction of aliphatic compounds is also present. Furthermore, temperature did not have a significant effect on the range of functional groups in the bio-oil, although their concentration is affected.

Given the high carbon content as identified in the elemental analysis, FTIR analysis of the residues was carried out. Figure 4-10 presents the FTIR spectra of residues obtained at a long residence time (80 min) for all temperatures. The corresponding spectra of residues obtained at a shorter residence time (20 min) are presented in Figure 5-21 in Appendix A.

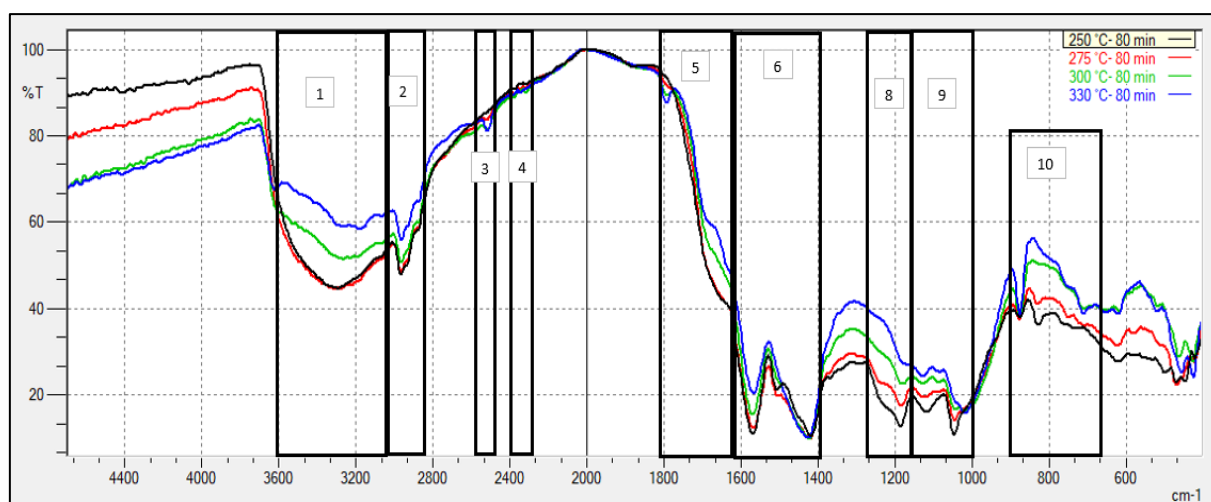


Figure 4-10: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 80 min for 250, 275, 300, and 330°C

The spectra of the residues comprised fewer peaks compared to the spectra of bio-oils because fewer functional groups and fewer organic molecules were present. As mentioned earlier, the organic fraction of the residues likely consists of epoxy resin that has not decomposed, as well as heavier organic compounds formed through the initial recombination of intermediates from the original epoxy and lignosulphonate, or through the cracking and repolymerisation of the bio-oils. The decomposition of the heavy organic molecules could also play a role.

In both Figure 4-10 and Figure 5-21, the peak intensities varied with temperature, which suggests that temperature has an impact on the composition of the residues. The peaks in notation 1 represent the -OH hydroxyl groups. The peak intensity was lower at increasing temperatures. This could indicate the loss of the hydroxyl groups from the epoxy resin through decomposition. A similar trend was noted at a 20 min residence time. Notation 2 comprises a single peak representing the sp^3 C-H symmetrical stretch group. This demonstrated minimal variation with temperature at both 20 and 80 min residence times, suggesting a wide range of compounds with tetrahedral single bonds. A small peak, designated as notation 3, was observed, indicating the S-H group in sulphur-containing compounds. For both 20 and 80 min, this peak was more pronounced at 330°C, indicating that higher temperatures facilitate the migration of sulphur to the residue, likely originating from the lignosulphonate. Similarly, at notation 4, slight vibrations for nitrile groups were evident; they corresponded to the low nitrogen content of residues.

The shoulder band in notation 5 represents the C=O groups. As established, these groups are an indication of various compounds, including carboxyl and carbonyl functional groups (these are advantageous for metal adsorption) (Li *et al.*, 2017). This shoulder peak was not very prominent, and it decreased with increasing temperature. The decomposition of ester bonds from the curing agents binding to the terminal epoxide groups could also play a part in the decrease. This trend

does not favour metal adsorption as it confirms only small concentrations of carboxyl and carbonyl groups in the residues. The peaks designated by notation 6 represent the aromatic rings. At 80 min, the peak intensities remained consistent; however, at 20 min, the peak intensity for 250°C decreased, likely due to low severity conditions. Notation 8 presents the peak for the C-O group, representative of the phenolic hydroxyl group. As the temperature increases, the peak intensity decreases, aligning with the trend observed in notation 1. The reduction in phenolic hydroxyl groups is also not advantageous for metal adsorption (Li, Yang, *et al.*, 2022). Similarly, the peak designated by notation 9 represents the ether groups, decreasing with increasing temperature. This could be an indication of the decomposition of the characteristic C-O-C group in the epoxy resin. Lastly, notation 10 indicates the sp² C-H asymmetrical groups typically bonded to aromatic rings. The peak intensities were higher at 330°C.

It is noteworthy that the decrease in C=O (carboxyl and carbonyl) and -OH (hydroxyl) groups produces molecules with less affinity towards metal adsorption. However, it is possible that compounds containing these functional groups undergo metal adsorption through complexation and cation exchange reactions during HTL, thus reducing the concentration and related peak intensities of these functional groups.

4.5.1.3 Compounds in bio-oils

FTIR spectra revealed a range of functional groups present in the bio-oils, including phenolic compounds, benzene derivatives, ketones, acids (carboxylic and fatty), alkenes, sulphur compounds, and nitrogen compounds. Through GC-MS analysis, the concentration of each could be semi-quantitatively determined as an area%, thus offering a better view of the composition than that achieved with FTIR analysis. To ensure accuracy, only compounds with a detected quality of 80% or higher were considered—they were normalised to 100.

The GC-MS findings for all temperatures at both a short (20 min) and a long (80 min) residence time are presented in Table 4-17. The findings for intermediate temperatures (40 and 60 min) are presented in Table 5-8 in Appendix A.

Table 4-17: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C

Compound groups (area%)	20 min				80 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Acids (± 1.25)	2.38	3.03	2.85	0.00	7.05	3.61	3.42	1.03
Alkenes (± 0.60)	2.59	0.00	0.33	1.76	0.97	0.19	0.40	5.12
Benzene derivatives (± 1.04)	0.00	0.13	0.59	0.00	0.55	0.00	0.55	0.90
Fatty acids (± 0.27)	3.10	2.51	1.04	0.34	0.92	0.80	0.71	0.19
Nitrogen compounds (± 1.64)	1.19	0.00	2.20	0.83	0.14	0.00	0.72	1.32
Ketones (± 2.17)	3.12	4.82	2.30	2.25	0.61	1.71	2.20	3.46
Phenolic compounds (± 4.50)	49.13	73.88	87.23	88.68	70.38	89.02	84.96	79.17
Sulphur compounds (± 0.09)	3.80	1.17	0.00	0.00	2.67	0.19	0.04	0.16
Others (± 4.35)	34.70	14.45	3.45	6.13	16.70	4.48	7.00	8.66
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Phenol (% of phenolics) (± 2.94)	4.23	14.99	26.02	10.92	15.80	22.54	19.11	7.93
Cresols (% of phenolics) (± 0.70)	0.60	0.91	3.73	7.66	0.62	2.79	7.57	7.61

According to Table 4-17 and Table 5-8, the largest fraction present in all bio-oils was the phenolic compounds. These findings are consistent with results of studies conducted by others during the hydrothermal treatment of epoxy resin (Xing & Zhang, 2013; Yildirim *et al.*, 2015; Yin *et al.*, 2011; Zhao *et al.*, 2019). This consistent pattern suggests that the underlying reactions responsible are the hydrolysis and thermal degradation pathways for epoxy resin because the primary products are phenolics (Yin *et al.*, 2011).

This confirmed the potential for valorisation of the organic fractions in waste PCBs via HTL as the phenolic compounds have shown many desirable traits (antiproliferative, anticancer, antiviral, anti-inflammatory, antimicrobial, and antioxidant activities) and applications (pharmaceutical, cosmetic, and food industries) (Albuquerque *et al.*, 2021).

Considering the effect of temperature on the phenolic compounds in the bio-oils, the following observations were made. At 20 min, temperature increases resulted in an increase in the phenolic content, which stabilised at 300°C and 330°C. At 40, 60, and 80 min, increased temperature led to an increase in phenolic content, however, this trend reached a turning point (300°C for 40 and 60 min; 275°C for 80 min), likely attributed to cracking of these compounds at higher reaction severities. The phenolic compounds comprised a notable fraction of pure phenol and cresols.

While phenol exhibited a similar trend to the overall phenolic content, the cresols exhibited a continuous increase with rising temperatures, thus favouring higher severity conditions.

Across all residence times, the bio-oils displayed their highest complexity at 250°C, as evidenced by the substantial area% assigned to compounds classified as 'others'. Increasing the temperature reduced these values significantly, correlating to the phenolic compounds increasing because an inversed trend can be observed. Similarly, the acids and fatty acids decreased with increasing temperatures as the cracking of these compounds became more significant. Results of FTIR analysis of residues (Figure 4-10) did not show a higher intensity for the C=O bonds with increasing temperature, suggesting that possibly these compounds favour conversion to light compounds in the gas product after cracking. Although concentrations of sulphur compounds were detected, their concentrations were relatively low. At 20 min, the concentration continually decreased with temperature, however at 40, 60, and 80 min a turning point was reached at 300°C, whereafter the sulphur compounds increased. FTIR data of residues also showed more intense peaks for the S-H thiol bond at 330°C, the sulphur likely originates from the lignosulphonate in the aqueous phase. Lastly, ketones exhibited fluctuations with changing temperatures, however, the area% remained within the bounds of statistical confidence.

4.5.2 Residence time

4.5.2.1 Water-soluble phenolic compounds

The effect of residence time on the phenolic content of the aqueous phases at 300°C is illustrated in Table 4-18. The data for other temperatures are presented in Table 5-9 in Appendix A.

Table 4-18: Total phenolic analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 300°C for 20, 40, 60, and 80 min

Operating parameters		g/l as phenol (±0.11)
Temperature (°C)	Residence time (min)	
300	20	6.45
	40	7.00
	60	6.53
	80	5.93

According to Table 4-18 and Table 5-9, the residence time had a comparable influence on the phenolic content of the aqueous phases to that of temperature. There was an overall slight decrease with increased time at 250°C, 275°C, and 330°C. At 300°C, the phenolic content began to decrease from 40 min. At 250°C, the rate of decrease was much higher compared to that at higher temperatures, likely attributed to dissolved lignosulphonate having a greater ability to decompose at increased times. Furthermore, longer residence times allowed for secondary

reactions, such as recombination or migration of phenolics to the bio-oils or heavy molecules in the solid product, to become more prominent.

4.5.2.2 Functional groups of bio-oils and residues

Figure 4-11 presents the FTIR spectra of the bio-oils obtained at 250°C at all residence times. The spectra obtained at 330°C for all residence times are presented in Figure 5-18 in Appendix A.

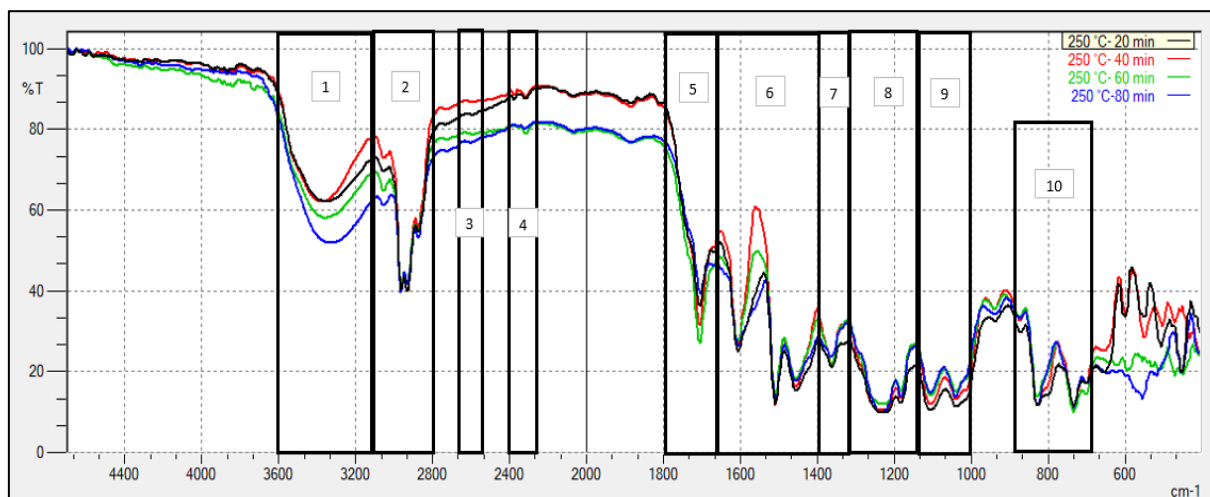


Figure 4-11: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C for 20, 40, 60, and 80 min

Upon comparing the spectra depicting changes in time (Figure 4-11) with those illustrating changes in temperatures (Figure 4-9), it was evident that the peak distribution remained consistent. This indicated that the range of functional groups in the bio-oils remained consistent with increasing reaction severity. The peaks in Figure 4-11 are not identified here—all notable peaks were identified during the earlier discussion of Figure 4-9. Only significant changes in peak intensities with varying residence times will now be discussed.

First, the hydroxyl group vibration, designated as notation 1, exhibited variations with longer residence time. At 250°C (Figure 4-11), this peak became more intense as a longer residence time was allowed, indicating a higher concentration of -OH groups, likely due to more phenolic compounds found in the bio-oils. Conversely, at 330°C, this trend was not noticed for the -OH peak; here, the peak intensity was similar, except at 60 min, where the intensity was lower. This suggests that at a higher temperature the phenolic compounds may have started to undergo cracking. At notation 5, representing the C=O group, slight variations in this peak were observed at 250°C, with the 20 and 80 min peak intensities being lower than those at intermediate times. This indicated that the formation of compounds such as acids, ketones, and aldehydes favoured intermediate times; a short residence time did not allow enough time for significant formation, while a longer residence time led to a decrease, likely due to secondary cracking reactions.

For all other peaks, at both 250°C and 330°C, no significant changes in intensity with respect to residence time were observed, suggesting that residence time had a less pronounced impact on the composition of the bio-oils than temperature did. The GC-MS findings provided a better understanding of changes in concentration with respect to residence time.

The FTIR spectra of the residues obtained at 250°C for all residence times are presented in Figure 4-12. As with the spectra of the bio-oils, the peak distributions of the residues remained mostly unchanged with increasing reaction severity, although there were some variations in the peak intensities and hence concentrations of groups. Consequently, only peaks where the intensity was affected by residence time will be discussed. The earlier discussion of Figure 4-10 has included the identification of each peak and group detected in the residues.

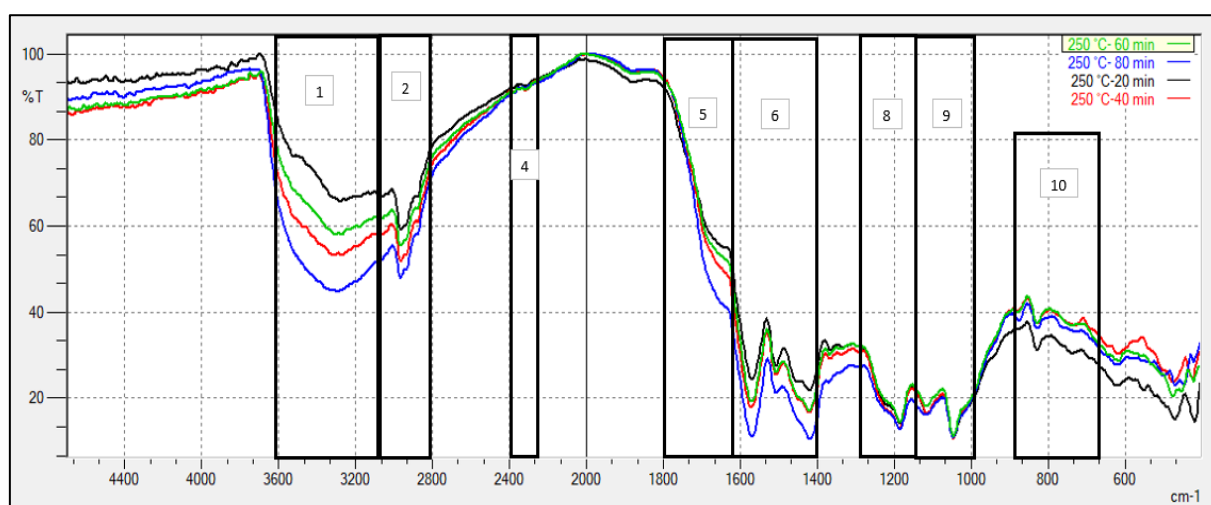


Figure 4-12: FTIR spectrum of residues from the HTL of waste PCBs and liginosulphonate at 250°C for 20, 40, 60, and 80 min

Figure 4-12 shows that increases in residence time resulted in more intense peaks for the -OH functional group in notation 1. This indicated that at 250°C the energy provided to the system was insufficient for the rate of decomposition of epoxy resin to overtake the recombination rate to form heavy compounds, which then convert to the residue. The intermediates likely originate from the liginosulphonate dissolved in the aqueous phase. A similar trend was noticed for other peaks, including notation 5 (C=O) and notation 6 (aromatic rings).

Conversely, Figure 5-20 in Appendix A presents the FTIR spectra of residues obtained at a higher temperature (330°C). There, no peak intensities were significantly affected by increases in the residence time. It was therefore concluded that the composition of the residues remains largely constant, with only small deviations, probably due to the dynamic equilibrium between the decomposition and repolymerisation reactions.

4.5.2.3 Compounds in bio-oils

GC-MS analysis enables a semi-quantitative assessment of how residence time influences the concentration of compounds in the bio-oils. Results obtained for all residence times at both a low (250°C) and a high (330°C) temperatures are presented in Table 4-19. Results for the intermediate temperatures (275°C and 300°C) are presented in Table 5-7 in Appendix A.

Table 4-19: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min

Compound groups (area%)	250°C				330°C			
	20 min	40 min	60 min	80 min	20 min	40 min	60 min	80 min
Acids (± 1.25)	2.38	11.08	13.96	7.05	0.00	1.75	2.17	1.03
Alkenes (± 0.60)	2.59	2.72	1.21	0.97	1.76	0.89	1.47	5.12
Benzene derivatives (± 1.04)	0.00	0.01	0.00	0.55	0.00	4.91	0.00	0.90
Fatty acids (± 0.27)	3.10	3.13	2.66	0.92	0.34	0.00	0.93	0.19
Nitrogen compounds (± 1.64)	1.19	0.92	0.82	0.14	0.83	0.55	0.28	1.32
Ketones (± 2.17)	3.12	1.42	0.79	0.61	2.25	1.99	2.47	3.46
Phenolic compounds (± 4.50)	49.13	61.73	58.35	70.38	88.68	83.45	86.52	79.17
Sulphur compounds (± 0.09)	3.80	0.67	0.17	2.67	0.00	0.28	0.26	0.16
Others (± 4.35)	34.70	18.32	22.05	16.70	6.13	6.18	5.88	8.66
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Phenol (% of phenolics) (± 2.94)	4.23	6.79	7.71	15.80	10.92	13.22	5.50	7.93
Cresols (% of phenolics) (± 0.70)	0.60	0.00	0.00	0.62	7.66	10.13	7.25	7.61

As previously mentioned, the phenolic compounds are the most abundant of all the identified compounds in the bio-oils—the likely reason for this is the decomposition of the epoxy resin through reaction pathways such as hydrolysis and thermal degradation (see Section 2.4.3.2). At the lower temperatures (250°C and 275°C), extending the residence time resulted in an increased phenolic content in the bio-oils (at 250°C, the production of phenolics was lower overall, compared to at the other temperatures). This was due to the slow rate of decomposition, due to the lower energy input. This slow rate was confirmed when considering that the rate of repolymerisation to form heavy molecules was faster than the decomposition rate, as observed in FTIR spectra (Figure 4-12). As a result, longer residence times allowed enough time for the slow decomposition rate to yield a significant number of intermediates that recombined into phenolics in the bio-oils. A similar occurrence was observed for 275°C, although at 40 min the rate of phenolic formation began to stagnate. At 300°C and 330°C, the phenolic content for the bio-oils remained within the confidence

level for up to 60 min, whereafter a decrease was observed at 80 min. This could be attributed to the higher temperatures enabling the accelerated decomposition of the epoxy resin as both hydrolysis and thermal degradation occurred, unlike the dominant depolymerisation reaction of hydrolysis at 250°C. Consequently, the rate of production of phenolics stagnated as the epoxy resin began to fully decompose at higher temperatures, while the rate of secondary cracking reactions increased at higher temperatures, ultimately overtaking phenolic formation after 60 min, and then decreasing the phenolic content in the bio-oils. Notably, pure phenol exhibited a similar trend. Cresols mimicked this trend, however, the rate of cracking and decrease overtook the formation rate at 330°C after 40 min, while consistently increasing with longer residence times at lower temperatures. Indications were therefore that cresol formation favoured higher severity conditions compared to phenol.

The trends for the category of compounds classified 'others' corresponded to the trends exhibited by the phenolic compounds, subsequently producing an inverse trend to the phenolics. The ketones showed a decrease with increasing residence time at both 250°C and 275°C, whereafter the concentration remained within the confidence levels. The increase in C=O bonds observed in the residues at low temperatures (Figure 4-12) indicated the potential migration of ketones (or their constituents), from the bio-oils to the residues at prolonged residence times. A similar trend was noticed for the fatty acids; however, after 275°C the area% began to fluctuate with longer residence times. Acids also began to fluctuate with extended residence times after 275°C. At 250°C and 275°C, an initial increase was observed, whereafter a decrease was then seen in the acid content. These acids likely originate from the decomposition of lignosulphonate. Lastly, low concentrations of the remaining compounds, including benzene derivatives, sulphur compounds, nitrogen compounds, and alkenes were noted, with changes in residence time resulting in fluctuating concentrations at all the investigated temperatures. These fluctuations primarily arise from the acceleration of complex secondary reactions when longer residence times are allowed.

4.5.3 Waste loading

4.5.3.1 Water-soluble phenolic compounds

Table 4-20 presents the phenolic content of the aqueous phases resulting from HTL experiments where the PCB waste loading was varied between 0 and 100 wt.%, with process parameters at 300°C and 80 min.

Table 4-20: Total phenolic analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

PCB loading (wt.%)	g/l as phenol (± 0.11)
0	2.61
10	2.77
30	4.74
50	5.93
70	7.02
90	6.22
100	5.56

Table 4-20 shows that the epoxy resin yields more polar phenolic compounds than lignosulphonate; the phenolic content is higher at a 100 wt.% PCB loading than at a 0 wt.% PCB loading. Furthermore, an incremental rise in PCB loading resulted in a consistent increase in the phenolic content up to 70 wt.%, whereafter the phenolic content decreased. The initial increase is justified by the fact that the epoxy resin produces more phenolic compounds than lignosulphonate. However, the decrease at 90 and 100 wt.% is contradictory. This suggests that, although the epoxy resin produces more phenolics, the lignosulphonate has a synergistic effect that results in more of the phenolics migrating to the aqueous phase, which is supported by the decrease in phenolic content at 90 and 100 wt.%, as less lignosulphonate is available. Although speculative, this synergistic relationship could be based on the abundance of free radicals provided by the lignosulphonate, subsequently allowing the formation of more phenolic compounds by reacting with the aromatic intermediates from the epoxy resin. Another plausible explanation could be that the lignosulphonate that has not degraded remains within the aqueous phase, thus increasing the total phenolic content, through the detection of phenolic groups present in the lignin molecules; therefore, at higher PCB loadings, less lignin remains in the aqueous phase.

4.5.3.2 Functional groups of bio-oils and residues

The FTIR spectra of the bio-oils obtained from the experiments in which the PCB loadings were varied from 0 to 100 wt.% are illustrated in Figure 4-13. In this case, the 10 and 90 wt.% loading spectra are not included in order to provide a clearer comparative view.

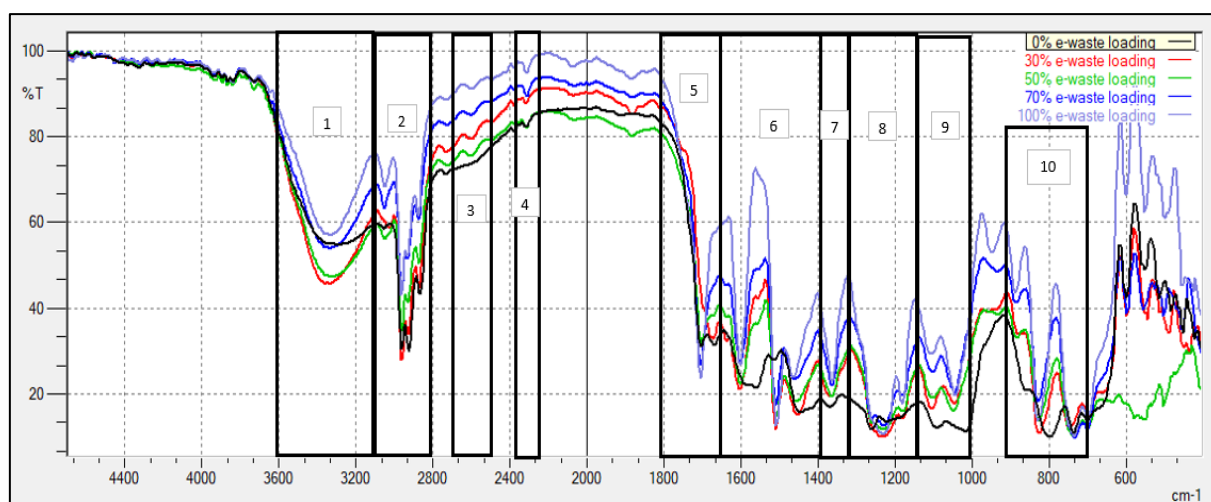


Figure 4-13: FTIR spectrum for bio-oils from the HTL of waste PCBs and lignosulphonate at 0, 30, 50, 70, and 100 wt.% PCB mass loading

While the distribution of functional groups remained consistent, their intensities were significantly affected by changes in the waste loading. The peak designated by notation 1 represents the hydroxyl groups. It showed an increase, where the initial intensity increased from 0 to 50 wt.% loading, whereafter the intensity decreased. Based on the notations 6 and 10 (aromatic rings), as well as notation 8 (phenol C-O), where the peak intensities increased with higher waste loadings, it was confirmed that a higher waste loading produces more phenolic compounds. This is similar to the trend seen for the phenolic content of the aqueous phase. Therefore, when the waste loading is increased to >50 wt.%, the decrease in the hydroxyl group in notation 1 could indicate the removal of -OH groups not bound to phenolics, such as organic acids or other alcohols.

The residues were also significantly affected by varying the waste loadings. Figure 4-14 presents the spectra of residues wherein the PCB loadings were varied from 0 to 100 wt.%.

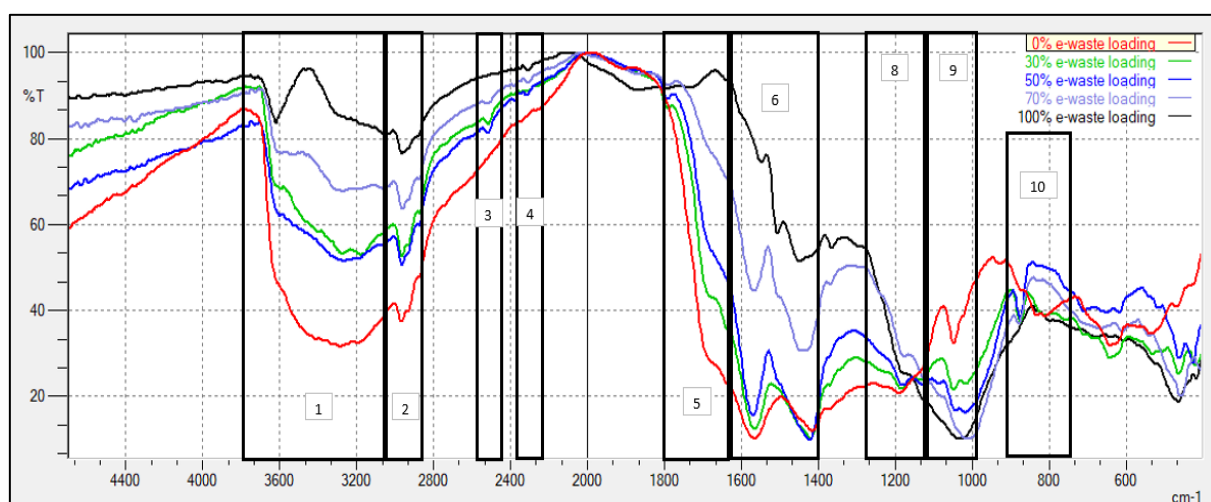


Figure 4-14: FTIR spectrum for residues from the HTL of waste PCBs and lignosulphonate at 0, 30, 50, 70, and 100 wt.% PCB mass loading

Figure 4-14 shows a general decline in intensity across all peaks as the waste loadings increase. This could be attributed to the epoxy resin favouring bio-oil and gas production, rather than recombination to heavy molecules that convert to solid residue. Considering that the carbon content of the residue derived at a 100 wt.% PCB loading was <5 wt.% (as seen in elemental analysis results, Table 4-12), it appeared that the majority of the residue consists of inorganic compounds, such as inert ceramics and metals. The spectrum of the residue at 100 wt.% was compared with a spectrum for fibreglass (see Figure 5-22 in Appendix A). The similarities were very clear, confirming the observation of inorganics in the residue. Conversely, lignosulphonate produced a significant amount of heavy organic molecules, which converted to the solid phase, as indicated by the carbon content at low PCB loadings (Table 4-12). Thus, with the decrease in lignosulphonate loading, the intensity of peaks at notations 1 (hydroxyl groups), 5 (C=O groups), 6 (aromatic rings), and 8 (phenolic C-O) decreased. This highlights the capability of subcritical HTL conditions to depolymerise waste PCBs, with subsequent removal of the organic epoxy resin in waste PCBs. The concentration of metals in the residue, as a consequence of the removal of the organic fraction, will be determined later. Furthermore, the spectra at 50 wt.% PCB loading confirmed that some biochar structures were produced in the residues, which could prove advantageous for metal adsorption.

4.5.3.3 Compounds in bio-oils

The GC-MS data for bio-oils obtained from the experiments wherein the PCB loadings were varied from 0 to 100 wt.% are presented in Table 4-21.

Table 4-21: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

Compound groups (area%)	0 (wt.%)	10 (wt.%)	30 (wt.%)	50 (wt.%)	70 (wt.%)	90 (wt.%)	100 (wt.%)
Acids (± 1.25)	48.13	8.82	5.96	3.42	2.49	2.62	3.79
Alkenes (± 0.60)	0.00	5.48	0.42	0.40	0.35	0.17	0.00
Benzene derivatives (± 1.04)	1.09	7.21	5.84	0.55	1.58	1.78	0.00
Fatty acids (± 0.27)	7.54	0.00	0.00	0.71	0.95	0.00	1.15
Nitrogen compounds (± 1.64)	10.26	6.17	1.49	0.72	0.00	1.42	0.00
Ketones (± 2.17)	5.74	4.07	1.98	2.20	0.00	0.60	0.00
Phenolics (± 4.50)	6.00	31.59	74.93	84.96	91.52	91.65	92.83
Sulphur compounds (± 0.09)	7.54	18.06	2.62	0.04	0.00	0.00	0.00
Others (± 4.35)	13.71	18.61	6.76	7.00	3.11	1.77	2.23
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Phenol (% of phenolics) (± 2.94)	0.00	0.00	8.87	19.11	37.26	44.99	61.17
Cresols (% of phenolics) (± 0.70)	0.00	0.00	8.39	7.57	3.36	1.22	0.00

These results confirmed that the epoxy resin yielded significantly more phenolic compounds than the lignosulphonate, since the phenolics increased with increasing waste loading. However, at a waste loading of ≥ 70 wt.%, the phenolics remained consistent within the confidence range. This trend may be attributed to a synergistic interaction between the two feedstocks, resembling the observed patterns of the phenolic content in the aqueous phase. However, since the phenolics remained within the confidence range at 70, 90, and 100 wt.% loading, this may indicate that the epoxy resin approaches complete degradation under these conditions, affording no further intermediates for recombination into phenolic compounds. This is due to less lignosulphonate competing for energy, or hydrogen and epoxy resin degrading more easily than the lignin molecules. Moreover, the intermediates originating from the lignosulphonate may favour the formation of heavy compounds, rather than the lighter compounds present in the bio-oils, therefore having an insignificant impact on the bio-oil composition at higher waste loadings.

The acids, ketones, sulphur, and nitrogen compounds all consistently decreased with increasing waste loading, thus confirming that these compounds mainly originate from the lignosulphonate. These trends confirmed that the organic fraction of waste PCBs primarily decomposes to phenolics, with a significant fraction of pure phenol (accounting for 61% of the phenolics at 100

wt.% PCB loading). This underscores the potential of HTL not only to eliminate the organic fraction from the PCBs but also to convert it into a valuable product.

4.6 Effect of operating parameters on the metal recovery

Having verified the capabilities of HTL to remove the organic fraction of waste PCBs, the effects of temperature, residence time, and waste loading on the elemental metal and mineral distributions in the residues, bio-oils, and aqueous phases were determined by ICP-OES analysis. Table 5-19 in Appendix B provides the list of elements detected by the ICP-OES analysis with the relevant detection limits, as well as the categorisation of these elements into minerals and metals. (It should be noted that some of these elements can be considered as both metals and minerals.) However, the list of metal elements was limited to the metalloids, transition-, and post-transition metals commonly detected in waste PCBs, whereas the mineral elements, apart from S, were mainly alkali- and alkaline-earth metals. In this section, both mineral and metal elements will be presented in the same tables but discussed separately. Given the wide range of minerals and metals identified, only notable trends are discussed.

4.6.1 Reaction temperature

As previously confirmed, HTL has the capability to decompose the organic fraction of the waste PCBs, with the epoxy resin favouring decomposition to phenolic intermediates, which recombined to the bio-oils or gas products, whereas a significant amount of the lignosulphonate recombined into heavy molecules in the residues. Higher degrees of reaction severities also favoured the decomposition of the epoxy resin, as confirmed by the slight decrease of carbon in the residues and the significant increase in bio-oil carbon (see Table 4-4), as well as the increase in phenolic compounds in the bio-oils (see Table 4-17). Furthermore, at 300°C and 80 min, almost all the carbon was removed from the residues when a 100 wt.% PCB loading was used (see Table 4-12). Consequently, for the decomposition of epoxy resin, it is necessary to study the concentration and potential migration of the minerals and metals to the HTL products. The overall yields of the HTL products only varied by small margins, ~3 wt.%, with changing severities (as demonstrated in Table 5-1). Thus, the fluctuations in the mineral and metal contents with changing severities are reported in milligrams per gram (mg/g). Table 4-22 presents the ICP-OES findings for the residues obtained at all temperatures for both 20 and 80 min. The findings at intermediate residence times are presented in Table 5-11 in Appendix A.

Table 4-22: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C

Element (mg/g)	20 min				80 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (± 1.41)	42.31	42.72	44.05	46.92	39.64	42.26	43.55	47.23
K (± 0.03)	1.00	1.21	1.36	1.49	1.28	1.30	1.75	1.39
Mg (± 0.16)	2.39	2.32	2.42	2.55	2.32	2.34	2.22	2.72
Na (± 2.28)	30.66	36.76	44.74	60.61	37.53	43.87	45.42	59.19
S (± 1.34)	29.10	31.94	38.11	37.77	36.86	35.63	34.40	39.37
P (± 0.07)	0.70	0.68	0.68	0.55	0.41	0.68	0.79	0.72
Al (± 1.95)	47.65	43.61	46.88	45.69	45.57	46.10	44.93	45.47
Ag (± 0.10)	0.43	0.36	0.49	0.41	0.47	0.82	0.71	0.65
Au (± 0.04)	0.24	0.16	0.18	0.19	0.18	0.20	0.19	0.21
Cu (± 6.12)	65.69	47.85	51.76	54.53	58.64	56.99	58.74	66.13
Fe (± 4.11)	47.81	37.11	38.78	40.97	42.52	42.33	44.37	49.44
Ni (± 0.46)	4.03	3.04	3.08	3.51	3.54	3.53	3.73	4.31
Pb (± 0.30)	3.77	3.43	3.49	3.65	3.42	3.55	3.85	3.68
Sb (± 0.01)	0.42	0.43	0.46	0.44	0.45	0.43	0.35	0.44
Sn (± 0.69)	27.05	25.32	25.54	26.27	25.53	25.16	25.80	28.48
Ti (± 0.30)	2.27	1.77	1.66	1.86	2.02	2.08	1.99	2.00
Zn (± 0.29)	5.03	3.94	3.98	4.41	4.47	4.17	4.29	5.18

It is of importance is to emphasise that the concentrations of most metals in the residues are lower than in the original sieved waste PCBs (see Table 4-3). This is due to the addition of lignosulphonate, which forms biochar structures and dilutes the metal concentration in the residues. The mineral elements will now be considered. High concentrations of Ca, Na, and S were observed in the residues, together with small amounts of K, Mg, and P (see Table 4-22 and Table 5-11). There was a general increase in concentration of these mineral elements with increasing temperature at all residence times, except for P, which fluctuated. The presence of Na and S can be attributed to lignosulphonate, with the increasing trend likely due to the formation of heavy molecules that contain these minerals and convert them to the residues. Meanwhile, the presence of Ca predominantly originates from the ceramics in the PCBs. The increase in Ca could be due to enhanced precipitation as a consequence of the higher pH resulting from the elevated temperatures. With increasing temperature, the residue had a higher ash content (as presented in Table 4-6) and less acidic functional groups, leading to an overall higher pH (Li *et al.*, 2017).

In terms of the metal content, the effect of temperature on the concentrations in the residues displayed a more inconsistent pattern. The majority of metals remained within the residues, confirming that they remained as stable metals bound to the residue matrix (F4 according to the BCR sequential extraction method); the Al, Cu, Fe, and Sn were the most abundant metals in the

residue. However, as will be discussed later, some of the metals did convert to a more reactive state, as confirmed by their detection in the bio-oils and aqueous phase. In most cases, no clear trends were observed for the metals in the residues, with the concentrations mostly fluctuating with increasing temperatures. This occurrence is most likely due to the wide range of metals and the complex reaction conditions having different effects on each. However, some exceptions were observed.

At 20 min, a temperature increase gave a trend for several metals, including Au, Cu, Fe, Ni, Pb, Sn, Ti, and Zn. At 250°C, relatively high concentrations of these metals were initially noted, whereafter the concentrations decreased at 275°C. At 300°C, the concentrations either remained similar or increased slightly compared to a temperature of 275°C. Lastly, at 330°C the concentration increased further but did not surpass the initial concentration reported at 250°C. This trend may suggest that at the lowest severity (250°C for 20 min) the majority of the metals remained in a stable state due to the lack of transformation attributed to lower energy input, as well as the decomposition of the waste PCBs. However, as the epoxy resin decomposed, more of these metals transitioned into a more reactive state through mechanisms such as ionisation, phase change, or secondary reactions, thus reducing their concentration in the residues. The subsequent increase in the concentrations could be attributed to the lignosulphonate decomposing and forming biochar structures in the residue, ultimately allowing for metal adsorption into the residues through various mechanisms such as reduction, electrostatic attraction, precipitation, cation exchange, and complexation. Additionally, higher operating temperatures could produce larger pores and subsequently a larger surface area, which could facilitate chemical adsorption (Li *et al.*, 2017). A more detailed study is required to determine the extent to which each mechanism facilitates the adsorption, as well as determine the influence of pore size and surface area.

A similar pattern was observed at 80 min for Au, Cu, Fe, Ni, Sn, and Zn, although in these cases the initial concentration at 250°C was always lower than at 330°C and, in certain cases, lower or similar than the concentrations at intermediate temperatures. This implies that at a longer residence time, more of the metals become reactive at a lower temperature, such as 250°C; however, at 330°C the higher metal concentration could suggest an elevated level of adsorption to the biochar structures within the residue. Alternatively, the metals could have formed complexes with the organic ligands or react with functional groups in the liquid products (F3 according to the BCR sequential extraction method), leading to their migration to the solid product at high temperatures.

Table 4-23 presents the reactive mineral and metal elements in the bio-oils obtained at all temperatures for both 20 and 80 min. The findings at intermediate residence times are presented in Table 5-13 in Appendix A.

Table 4-23: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C

Element (mg/g)	20 min				80 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (± 0.63)	2.16	0.94	0.69	0.93	1.05	0.90	1.19	1.14
K (± 0.10)	0.20	0.17	0.21	0.24	0.17	0.17	0.19	0.28
Mg (± 0.07)	0.10	0.14	0.10	0.17	0.16	0.11	0.12	0.17
Na (± 2.70)	17.28	11.37	15.58	15.59	10.31	18.24	15.62	17.44
S (± 4.73)	16.36	21.02	12.72	18.44	18.84	17.91	14.22	17.43
P (± 0.02)	0.03	0.05	3.11E-03	0.05	0.05	0.02	8.51E-03	0.05
Al (± 0.08)	0.29	0.43	0.19	0.14	0.60	0.32	0.10	0.18
Ag (± 0.01)	7.26E-03	5.04E-03	9.50E-03	5.27E-03	0.02	7.51E-03	9.34E-03	0.02
Au (± 3.81 E-03)	5.31E-03	ND	4.32E-03	7.26E-03	ND	6.92E-03	6.75E-03	7.24E-03
Cu (± 0.09)	0.33	0.33	0.27	0.44	0.28	0.37	0.24	0.40
Fe (± 0.05)	0.07	0.06	0.10	0.30	0.22	0.08	0.12	0.30
Ni (± 0.01)	7.76E-03	1.06E-02	7.96E-03	0.02	1.36E-02	3.47E-03	1.39E-02	0.03
Pb (± 0.04)	BDL	3.33E-03	3.63E-03	9.95E-03	8.93E-03	6.32E-03	1.47E-02	0.03
Sb (± 0.05)	0.08	0.07	0.05	0.21	BDL	0.09	0.07	0.19
Sn (± 0.58)	1.50	1.09	1.87	0.72	0.91	1.64	1.53	0.89
Ti (± 0.05)	4.96E-03	0.04	1.32E-02	0.38	0.14	1.45E-02	0.05	0.20
Zn (± 0.02)	ND	ND	1.39E-02	0.09	0.05	ND	1.24E-02	0.06

BDL: Below the detection limit; ND: Not detected

Table 4-23 shows that the concentrations of metals in the bio-oils exhibit inconsistencies, likely attributed to the complex nature of metals under HTL conditions, as well as the organic composition of the bio-oils. As expected, the overall concentrations of the mineral and metal elements in the bio-oils were notably lower than those in the residues, indicating that the majority of the metals remained in a stable state. Furthermore, the metal concentrations in the bio-oils were higher than in the aqueous phases, as will be discussed later, leading to the conclusion that the bio-oils had certain adsorption properties, possibly due to the high phenolic concentrations and the presence of hydroxyl groups which facilitate metal adsorption (Li *et al.*, 2022).

Regarding the mineral elements, Na and S (from the lignosulphonate) were the most significant in the bio-oils, followed by Ca (from the ceramics in the PCBs). Trace amounts of K, Mg, and S were also detected. The temperature changes did not produce very clear trends for the minerals, although some observations were noted. At residence times of 20, 40, and 60 min, the Ca concentrations at 250°C were higher than at other temperatures, where only fluctuations within the confidence level were observed. At 80 min, the concentration remained within the confidence level for all temperatures. Thus, low severities favoured the removal of Ca from the residues to the bio-

oils, correlating with the lower Ca concentrations in the residues at low severities. Conversely, the Na, and S did not yield any conclusive trends.

From Table 4-23, it was evident that Cu, Fe, Al, and Sn had comparatively high concentrations, correlating to their abundance in the waste PCBs, while trace amounts of the other metals were detected. Some trends were observed, for example, at 20 min several metals, including Cu, Fe, Ni, Zn, and Ti, showed similar changes in concentration with increasing temperature. At 250, 275, and 300°C, these metal concentrations remained within the confidence levels, however, at 330°C, a significant increase was observed. These occurrences indicate that the bio-oils contained more metals at 330°C, possibly due to the increased formation of phenolic compounds in the bio-oils at the short residence time (20 min) and the corresponding adsorption of the phenolic hydroxyl groups. This occurrence could also be due to the reactive metals being released from the residues at high temperature. At a long residence time (80 min), several metals, including Ag, Fe, Ni, Pb, Ti, and Zn, showed a similar trend. At 275°C, the concentrations were lower than observed at 250°C, followed by a consistent increase up to 330°C, with 330°C again yielding the highest metal concentrations at this residence time.

Based on the findings pertaining to the bio-oils, it was concluded that migration from the residues is in relation to the initial metal concentration of the feedstocks, since Cu, Fe, Al, and Sn were the most abundant in the PCBs. Furthermore, certain metals showed similar trends, whilst some only fluctuated with increasing severities. Although there could be various reasons for this phenomenon, the high phenolic concentration of the bio-oils may play a role in facilitating the transfer of these metals to the bio-oils. From the trends observed, it emerged that 330°C gave the highest concentration of metals at both 20 and 80 min. Further research is required to determine the migration mechanisms behind each of these metals.

The mineral and metal element distribution in the aqueous phases obtained at 20 and 80 min for all temperatures is presented in Table 4-24.

Table 4-24: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 20 min and 80 min for 250, 275, 300, and 330°C

Element (mg/g)	20 min				80 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (± 0.10)	1.15	0.13	0.32	0.22	0.45	0.41	0.28	0.20
K (± 0.05)	0.61	0.36	0.39	0.25	0.41	0.28	0.24	0.27
Mg ($\pm 2.38\text{E-}03$)	0.03	8.16E-03	7.21E-03	7.38E-03	0.02	1.14E-02	6.19E-03	3.45E-03
Na (± 0.64)	36.67	35.98	33.54	25.55	30.75	31.75	29.54	24.59
S (± 0.29)	14.81	9.32	7.45	2.80	9.02	6.80	3.42	2.44
P ($\pm 8.89\text{E-}05$)	3.01E-03	5.40E-04	ND	1.34E-04	1.28E-03	3.27E-04	5.79E-05	ND
Al ($\pm 9.64\text{E-}04$)	0.24	0.10	5.17E-03	4.16E-05	0.13	0.02	7.35E-04	ND
Ag (± 0.00)	2.76E-04	ND	ND	ND	1.70E-04	ND	ND	ND
Au ($\pm 2.51\text{E-}04$)	9.33E-04	6.32E-04	9.50E-04	3.76E-04	1.31E-03	4.41E-04	5.40E-04	7.02E-04
Cu ($\pm 1.99\text{E-}03$)	8.77E-03	1.03E-02	7.25E-03	7.91E-03	7.62E-03	5.92E-03	9.69E-03	1.08E-02
Fe ($\pm 3.84\text{E-}05$)	8.23E-03	1.54E-03	5.36E-04	1.09E-04	6.64E-03	5.42E-04	1.73E-04	1.55E-04
Ni ($\pm 2.21\text{E-}04$)	1.58E-03	1.04E-03	4.82E-04	3.64E-04	7.99E-04	6.42E-04	5.40E-04	8.20E-04
Pb ($\pm 6.93\text{E-}05$)	4.33E-04	1.27E-04	5.67E-05	2.10E-05	2.82E-04	3.10E-05	2.49E-05	1.01E-04
Sb ($\pm 2.23\text{E-}03$)	4.11E-03	2.81E-03	6.78E-03	6.04E-03	4.56E-03	2.34E-03	5.02E-03	6.34E-03
Sn (± 0.01)	0.53	0.03	0.03	1.11E-02	0.10	0.03	0.02	1.16E-02
Ti ($\pm 2.15\text{E-}05$)	2.30E-03	2.72E-04	9.51E-05	2.38E-05	7.86E-04	1.21E-04	2.88E-05	3.55E-05
Zn (± 0.00)	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not detected

Table 4-24 shows that the mineral elements were the most prevalent, with Na and S from the lignosulphonate the most abundant, in agreement with the findings reported in literature (Panisko *et al.*, 2015). A consistent decrease in both Na and S was noted with increasing temperature at all residence times. This could be an indication of the dissolved lignosulphonate decomposing at elevated temperatures, with the consequent removal of these two elements from the aqueous phases. Furthermore, only trace amounts of metals were detected. This is a favourable observation as this means that less treatment of the aqueous phase would be required. Of all the HTL products, the most consistent trends were observed for metals in the aqueous phases. Almost none of the Ag or Zn migrated to the aqueous phases with changing temperatures. The Al, Fe, Pb, Sn, and Ti all consistently decreased with increasing temperature at all residence times, suggesting that these metals initially migrated to the aqueous phase at 250°C; however, at increasing temperatures these metals were removed. Possible causes include the adsorption mechanisms of the biochar structures in the residues or the phenolic compounds in the bio-oils, as well as secondary reactions leading to stable ligands.

4.6.2 Residence time

The ICP-OES findings for the mineral and metal elements in the residues for all residence times at both a low (250°C) and a high (330°C) temperature are presented in Table 4-25. The findings at intermediate temperatures (275°C and 300°C) are presented in Table 5-10 in Appendix A.

Table 4-25: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min

Element (mg/g)	250°C				330°C			
	20 min	40 min	60 min	80 min	20 min	40 min	60 min	80 min
Ca (±1.41)	42.31	41.24	42.38	39.64	46.92	47.20	46.06	47.23
K (±0.03)	1.00	1.05	1.16	1.28	1.49	1.46	1.46	1.39
Mg (±0.16)	2.39	2.26	2.38	2.32	2.55	2.65	2.54	2.72
Na (±2.28)	30.66	33.28	33.93	37.53	60.61	53.00	57.00	59.19
S (±1.34)	29.10	30.31	32.07	36.86	37.77	38.44	39.63	39.37
P (±0.07)	0.70	0.56	0.65	0.41	0.55	0.82	0.62	0.72
Al (±1.95)	47.65	45.97	45.13	45.57	45.69	49.08	46.28	45.47
Ag (±0.10)	0.43	0.49	0.29	0.47	0.41	0.51	0.66	0.65
Au (±0.04)	0.24	0.20	0.23	0.18	0.19	0.33	0.21	0.21
Cu (±6.12)	65.69	63.91	62.33	58.64	54.53	63.11	59.52	66.13
Fe (±4.11)	47.81	44.99	47.08	42.52	40.97	51.68	45.11	49.44
Ni (±0.46)	4.03	3.73	4.05	3.54	3.51	4.45	3.94	4.31
Pb (±0.30)	3.77	3.73	3.67	3.42	3.65	3.96	3.65	3.68
Sb (±0.01)	0.42	0.44	0.45	0.45	0.44	0.41	0.42	0.44
Sn (±0.69)	27.05	26.21	26.20	25.53	26.27	29.24	34.26	28.48
Ti (±0.30)	2.27	2.20	2.16	2.02	1.86	2.53	2.10	2.00
Zn (±0.29)	5.03	4.80	5.06	4.47	4.41	5.22	4.68	5.18

As mentioned earlier, the majority of minerals and metals remain in a stable state within the residues. Similar to the effects of temperature changes, very few trends are clear since most of the concentrations fluctuated, likely due to the complex nature of HTL reactions and conditions. Ca was the most abundant mineral in the residues. Longer residence times at 250°C resulted in its decrease, whereas at higher temperatures the concentration began to fluctuate, or remain within the confidence level. Similarly, at 250°C, the Na and S increased with increasing residence time; at 330°C, the concentration fluctuated with time changes. This observation appears to be in line with the organic composition, as the composition of residues at 250°C (see Figure 4-12) varies with changes in residence time, in contrast to the composition at 330°C (see Figure 5-20), which remains largely unchanged with longer residence times.

Regarding the metal content, only a few obvious trends were evident. At 250°C, all metals except Ag and Sb exhibited a similar trend. For these metals, at 20 min the concentration was always

comparatively high, whereas at 80 min the concentration was always lower. At the intermediate residence times (40 and 60 min), the concentrations were either lower than at 250°C or within the confidence levels. It was concluded that at the lowest severity, the lowest proportions of metals were released from the residues, while at 80 min more of the metals entered a reactive state and migrated to other HTL products.

For residues obtained at 330°C, there was greater fluctuation in concentrations compared to at 250°C. In all cases, except Sb, the concentration at 40 min was higher than at 20 min, possibly indicating the stabilisation of metals through adsorption or secondary reactions. From 40 to 80 min, these trends diverged. The Al, Au, Pb, and Ti decreased to concentrations within the confidence level of the value at 20 min, likely due to secondary reactions. Conversely, the concentrations of Ag, Cu, Fe, Ni, Sn, and Zn remained similar or increased slightly. Since various mechanisms could be involved in these trends, further study is warranted for each metal.

The findings for the mineral and metal elements detected in the bio-oils at all residence times, for both 250°C and 330°C, are presented in Table 4-26. The findings at the intermediate temperatures are presented in Table 5-12 in Appendix A.

Table 4-26: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min

Element (mg/g)	250°C				330°C			
	20 min	40 min	60min	80 min	20 min	40 min	60 min	80 min
Ca (±0.63)	2.16	1.31	1.21	1.05	0.93	1.01	0.60	1.14
K (±0.1)	0.20	0.22	0.18	0.17	0.24	0.26	0.18	0.28
Mg (±0.07)	0.10	0.13	0.10	0.16	0.17	0.17	0.15	0.17
Na (±2.7)	17.28	13.25	12.17	10.31	15.59	15.91	13.85	17.44
S (±4.73)	16.36	15.18	14.53	18.84	18.44	17.70	12.19	17.43
P (±0.02)	0.03	0.04	0.04	0.05	0.05	0.03	1.30E-02	0.05
Al (±0.08)	0.29	0.43	0.41	0.60	0.14	0.10	0.07	0.18
Ag (±0.01)	7.26E-03	7.66E-03	8.24E-03	0.02	5.27E-03	6.51E-03	7.69E-03	0.02
Au (±3.81E-03)	5.31E-03	ND	7.07E-04	ND	7.26E-03	1.11E-02	6.91E-03	7.24E-03
Cu (±0.09)	0.33	0.43	0.51	0.28	0.44	0.29	0.43	0.40
Fe (±0.05)	0.07	0.07	0.09	0.22	0.30	0.19	0.22	0.30
Ni (±0.01)	7.76E-03	2.62E-03	5.88E-03	1.36E-02	0.02	1.32E-02	6.82E-03	0.03
Pb (±0.04)	BDL	BDL	3.83E-03	8.93E-03	9.95E-03	1.23E-02	1.02E-02	0.03
Sb (±0.05)	0.08	0.05	0.06	BDL	0.21	0.16	0.17	0.19
Sn (±0.58)	1.50	1.55	1.49	0.91	0.72	0.92	0.36	0.89
Ti (±0.05)	4.96E-03	0.02	4.31E-03	0.14	0.38	0.20	0.08	0.20
Zn (±0.02)	ND	9.54E-03	ND	0.05	0.09	0.05	0.02	0.06

BDL: Below the detection limit, ND: Not detected

From Table 4-26, it can be inferred that the residence time has a limited impact on the mineral composition of the bio-oils, similar to the effects of temperature; some observations were nonetheless noted. At 250°C, the Ca content decreased with increasing residence time from 20 to 40 min, but it fluctuated within the confidence level at all other residence times. The Na content also decreased with a longer residence time at 250°C, potentially indicating that the bio-oil molecules originating from the lignosulphonate intermediates undergo thermal cracking at a lower temperature.

Considering the influence of residence time on the metal concentrations within the bio-oils, some trends were noted. At 250°C, the Al, Ag, Fe, Ni, Pb, Ti, and Zn produced a general increase from 20 to 80 min. This confirmed that more metals become reactive at low temperatures with longer residence times. At 250°C, longer residence times gave the largest increases in phenolic content of the bio-oils, while at higher temperatures the phenolic content stagnated with longer residence times (see Table 4-19). The stagnation could also account for the fluctuations observed for Al, Au, Cu, Fe, Ni, Sn, Zn, and Sb at 330°C, when comparing the results of 20 and 80 min.

In conclusion, the metal distributions of the residue and bio-oils did not yield many consistent trends when changing the residence time. For both the residues and bio-oils, residence time changes at a low temperature (250°C) showed more consistent trends than at higher temperatures. At 250°C, most of the metal concentrations in the residues decreased with increasing time (20-80 min), while that of the bio-oils increased over the same period. At 330°C, fluctuations are noted for both products.

The mineral and metal distribution in the aqueous phases obtained at 250°C and 330°C for all residence times is presented in Table 4-27. The distribution at intermediate temperatures (275°C and 300°C) is presented in Table 5-14 in Appendix A.

Table 4-27: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 250°C and 330°C for 20, 40, 60, and 80 min

Element (mg/g)	250°C				330°C			
	20 min	40 min	60 min	80 min	20 min	40 min	60 min	80 min
Ca (± 0.10)	1.15	0.76	0.64	0.45	0.22	0.22	0.26	0.20
K (± 0.05)	0.61	0.49	0.40	0.41	0.25	0.25	0.27	0.27
Mg ($\pm 2.38\text{E-}03$)	0.03	0.02	1.39E-02	0.02	7.38E-03	4.85E-03	7.36E-03	3.45E-03
Na (± 0.64)	36.67	34.57	34.06	30.75	25.55	27.73	26.21	24.59
S (± 0.29)	14.81	12.68	12.34	9.02	2.80	2.50	2.62	2.44
P ($\pm 8.89\text{E-}05$)	3.01E-03	2.03E-03	1.11E-03	1.28E-03	1.34E-04	2.59E-04	ND	ND
Al ($\pm 9.64\text{E-}04$)	0.24	0.20	0.17	0.13	4.16E-05	ND	2.83E-05	ND
Ag (± 0.00)	2.76E-04	ND	ND	1.70E-04	ND	ND	ND	ND
Au ($\pm 2.51\text{E-}04$)	9.33E-04	1.03E-03	8.52E-04	1.31E-03	3.76E-04	8.41E-04	4.44E-04	7.02E-04
Cu ($\pm 1.99\text{E-}03$)	8.77E-03	9.84E-03	9.77E-03	7.62E-03	7.91E-03	8.43E-03	7.97E-03	1.08E-02
Fe ($\pm 3.84\text{E-}05$)	8.23E-03	4.99E-03	4.77E-03	6.64E-03	1.09E-04	5.89E-05	ND	1.55E-04
Ni ($\pm 2.21\text{E-}04$)	1.58E-03	1.08E-03	9.88E-04	7.99E-04	3.64E-04	5.02E-04	6.48E-04	8.20E-04
Pb ($\pm 6.93\text{E-}05$)	4.33E-04	3.29E-04	8.66E-04	2.82E-04	2.10E-05	ND	1.38E-04	1.01E-04
Sb ($\pm 2.23\text{E-}03$)	4.11E-03	4.06E-03	4.10E-03	4.56E-03	6.04E-03	7.14E-03	3.26E-03	6.34E-03
Sn (± 0.01)	0.53	0.39	0.34	0.10	1.11E-02	8.97E-03	9.05E-03	1.16E-02
Ti ($\pm 2.15\text{E-}05$)	2.30E-03	2.16E-03	1.62E-03	7.86E-04	2.38E-05	1.47E-05	2.88E-05	3.55E-05
Zn (± 0.00)	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not detected

According to Table 4-27 and Table 5-14, the residence time has a more consistent influence on the mineral composition of the aqueous phases at lower temperatures. For instance, the Ca, Na, K, and S exhibit a decrease with longer residence times at 250°C; however, at 330°C, these concentrations mostly fluctuate. This could be a result of the dissolved lignosulphonate decomposing at a slower rate due to the lower energy input. Consequently, longer residence times allow the decomposition to progress further, whereas at higher temperatures, the decomposition rate is increased, therefore the migration of these minerals is less apparent when increasing the residence time, since most of the available minerals have been removed before 20 min.

Regarding the metals, once again almost no Ag or Zn was detected in the aqueous phases; trace amounts of the other metals were observed. Some metals, including Al, Fe, Sn, and Ti showed an overall decrease in concentration with longer residence times. However, since temperature has a more pronounced effect on the metal concentrations in the aqueous phase, the rate of decline was higher at 250°C than at 330°C, as most metals have already been removed from the aqueous phase before 20 min. No consistent trends for the Cu, Sb, and Au were evident.

4.6.3 Waste loading

The ICP-OES analysis results of the HTL products at various waste loadings provide insight into the migration of minerals and metals as the input of metals is increased through higher waste loadings, as well as the potential metal adsorption from the liquid products from the lignosulphonate. The distribution of minerals and metals in the residues that resulted from HTL experiments in which the PCB waste loading was varied between 0 and 100 wt.%, with process parameters of 300°C and 80 min, is presented in Table 4-28.

Table 4-28: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

Element (mg/g)	0 (wt.%)	10 (wt.%)	30 (wt.%)	50 (wt.%)	70 (wt.%)	90 (wt.%)	100 (wt.%)
Ca (± 1.41)	0.96	12.44	26.60	43.55	57.13	72.64	70.76
K (± 0.03)	1.51	1.41	1.32	1.75	1.08	0.49	0.30
Mg (± 0.16)	1.16	1.79	2.13	2.22	2.62	3.11	3.27
Na (± 2.28)	109.78	92.30	64.13	45.42	22.24	4.89	1.21
S (± 1.34)	62.74	61.89	50.08	34.40	25.95	9.26	3.22
P (± 0.07)	0.22	0.61	0.77	0.79	0.88	0.93	1.01
Al (± 1.95)	0.13	12.39	27.58	44.93	65.53	78.84	82.32
Ag (± 0.10)	6.12E-03	0.25	0.43	0.71	0.76	0.60	0.55
Au (± 0.04)	3.83E-03	0.06	0.07	0.19	0.28	0.29	0.40
Cu (± 6.12)	0.04	16.38	29.79	58.74	84.10	90.20	114.78
Fe (± 4.11)	0.28	11.60	20.37	44.37	66.31	68.82	82.64
Ni (± 0.46)	0.02	0.94	1.66	3.73	5.21	5.73	6.42
Pb (± 0.30)	0.03	0.99	2.25	3.85	4.73	5.64	6.02
Sb (± 0.01)	ND	0.15	0.30	0.35	0.54	0.63	0.67
Sn (± 0.69)	0.49	7.32	14.82	25.80	32.56	39.15	42.66
Ti (± 0.30)	8.19E-03	0.71	1.15	1.99	2.77	3.48	3.21
Zn (± 0.29)	ND	1.09	2.29	4.29	6.34	7.11	8.59

ND: Not detected

It is evident from Table 4-28 that the mineral and metal distributions within the residues are contingent upon the feedstocks. As previously noted, Ca, Na, and S are the most dominant minerals in the residues. The Ca content increases with increasing waste loading, confirming that it originates from the ceramic materials in the PCBs. Conversely, the Na and S continually decrease with increasing waste loading, confirming that they originate from the lignosulphonate. Regarding the metal content, all metals except Ag and Ti continually increase with increasing waste loading due to the high concentrations of these metals in the PCBs. This confirmed that most of the metals remain in the stable phase, regardless of the biomass loading. This confirmation presents a key step towards the valorisation of waste PCBs since the yield of residue is less than the input of

waste PCBs (Section 4.3.3), and metals are conserved in a stable phase, ultimately leading to a metal-rich residue that would require less hydrometallurgical treatment to extract the same amount of metals compared to the waste PCB feedstock. Furthermore, considering the non-linear increase in trends for most metals, it can be inferred that metal adsorption or secondary reactions could have played a part, the extent to which was possibly influenced by the lignosulphonate loading.

The mineral and metal distributions of the bio-oils obtained from HTL experiments where the PCB waste loading was varied between 30 and 100 wt.% are presented in Table 4-29. The bio-oil yields at 0 and 10 wt.% were insufficient to be able to conduct ICP-OES analysis.

Table 4-29: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

Element (mg/g)	0 (wt.%)	10 (wt.%)	30 (wt.%)	50 (wt.%)	70 (wt.%)	90 (wt.%)	100 (wt.%)
Ca (± 0.63)	N/A	N/A	0.86	1.19	1.89	2.34	3.48
K (± 0.10)	N/A	N/A	0.74	0.19	0.07	0.04	0.03
Mg (± 0.07)	N/A	N/A	0.14	0.12	0.16	0.10	0.11
Na (± 2.70)	N/A	N/A	49.71	15.62	7.52	1.75	0.38
S (± 4.73)	N/A	N/A	31.11	14.22	6.44	0.26	0.10
P (± 0.02)	N/A	N/A	7.06E-03	8.51E-03	0.03	1.49E-02	0.02
Al (± 0.08)	N/A	N/A	0.12	0.10	0.37	0.07	0.06
Ag (± 0.01)	N/A	N/A	1.16E-03	9.34E-03	0.13	0.03	ND
Au ($\pm 3.81E-03$)	N/A	N/A	8.86E-03	6.75E-03	2.07E-03	1.97E-03	1.98E-03
Cu (± 0.09)	N/A	N/A	0.14	0.24	0.84	0.49	0.64
Fe (± 0.05)	N/A	N/A	0.10	0.12	0.71	0.25	0.77
Ni (± 0.01)	N/A	N/A	0.02	1.39E-02	0.02	6.89E-03	3.95E-03
Pb (± 0.04)	N/A	N/A	4.37E-03	1.47E-02	0.08	0.20	0.64
Sb (± 0.05)	N/A	N/A	0.02	0.07	0.08	0.02	0.03
Sn (± 0.58)	N/A	N/A	1.31	1.53	2.02	0.34	0.04
Ti (± 0.05)	N/A	N/A	0.07	0.05	0.04	2.16E-03	ND
Zn (± 0.02)	N/A	N/A	ND	1.24E-02	0.03	1.35E-02	0.13

ND: Not detected

Several noteworthy observations were made from the data presented in Table 4-29. The Ca, Na, and S content showed the same trend as for the residues, i.e., an increased waste loading led to more Ca in the bio-oils, while less Na and S was detected in the bio-oils.

The metal content of the bio-oils revealed some significant trends. First, both the Pb and Zn gradually increased with escalating waste loadings, likely attributed to the increased availability of these metals within the system. Second, the Au and Ti gradually decreased with increasing waste loadings. This trend suggests that these metals are more prone to adsorption into the bio-oil constituents stemming from the lignosulphonate. The removal of minerals such as Na and S could

have influenced the adsorption as fewer cation exchange reactions could occur (Cao *et al.*, 2009). Several metals have comparatively high concentrations at 70 wt.% loadings. This loading produced the highest metal concentrations of most of the metals (Al, Ag, Cu, Fe, Ni, Sn, Sb, and Zn; excluding Fe and Zn). Hereafter, a decrease in the concentrations was observed. The amount of phenolic compound in the bio-oils stagnated at 70 wt.%, with similar results at 90 and 100 wt.% (Table 4-21), therefore justifying the high concentration at 70 wt.%. The decrease in the metal concentrations at 90 and 100 wt.% could be attributed to the reduction in compounds originating from the lignosulphonate, which may have facilitated the adsorption of these metals, possibly involving carboxylic groups.

The mineral and metal distributions of the aqueous phases obtained from HTL experiments where the PCB waste loading was varied between 0 and 100 wt.% are presented in Table 4-30.

Table 4-30: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at waste PCB mass loadings of 0 to 100 wt.%

Element (mg/g)	0 (wt.%)	10 (wt.%)	30 (wt.%)	50 (wt.%)	70 (wt.%)	90 (wt.%)	100 (wt.%)
Ca (± 0.10)	0.02	4.48E-03	1.27E-02	0.28	2.83	2.98	3.30
K (± 0.05)	1.45	1.42	0.77	0.24	0.09	0.07	0.03
Mg ($\pm 2.38E-03$)	0.06	5.82E-03	3.91E-03	6.19E-03	9.31E-03	8.02E-03	9.25E-03
Na (± 0.64)	60.65	59.41	41.93	29.54	22.97	10.23	0.21
S (± 0.29)	8.96	0.82	4.40	3.42	2.96	0.95	0.15
P ($\pm 8.89E-05$)	0.11	7.22E-03	8.88E-04	5.79E-05	ND	6.77E-04	ND
Al ($\pm 9.64E-04$)	ND	ND	ND	7.35E-04	1.36E-02	9.76E-04	7.70E-04
Ag (± 0.00)	ND	ND	ND	ND	2.15E-03	2.47E-03	ND
Au ($\pm 2.51E-04$)	8.63E-04	2.36E-03	8.69E-04	5.40E-04	5.71E-04	7.20E-04	8.25E-04
Cu ($\pm 1.99E-03$)	8.70E-03	6.88E-03	8.96E-03	9.69E-03	6.45E-03	8.20E-03	1.29E-02
Fe ($\pm 3.84E-05$)	2.50E-04	9.77E-06	2.16E-04	1.73E-04	9.90E-03	3.60E-03	2.15E-03
Ni ($\pm 2.21E-04$)	5.15E-04	8.88E-04	4.40E-04	5.40E-04	1.38E-03	1.74E-03	1.23E-03
Pb ($\pm 6.93E-05$)	ND	ND	ND	2.49E-05	8.76E-03	0.05	0.23
Sb ($\pm 2.23E-03$)	1.66E-03	1.16E-02	5.23E-03	5.02E-03	4.13E-03	2.13E-03	2.63E-03
Sn (± 0.01)	0.05	0.02	0.02	0.02	0.02	7.37E-03	9.66E-03
Ti ($\pm 2.15E-05$)	ND	ND	1.66E-05	2.88E-05	7.89E-05	3.24E-05	4.41E-05
Zn (± 0.00)	ND	ND	ND	ND	ND	2.18E-03	0.04

ND: Not detected

Table 4-30 shows that the mineral content follows the same trend in the residues, compared to the bio-oils. As the waste loadings increase, the Ca increases, whereas Na and S decrease (due to a decrease of lignosulphonate feed). When considering the metal content of the aqueous phases, it is evident that only trace amounts of all metals are detected in the aqueous phase, irrespective of waste loadings. This indicates the potential of HTL to valorise the waste PCBs as only trace

amounts migrated to the aqueous phase, then ultimately requiring less treatment before being released into the environment. A few trends were apparent. The Pb and Zn gradually increased with waste loading, similar to the trends seen in the bio-oils, mainly due to the increased input of these metals. At a waste loading of 70 wt.%, the Al, Ag, and Fe reached peak concentrations, whereafter the concentrations decreased.

Considering the findings pertaining to the waste loading changes, the non-linear increase of the metal concentrations in the residues together with the significant trends observed for metals in the bio-oils serve to confirm that metal adsorption and secondary reactions, such as ligand formation, did occur. The addition of lignosulphonate had an impact on mineral and metal distributions, although the extent of biochar adsorption does necessitate further study. Lastly, the trace amounts of metals detected in the aqueous phases, as well as the overall low metal concentrations in the bio-oils, at all waste loadings, confirmed that the majority of the metals remained in a stable state within the residues.

This ultimately validates the valorisation of waste PCBs through the decomposition of the organic fractions into valuable phenolic compounds, whilst producing a residue that contains the vast majority of metals from the waste PCBs.

4.7 Summary of results

From this study, it is seen that reaction temperature, residence time, and waste loading had significant effects on the recovery of metals and the formation of organic compounds.

The bio-oil yield exhibited a temperature-dependent trend, increasing until 300°C, after which cracking reactions surpassed repolymerization. The predominant compounds in bio-oils were phenolics, with molecular weight and O/C ratio decreasing as temperatures rose. Residence time, particularly at 250°C, influenced bio-oil and residue yields, while at 330°C, a dynamic equilibrium between cracking and repolymerization led to yield fluctuations. Optimal conditions for bio-oil production was identified at 300°C for 80 minutes.

The impacts of increasing waste loadings were noteworthy, resulting in decreased aqueous phase yields and elevated bio-oil and residue yields, as well as a reduction in carbon content in residues. This indicated depolymerization of epoxy resin in the waste material. Additionally, higher waste loadings led to non-linear increases in metal concentrations in residues, suggesting potential contributions from metal adsorption and secondary reactions, although most metals remained in a stable state within the residue. Temperature exerted a more consistent impact on metal distributions than residence time. At 90 and 100 wt.% waste loadings, residues with the highest concentrations of metals were obtained through the HTL of sieved waste PCBs.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

This final chapter provides the outcomes for the HTL of waste PCBs and lignosulphonate. Section 5.2 presents the key findings pertaining to the characterisation of the feedstocks, as well as the influence of residence time, temperature, and waste loading on the HTL products and their composition. Section 5.3 offers some limitations and recommendations for future studies.

5.2 Conclusion

The overall aim of this study was to determine the suitability of HTL as a treatment method for locally obtained PCB e-waste co-processed with lignosulphonate biomass.

This was achieved by evaluating the recovery of metals and the formation of organic compounds in the HTL products at various temperatures, residence times, and waste loadings. Furthermore, the feedstocks were characterised and the combined effect of residence time and operating temperature on the product yields was investigated using SFs.

Characterisation of the waste PCBs revealed that high concentrations of metals were present in the sieved waste PCBs, particularly Cu, Fe, Al, and Sn, along with notable concentrations of other metals such as, Ag, Au, Ni, Pb, Ti, and Zn. There was also a significant organic fraction; it was identified as the epoxy resin, commonly used to manufacture PCB substrates. Lignosulphonate was utilised for its potential metal adsorption capabilities in the biochar from HTL of this biomass. The adsorption potential was highlighted by the presence of hydroxyl, carboxyl, and carbonyl groups in the large lignin molecules of the lignosulphonate, along with high concentrations of mineral elements such as S and Na.

The study found that the reaction temperature played a crucial role in influencing the product yields and composition of the HTL products. The bio-oil yield increased with increasing temperature until reaching a turning point at 300°C for both short and long residence times, where cracking surpassed repolymerisation reactions. The bio-oils consisted of mostly phenolic compounds. The latter followed a similar trend; they also reached a turning point due to cracking reactions. Furthermore, the molecular weight and O/C ratio of the bio-oils consistently decreased with increasing temperatures at all residence times. The organic composition of residues was primarily unreacted epoxy resin and heavy carbonaceous compounds formed by repolymerisation reactions. The overall residue yield decreased with increasing temperature at 40, 60, and 80 min. Waste PCB decomposed at a faster rate than the repolymerisation of intermediates into solids. The organic

composition of the residues was influenced by increased temperature, through the increased decomposition of the epoxy resin and increased repolymerisation into solid molecules. The volatile content in the residues also decreased at elevated temperatures as the volatile organic matter in the epoxy resin was decomposed.

Residence time had a lesser impact on the HTL products compared to temperature. At 250°C, longer residence times led to slow decomposition and repolymerisation rates to progress which resulted in increasing bio-oil and residue yields. However, at 330°C, longer residence times resulted in a dynamic equilibrium between cracking and repolymerisation reactions causing fluctuations in the bio-oil, gas, and residue yields. Phenolic compounds increased with longer residence times at lower temperatures reaching a turning point at higher temperatures. Overall, it emerged that an increased residence time mostly affected the HTL reactions by allowing reactions to progress, whereas temperature heavily influenced the rate of these reactions. This was evident from the molecular weights of the bio-oils; longer residence times at low temperatures did not significantly affect the weights since the rate of cracking reactions was too slow. The optimum process conditions for the bio-oil yield were determined to be 300°C at 80 min.

Increasing waste loading resulted in decreased aqueous phase yields, indicating lignosulphonate dissolution in the water solvent, while both the bio-oil and residue yields increased. With rising waste loading, the carbon content of the residues decreased from 49 wt.% to 5 wt.%. This confirmed that most of the epoxy resin was depolymerised. This observation also establishes that the lignosulphonate produces carbon-rich biochar structures during HTL. Furthermore, the phenolic content of the bio-oils increased from 6 to 93 area%, validating that the epoxy resin primarily underwent depolymerisation through thermal degradation and hydrolysis reactions, after which recombination reactions resulted in the formation of phenolic compounds.

The majority of metals were found to remain in a stable state within the residues; only small concentrations were detected in the bio-oils and aqueous phases. Slightly higher metal concentrations were observed in the bio-oils compared to the aqueous phases. This study concluded that the migration from the residues is linked to the initial metal concentration of the feedstocks. Temperature and residence time had inconsistent effects on the metal concentrations in most cases, likely due to the diverse range of metals and complex reaction conditions, leading to different interactions and pathways for each metal. At a short residence time, certain metals (Au, Cu, Fe, Ni, Sn, and Zn) exhibited high concentrations in the residues at 250°C, attributed to the slow decomposition rate of the waste PCBs. However, with increasing temperature, there was an initial decrease in concentrations as more metals were released, following by a slight increase, possibly due to the adsorption from the biochar structures. A similar trend was observed at a long residence time, although at 250°C the metal concentrations were lower.

Temperature exerted a more noticeable and consistent impact on the metal distributions compared to residence time. Notwithstanding this, most of the metal concentrations in the residues decreased with increasing time at 250°C, whereas these concentrations mostly fluctuated with increased residence time at 330°C. Furthermore, increasing the waste loadings led to a non-linear increase in most metal concentrations, indicating potential contributions from metal adsorption or secondary reactions, with the extent potentially influenced by the lignosulphonate loading. At 70 wt.% loading, the metal concentrations of the residues were comparable to the original PCB feedstock, with 90 and 100 wt.% loadings being significantly higher than the original feedstock with <6 wt.% carbon in the residues.

This study has demonstrated that HTL is indeed a suitable treatment method for waste PCBs through the conversion of waste organics to valuable phenolic compounds and the production of metal-rich residues, where the outcomes of HTL are significantly influenced by temperature, residence time, and waste loading. Consequently, this study shows the potential of a novel end-processing method for e-waste which can simultaneously convert the commonly discarded organic fraction of waste PCBs to valuable compounds, while directing both harmful and desired metals to a residue where it can be extracted via hydrometallurgical routes. This, along with less energy-intensive processing, infers the superiority of HTL as an e-waste valorisation method when compared to traditional methods. Although this study concludes the viability of HTL, much more study is required before HTL can truly overcome all the disadvantages of current methods and evolve into an effective solution for the challenge of e-waste.

5.3 Limitations and recommendations

This study faced operational limitations that prevented the examination of HTL gas products. To fully understand the viability of the liquefaction of e-waste, it is crucial to capture and study the gas products, and then determine the potentially harmful and useful substances released from the HTL reactions. Furthermore, the maximum operational parameters of the batch reactor used in this study limited the HTL of waste PCBs to subcritical conditions, therefore the effect of supercritical conditions on the organic products and metal distributions should also be studied. Then, other variables, such as the liquid-to-solid feed ratio, volume loading, heating rate, and initial pressure should also be investigated.

The bio-oil yields remained relatively low under all process conditions used in this study. Therefore, the effect of catalysts should be studied in efforts to potentially increase the bio-oil yields. However, as the presence of various metals during the HTL of e-waste could lead to deactivation, poisoning, competitive adsorption, or the formation of complexes. Therefore, catalyst selection should be carefully considered based on both the bio-oil yields and the metal–catalyst interactions.

Lignosulphonate was co-liquefied with waste PCBs to explore the potential metal adsorption through biochar formation; however, the extent of the adsorption capabilities was not subject to detailed study. Nuclear magnetic resonance spectroscopy could be implemented, in conjunction with FTIR analysis, to gain a better understanding of the functional groups present and the subsequent adsorption mechanisms involved in the residues. Similarly, employing X-ray photoelectron and adsorption spectroscopy, as well as scanning tunnelling microscopy, could provide a more in-depth understanding of metal adsorption by studying the interactions between individual metals and the residue surface. Then, in the pursuit of retaining all available metals in the solid products, studying the co-liquefaction of e-waste with other biomass sources, and their potential metal adsorption capabilities, could be advantageous. It would also be beneficial to explore the interactions of individual metals during the complex conditions of HTL.

Due to the wide range of metals and mineral elements analysed in this study, the ICP-OES analysis presented a limitation in the form of spectral interference from overlapping wavelengths from the wide range of metals. This could have resulted in inaccurate results in certain samples. Thus, it is recommended that further study should be conducted to validate these results, as well as focus on single elements and their relevant behaviour during HTL. This would make important contributions to the optimisation of metal recovery, especially during large-scale applications.

Having confirmed the decomposition of the waste PCB organic fraction and conversion to valuable phenolic compounds via HTL, the applicability of HTL to decompose the organic fractions of other WEEE should be investigated. Then, consideration should be given to employing large-scale HTL for e-waste valorisation, and the extraction of valuable compounds (phenolics in the case of waste PCBs) from the liquid HTL products should be considered. Exploring the viability of semi-continuous or continuous HTL of e-waste is a required step before the challenge of e-waste can be effectively addressed via HTL. Lastly, the hydrometallurgical extraction routes of the metal-rich residues should be investigated for the optimum recovery and purification of valuable metals.

This ultimately address the challenge of e-waste, determining the most effective and environmentally friendly end-processing method is required. Although this study determines the suitability of HTL as an end-processing method, a stringent study of the various end-processing methods compared to the HTL of various e-waste feedstocks could prove to be exceptionally valuable. Furthermore, the economic feasibility of HTL as an end-processing method was not determined in this study, thus studying the economic feasibility of HTL, as well as other methods, would be highly advantageous to establish a desirable solution for the ongoing e-waste issue.

REFERENCES

- Abdelaziz, O.Y., Meier, S., Prothmann, J., Turner, C., Riisager, A. & Hulteberg, C.P. 2019. Oxidative Depolymerisation of Lignosulphonate Lignin into Low-Molecular-Weight Products with Cu–Mn/ δ -Al₂O₃. *Topics in Catalysis*. 62(7–11):639–648.
- Adeleke, O., Akinlabi, S., Jen, T.C. & Dunmade, I. 2021. Towards sustainability in municipal solid waste management in South Africa: a survey of challenges and prospects. *Transactions of the Royal Society of South Africa*. 76(1):53–66.
- Ahmedna, M., Marshall, W.E., Husseiny, A.A., Rao, R.M. & Goktepe, I. 2004. The use of nutshell carbons in drinking water filters for removal of trace metals. *Water Research*. 38(4):1062–1068.
- Akhtar, J. & Amin, N.A.S. 2011. A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 15(3):1615–1624.
- Al-Salem, S.M., Leeke, G.A., El-Eskandarany, M.S., Van Haute, M., Constantinou, A., ... Baeyens, J. 2022. On the implementation of the circular economy route for E-waste management: A critical review and an analysis for the case of the state of Kuwait. *Journal of Environmental Management*. 323:116181.
- Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M. & Usman, A.R.A. 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. *Bioresource Technology*. 131:374–379.
- Albuquerque, B.R., Heleno, S.A. 8., Oliveira, M.B.P.P., Barros, L. & Ferreira, I.C.F.R. 2021. Phenolic compounds: Current industrial applications, limitations and future challenges. *Food and Function*. 12(1):14–29.
- Alper, K., Tekin, K., Karagöz, S. & Ragauskas, A.J. 2020. Sustainable energy and fuels from biomass: A review focusing on hydrothermal biomass processing. *Sustainable Energy and Fuels*. 4(9):4390–4414.
- Andooz, A., Egbalpour, M., Kowsari, E., Ramakrishna, S. & Cheshmeh, Z.A. 2022. A comprehensive review on pyrolysis of E-waste and its sustainability. *Journal of Cleaner Production*. 333:130191.
- Andrade, L.M., Botelho Junior, A.B., Rosario, C.G.A., Hashimoto, H., Andrade, C.J. & Tenório, J.A.S. 2022. Copper recovery through biohydrometallurgy route: chemical and physical characterization of magnetic (m), non-magnetic (nm) and mix samples from obsolete smartphones. *Bioprocess and Biosystems Engineering*. 46(8):1121–1131.
- Anouti, S., Haarlemmer, G., Déniel, M. & Roubaud, A. 2016. Analysis of Physicochemical Properties of Bio-Oil from Hydrothermal Liquefaction of Blackcurrant Pomace. *Energy and Fuels*. 30(1):398–406.
- Aro, T. & Fatehi, P. 2017. Production and Application of Lignosulfonates and Sulfonated Lignin. *ChemSusChem*. 10(9):1861–1877.
- Arun, J. & Gopinath, K.P. 2020. Chemical Recycling of Electronic-Waste for Clean Fuel Production. In: Springer, Cham. pp. 111–126.
- Asante, K.A., Amoyaw-Osei, Y. & Agusa, T. 2019. E-waste recycling in Africa: risks and opportunities. *Current Opinion in Green and Sustainable Chemistry*. 18:109–117.
- Ashiq, A., Kulkarni, J. & Vithanage, M. 2019. Chapter 10 - Hydrometallurgical Recovery of Metals From E-waste. In: M.N.V. Prasad & M. Vithanage, eds. *Electronic Waste Management and Treatment Technology*. Butterworth-Heinemann. pp. 225–246.

- Baldé, C.P., Forti, V., Gray, V.J., Kuehr, R. & Stegmann, P. 2015. The Global E-waste Monitor 2017: Quantities, Flows and Resources. In: Bonn/Geneva/Vienna: United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA).
- Barontini, F., Cozzani, V., Marsanich, K., Raffa, V. & Petarca, L. 2004. An experimental investigation of tetrabromobisphenol A decomposition pathways. *Journal of Analytical and Applied Pyrolysis*. 72(1):41–53.
- Basar, I.A., Liu, H., Carrere, H., Trabaly, E. & Eskicioglu, C. 2021. A review on key design and operational parameters to optimize and develop hydrothermal liquefaction of biomass for biorefinery applications. *Green Chemistry*. 23(4):1404–1446.
- Basar, I.A., Liu, H. & Eskicioglu, C. 2023. Incorporating hydrothermal liquefaction into wastewater treatment – Part III: Aqueous phase characterization and evaluation of on-site treatment. *Chemical Engineering Journal*. 467.
- Benzal, E., Cano, A., Solé, M., Lao-Luque, C., Gamisans, X. & Dorado, A.D. 2020. Copper Recovery from PCBs by Acidithiobacillus ferrooxidans: Toxicity of Bioleached Metals on Biological Activity. *Waste and Biomass Valorization*. 11(10):5483–5492.
- Betts, K. 2008. Producing usable materials from e-waste. *Environmental Science & Technology*. 42(18):6782–6783.
- Biller, P. & Ross, A.B. 2011. Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource Technology*. 102(1):215–225.
- Biller, P., Madsen, R.B., Klemmer, M., Becker, J., Iversen, B.B. & Glasius, M. 2016. Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition. *Bioresource Technology*. 220:190–199.
- Bizzo, W.A., Figueiredo, R.A. & Andeade, V.F.D. 2014. Characterization of Printed Circuit Boards for Metal and Energy Recovery after Milling and Mechanical Separation. *Materials*. 7 (6):4555–4566.
- Bychkov, A.L., Denkin, A.I., Tikhova, V.D. & Lomovsky, O.I. 2017. Prediction of higher heating values of plant biomass from ultimate analysis data. *Journal of Thermal Analysis and Calorimetry*. 130(3):1399–1405.
- Cao, L., Luo, G., Zhang, S. & Chen, J. 2016. Bio-oil production from eight selected green landscaping wastes through hydrothermal liquefaction. *RSC Advances*. 6(18):15260–15270.
- Cao, L., Zhang, C., Chen, H., Tsang, D.C.W., Luo, G., ... Chen, J. 2017. Hydrothermal liquefaction of agricultural and forestry wastes: state-of-the-art review and future prospects. *Bioresource Technology*. 245:1184–1193.
- Cao, X., Ma, L., Gao, B. & Harris, W. 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environmental Science and Technology*. 43(9):3285–3291.
- Caprariis, B., Filippis, P., Petrullo, A., Scarsella, M., de Caprariis, B., ... Scarsella, M. 2017. Hydrothermal liquefaction of biomass: Influence of temperature and biomass composition on the bio-oil production. *Fuel*. 208:618–625.
- Chauhan, G., Jadhao, P.R., Pant, K.K. & Nigam, K.D.P. 2018. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment: Challenges & opportunities – A review. *Journal of Environmental Chemical Engineering*. 6(1):1288–1304.
- Chen, Y., Wu, Y., Zhang, P., Hua, D., Yang, M., ... Liu, J. 2012. Direct liquefaction of *Dunaliella tertiolecta* for bio-oil in sub/supercritical ethanol-water. *Bioresource*

Technology. 124:190–198.

- Chow, K., Mun, M., Yhaya, M. & Azahari, B. 2016. Heat-Induced Hardening and the Effect of Aromatic Ring in Epoxy Resins. *Imperial Journal of Interdisciplinary Research*. 2(5):1557–1562.
- Ciuffi, B., Rosi, L., Miliotti, E., Lotti, G., Rizzo, A.M. & Chiaramonti, D. 2021. Batch Hydrothermal liquefaction of end-of-life plastic and oil characterization. In: Vol. 238. *E3S Web of Conferences*.
- Cui, J. & Forssberg, E. 2003. Mechanical recycling of waste electric and electronic equipment: a review. *Journal of Hazardous Materials*. 99(3):243–263.
- Cui, J. & Zhang, L. 2008. Metallurgical recovery of metals from electronic waste: A review. *Journal of Hazardous Materials*. 158(2):228–256.
- D'Adamo, I., Ferella, F., Gastaldi, M., Maggiore, F., Rosa, P. & Terzi, S. 2019. Towards sustainable recycling processes: Wasted printed circuit boards as a source of economic opportunities. *Resources, Conservation and Recycling*. 149:455–467.
- Das, S. & Ting, Y.P. 2017. Evaluation of wet digestion methods for quantification of metal content in electronic scrap material. *Resources*. 6(4):64.
- Daud, N.M.A.N., Jaafar, W.M.K.W., Ismail, N., Junin, R., Manan, M.A. & Idris, A.K. 2021. Utilizing lignosulfonate from coconut husk as sacrificial agent to reduce surfactant adsorption. In: Vol. 765. *IOP Conference Series: Earth and Environmental Science*.
- Demirbas, A., Ak, N., Aslan, A. & Sen, N. 2018. Calculation of higher heating values of hydrocarbon compounds and fatty acids. *Petroleum Science and Technology*. 36(11):712–717.
- Department of Environmental Affairs (DEA). 2018. *South Africa State of Waste: A report on the state of the environment*. Pretoria. <https://remade.co.za/wp-content/uploads/2020/01/South-Africa-State-of-Waste-Report.pdf> Date of access: 28 Feb. 2021.
- Devore, J., Farnum, N. & Doi, J. 2013. *Applied Statistics for Engineers and Scientists*. 3, ed. Stamford, CT: Cengage Learning EMEA.
- Dimitriadis, A. & Bezergianni, S. 2017. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renewable and Sustainable Energy Reviews*. 68:113–125.
- Duan, H., Hou, K., Li, J. & Zhu, X. 2011. Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns. *Journal of Environmental Management*. 92(3):392–399.
- Durak, H. & Aysu, T. 2016. Structural analysis of bio-oils from subcritical and supercritical hydrothermal liquefaction of *Datura stramonium* L. *Journal of Supercritical Fluids*. 108:123–135.
- Dutta, D., Rautela, R., Gujjala, L.K.S., Kundu, D., Sharma, P., ... Kumar, S. 2023. A review on recovery processes of metals from E-waste: A green perspective. *Science of The Total Environment*. 859:160391.
- Ebin, B. & Isik, M.I. 2016. Chapter 5 - Pyrometallurgical Processes for the Recovery of Metals from WEEE. In: A. Chagnes, G. Cote, C. Ekberg, M. Nilsson, & T. Retegan, eds. *WEEE Recycling*. Elsevier. pp. 107–137.
- Elliott, D.C., Biller, P., Ross, A.B., Schmidt, A.J. & Jones, S.B. 2015. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresource Technology*. 178:147–156.

- Elumalai, S. & Pan, X.J. 2011. Chemistry and reactions of forest biomass in biorefining. *ACS Symposium Series*. 1067:109–144.
- eWaste Recycling Authority (ERA). 2018. *South African E-waste Industry Waste Management Plan (V.1) 2019-2024*. Cape Town.
- Ezema Ike-Eze, I.C., Ucheji, O.N., Ubi, P.A., Oji, E.O., Aigbodion, V.S., ... Ogbuefi, U.C. 2023. An Overview of Flame Retardants in Printed Circuit Boards for LEDs and other Electronic Devices. *Journal of Materials and Environmental Science*. 14(4):410–420.
- Ferella, F., De Michelis, I., Scocchera, A., Pelino, M. & Vegliò, F. 2015. Extraction of metals from automotive shredder residue: Preliminary results of different leaching systems. *Chinese Journal of Chemical Engineering*. 23(2):417–424.
- Forti, V., Balde, C.P., Kuehr, R. & Bel, G. 2020. *The Global E-waste Monitor 2020: Quantities, flows and the circular economy potential. Quantities, flows, and the circular economy potential*. Bonn/Geneva/Rotterdam: United Nations University (UNU)/ United Nations Institute for Training and Research (UNITAR) - co-hosted SCYCLE Programme, International Telecommunication Union (ITU) & International Solid Waste Association (ISWA).
- Forti, V., Balde, C.P. & Kuehr, R. 2018. *E-waste statistics: guidelines on classifications, reporting and indicators*. 2nd ed. Bonn: United Nations University (UNU).
- Freegard, K., Tan, G. & Morton, R. 2006. Develop a process to separate BFRs from WEEE polymers – Final report. *Waste & Resources Action Programme (WRAP)*. 335.
- Ghavami, N., Özdenkçi, K., Salierno, G., Björklund-Sänkiahö, M. & De Blasio, C. 2021. Analysis of operational issues in hydrothermal liquefaction and supercritical water gasification processes: a review. *Biomass Conversion and Biorefinery*.
- Ghosh, B., Ghosh, M.K., Parhi, P., Mukherjee, P.S. & Mishra, B.K. 2015. Waste Printed Circuit Boards recycling: an extensive assessment of current status. *Journal of Cleaner Production*. 94:5–19.
- Ghosh, S.K., Debnath, B., Baidya, R., De, D., Li, J., ... Tavares, A.N. 2016. Waste electrical and electronic equipment management and Basel Convention compliance in Brazil, Russia, India, China and South Africa (BRICS) nations. *Waste Management and Research*. 34(8):693–707.
- Gollakota, A.R.K., Kishore, N. & Gu, S. 2018. A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 81:1378–1392.
- Guo, Y. & Rockstraw, D.A. 2007. Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. *Bioresource Technology*. 98(8):1513–1521.
- Guo, J., Jiang, Y., Hu, X. & Xu, Z. 2012. Volatile organic compounds and metal leaching from composite products made from fiberglass-resin portion of printed circuit board waste. *Environmental Science and Technology*. 46(2):1028–1034.
- Guo, X., Zhang, S. & Shan, X. quan. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials*. 151(1):134–142.
- Hadi, P., Xu, M., Lin, C.S.K., Hui, C.-W. & McKay, G. 2015. Waste printed circuit board recycling techniques and product utilization. *Journal of Hazardous Materials*. 283:234–243.
- Hagelüken, C. 2006. Recycling of electronic scrap at umicore's integrated metals smelter and refinery. *World of Metallurgy - ERZMETALL*. 59(3):152–161.
- Hall, W.J. & Williams, P.T. 2007. Separation and recovery of materials from scrap printed circuit boards. *Resources, Conservation and Recycling*. 51(3):691–709.

- He, C., Zhang, Z., Xie, C., Giannis, A., Chen, Z., ... Qiu, R. 2021. Transformation behaviors and environmental risk assessment of heavy metals during resource recovery from *Sedum plumbizincicola* via hydrothermal liquefaction. *Journal of Hazardous Materials*. 410:124588.
- Hoornweg, D. & Bhada-Tata, P. 2012. *What a Waste: A Global Review of Solid Waste Management*. Washington, DC: World bank. <https://openknowledge.worldbank.org/handle/10986/17388> Date of access: 28 Feb. 2021.
- Hopewell, J., Dvorak, R. & Kosior, E. 2009. Plastics recycling: Challenges and opportunities. *Philosophical Transactions of the Royal Society B: Biological Sciences*. 364(1526):2115–2126.
- Hou, Q.Q., Liu, X., Gong, W., Xu, F., Zhang, W.S., ... Ji, K.J. 2023. Development of Methods for Determining Molecular Weights of Epoxy Resin. *Journal of Physics: Conference Series*. 2460(1).
- Hu, D., Jia, Z., Li, J., Zhong, B., Fu, W., ... Jia, D. 2018. Characterization of Waste Printed Circuit Boards Nonmetals and its Reutilization as Reinforcing Filler in Unsaturated Polyester Resin. *Journal of Polymers and the Environment*. 26(4):1311–1319.
- Huang, H. & Yuan, X. 2016. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. *Bioresource Technology*. 200:991–998.
- Huang, X., Yin, H., Zhang, H., Mei, N. & Mu, L. 2022. Pyrolysis characteristics, gas products, volatiles, and thermo-kinetics of industrial lignin via TG/DTG–FTIR/MS and in-situ Py–PI–TOF/MS. *Energy*. 259:125062.
- Hudson, C., Reuter, M., Van Schaik, A., Heishanen, K., Meskers, C., ... UNEP. 2013. *Metal Recycling: Opportunities, Limits, Infrastructure, A Report of the Working Group on the Global Metal Flows to the International Resource Panel*. United Nations Environmental Programme. Nairobi, Kenya: United Nations Environment Programme.
- Ilanakoon, I.M.S.K., Ghorbani, Y., Chong, M.N., Herath, G., Moyo, T. & Petersen, J. 2018. E-waste in the international context – A review of trade flows, regulations, hazards, waste management strategies and technologies for value recovery. *Waste Management*. 82:258–275.
- Ilić, P., Nišić, T., Ilić, S. & Stojanović Bjelić, L. 2020. Identifying new 'hotspot' heavy metal contamination in industrial zone soil. *Polish Journal of Environmental Studies*. 29(4):2987–2993.
- Iroba, K.L., Tabil, L.G., Sokhansanj, S. & Dumonceaux, T. 2014. Pretreatment and fractionation of barley straw using steam explosion at low severity factor. *Biomass and Bioenergy*. 66:286–300.
- Islam, A., Ahmed, T., Awual, M.R., Rahman, A., Sultana, M., ... Hasan, M. 2020. Advances in sustainable approaches to recover metals from e-waste-A review. *Journal of Cleaner Production*. 244:118815.
- Islam, M.N., Taki, G., Rana, M. & Park, J.H. 2018. Yield of Phenolic Monomers from Lignin Hydrothermolysis in Subcritical Water System. *Industrial and Engineering Chemistry Research*. 57(14):4779–4784.
- Jazrawi, C. 2014. Hydrothermal treatment of algal biomass: From batch to continuous pilot. University of Sydney.
- Jiang, W., Jia, L. & Zhen-ming, X. 2009. A new two-roll electrostatic separator for recycling of metals and nonmetals from waste printed circuit board. *Journal of Hazardous Materials*. 161(1):257–262.

- Jianzhi, L., Shrivastava, P., Gao, Z. & Zhang, H.C. 2004. Printed circuit board recycling: A state-of-the-art survey. *IEEE Transactions on Electronics Packaging Manufacturing*. 27(1):33–42.
- Jin, B., Duan, P., Xu, Y., Wang, F. & Fan, Y. 2013. Co-liquefaction of micro- and macroalgae in subcritical water. *Bioresource Technology*. 149:103–110.
- Jin, B., Duan, P., Zhang, C., Xu, Y., Zhang, L. & Wang, F. 2014. Non-catalytic liquefaction of microalgae in sub-and supercritical acetone. *Chemical Engineering Journal*. 254:384–392.
- Jin, H., Bai, B., Wei, W., Chen, Y., Ge, Z. & Shi, J. 2020. Hydrothermal Liquefaction of Polycarbonate (PC) Plastics in Sub-/Supercritical Water and Reaction Pathway Exploration. *ACS Sustainable Chemistry and Engineering*. 8(18):7039–7050.
- Jindal, M.K. & Jha, M.K. 2016a. Catalytic Hydrothermal Liquefaction of Waste Furniture Sawdust to Bio-oil. *Indian Chemical Engineer*. 58(2):157–171.
- Jindal, M.K. & Jha, M.K. 2016b. Hydrothermal liquefaction of wood: A critical review. *Reviews in Chemical Engineering*. 32(4):459–488.
- Kaharn, J., Khaobang, C., Suemanotham, A., Punsuvon, V. & Areeprasert, C. 2022. Investigation of the molecular characterization and antioxidant activity of bio-oil produced from high moisture oil palm residues employing hydrothermal liquefaction. *Biomass and Bioenergy*. 163.
- Kai, D., Tan, M.J., Chee, P.L., Chua, Y.K., Yap, Y.L. & Loh, X.J. 2016. Towards lignin-based functional materials in a sustainable world. *Green Chemistry*. 18(5):1175–1200.
- Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y. & Uddin, M.A. 2004. Low-temperature hydrothermal treatment of biomass: Effect of reaction parameters on products and boiling point distributions. *Energy and Fuels*. 18(1):234–241.
- Kaya, M. 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. *Waste Management*. 57:64–90.
- Kaya, M. 2018. *Current WEEE recycling solutions. Waste Electrical and Electronic Equipment Recycling: Aqueous Recovery Methods*. Amsterdam, The Netherlands: Elsevier.
- Kaya, M. & Şzeri, A. 2009. A review of electronic waste (E-Waste) recycling technologies “is E-Waste an opportunity or treat?” *TMS Annual Meeting*. 1055–1060.
- Khaliq, A., Rhamdhani, M.A., Brooks, G. & Masood, S. 2014. Metal extraction processes for electronic waste and existing industrial routes: A review and Australian perspective. *Resources*. 3(1):152–179.
- Khan, Q. uz Z., El Ouni, M.H., Raza, A. & Alomayri, T. 2022. Mechanical behavior of electronic waste concrete columns reinforced with structural fibers and glass fiber reinforced polymer bars: Experimental and analytical investigation. *Advances in Structural Engineering*. 25(2):374–391.
- Kumar, R. 2022. A review on the modelling of hydrothermal liquefaction of biomass and waste feedstocks. *Energy Nexus*. 5:100042.
- Kumar, D. & Pant, K.K. 2015. Production and characterization of biocrude and biochar obtained from non-edible de-oiled seed cakes hydrothermal conversion. *Journal of Analytical and Applied Pyrolysis*. 115:77–86.
- Kumar, A., Holuszko, M. & Espinosa, D.C.R. 2017. E-waste: An overview on generation, collection, legislation and recycling practices. *Resources, Conservation and Recycling*. 122(1):32–42.

- Kumar, M., Morya, R., Gupta, A., Kumar, V. & Thakur, I.S. 2020. Bacterial-Mediated Depolymerization and Degradation of Lignin. *Environmental Microbiology and Biotechnology: Volume 2: Bioenergy and Environmental Health*. 83–103.
- Ladou, J. 2006. Printed circuit board industry. *International Journal of Hygiene and Environmental Health*. 209(3):211–219.
- Lange, H., Decina, S. & Crestini, C. 2013. Oxidative upgrade of lignin - Recent routes reviewed. *European Polymer Journal*. 49(6):1151–1173.
- Lanphear, B.P. & Roghmann, K.J. 1997. Pathways of lead exposure in urban children. *Environ. res.* 74(1):67–73.
- Laredo, G.C., Reza, J. & Meneses Ruiz, E. 2023. Hydrothermal liquefaction processes for plastics recycling: A review. *Cleaner Chemical Engineering*. 5:100094.
- Lee, D., Offenhuber, D., Duarte, F., Biderman, A. & Ratti, C. 2018. Monitour: Tracking global routes of electronic waste. *Waste Management*. 72:362–370.
- Leng, L., Yuan, X., Huang, H., Shao, J., Wang, H., ... Zeng, G. 2015. Bio-char derived from sewage sludge by liquefaction: Characterization and application for dye adsorption. *Applied Surface Science*. 346:223–231.
- Leng, L.J., Yuan, X.Z., Huang, H.J., Wang, H., Wu, Z. Bin, ... Zeng, G.M. 2015. Characterization and application of bio-chars from liquefaction of microalgae, lignocellulosic biomass and sewage sludge. *Fuel Processing Technology*. 129:8–14.
- Li, K. & Xu, Z. 2015. Application of supercritical water to decompose brominated epoxy resin and environmental friendly recovery of metals from waste memory module. *Environmental Science and Technology*. 49(3):1761–1767.
- Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y. & Ma, L.Q. 2017. Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere*. 178:466–478.
- Li, M., Hu, Y., Zhou, N., Wang, S. & Sun, F. 2022. Hydrothermal treatment coupled with pyrolysis and calcination for stabilization of electroplating sludge: Speciation transformation and environmental risk of heavy metals. *Journal of Hazardous Materials*. 438.
- Li, Y., Yang, D., Li, P. & Li, Z. 2022. Lignin as a multi-functional agent for the synthesis of Ag nanoparticles and its application in antibacterial coatings. *Journal of Materials Research and Technology*. 17:3211–3220.
- Liu, Z. & Zhang, F.-S. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *Journal of Hazardous Materials*. 167(1):933–939.
- Liu, Z. & Zhang, F.-S.S. 2011. Removal of copper (II) and phenol from aqueous solution using porous carbons derived from hydrothermal chars. *Desalination*. 267(1):101–106.
- Liu, A., Park, Y.K., Huang, Z., Wang, B., Ankumah, R.O. & Biswas, P.K. 2006. Product identification and distribution from hydrothermal conversion of walnut shells. *Energy and Fuels*. 20(2):446–454.
- Liu, K., Tan, Q., Yu, J. & Wang, M. 2023. A global perspective on e-waste recycling. *Circular Economy*. 2(1):100028.
- Liu, Z., Zhang, F.S. & Wu, J. 2010. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. *Fuel*. 89(2):510–514.
- Lloyd, T.A. & Wyman, C.E. 2005. Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresource Technology*. 96(18 SPEC. ISS.):1967–1977.

- Lu, J., Zhang, J., Zhu, Z., Zhang, Y., Zhao, Y., ... Liu, Z. 2017. Simultaneous production of biocrude oil and recovery of nutrients and metals from human feces via hydrothermal liquefaction. *Energy Conversion and Management*. 134:340–346.
- Lu, J., Watson, J., Zeng, J., Li, H., Zhu, Z., ... Liu, Z. 2018. Biocrude production and heavy metal migration during hydrothermal liquefaction of swine manure. *Process Safety and Environmental Protection*. 115:108–115.
- Luda, M.P., Balabanovich, A.I. & Camino, G. 2002. Thermal decomposition of fire retardant brominated epoxy resins. *Journal of Analytical and Applied Pyrolysis*. 65(1):25–40.
- Ma, E. 2019. Recovery of waste printed circuit boards through pyrometallurgy. *Electronic Waste Management and Treatment Technology*. 247–267.
- Ma, C., Yu, J., Wang, B., Song, Z., Xiang, J., ... Sun, L. 2016. Chemical recycling of brominated flame retarded plastics from e-waste for clean fuels production: A review. *Renewable and Sustainable Energy Reviews*. 61:433–450.
- Macleod, P. 2002. A review of flexible circuit technology and its applications. *Technology Watch*. (June 2002):54. https://www.lboro.ac.uk/microsites/mechman/research/ipm-ktn/pdf/Technology_review/flexible-circuit-technology-and-its-applications.pdf.
- Magdeldin, M., Kohl, T. & Järvinen, M. 2017. Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues. *Energy*. 137:679–695.
- Marais, H.B., Marx, S. & Venter, R.J. 2019. Valorisation of waste lignin for phenol derivative compounds using hydrothermal liquefaction. In: *European Biomass Conference and Exhibition*. Lisbon, Portugal.
- Mateus, M.M., Bordado, J.M. & Galhano dos Santos, R. 2021. Estimation of higher heating value (HHV) of bio-oils from thermochemical liquefaction by linear correlation. *Fuel*. 302.
- Mathanker, A., Das, S., Pudasainee, D., Khan, M., Kumar, A. & Gupta, R. 2021. A review of hydrothermal liquefaction of biomass for biofuels production with a special focus on the effect of process parameters, co-solvents and extraction solvents. *Energies*. 14(16).
- Matsumoto, Y. & Oshima, Y. 2014. Au and Cu recovery from printed boards by decomposition of epoxy resin in supercritical water. *Journal of Supercritical Fluids*. 95:462–467.
- Mazaheri, H., Lee, K.T., Bhatia, S. & Mohamed, A.R. 2010. Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: An optimisation study using response surface methodology. *Bioresource Technology*. 101(23):9335–9341.
- Megiatto, J.D., Cerrutti, B.M. & Frollini, E. 2016. Sodium lignosulfonate as a renewable stabilizing agent for aqueous alumina suspensions. *International Journal of Biological Macromolecules*. 82:927–932.
- Mei, C., Hu, C., Hu, Q., Sun, C., Li, L., ... Gu, X. 2020. Effective depolymerization of sodium lignosulfonate over SO₄²⁻/TiO₂ catalyst. *Catalysts*. 10(9):1–12.
- Menon, V. & Rao, M. 2012. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*. 38(4):522–550.
- Mihai, F.C., Gnoni, M.G., Meidiana, C., Ezeah, C. & Elia, V. 2019. Waste electrical and electronic equipment (WEEE): Flows, quantities, and management-a global scenario. *Electronic Waste Management and Treatment Technology*. 1–34.
- Minowa, T., Kondo, T. & Sudirjo, S.T. 1998. Thermochemical liquefaction of Indonesian biomass residues. *Biomass and Bioenergy*. 14(5–6):517–524.

- Moroni, M., Lupo, E., Della Pelle, V., Pomponi, A. & La Marca, F. 2018. Experimental investigation of the productivity of a wet separation process of traditional and bio-plastics. *Separations*. 5(2).
- Nagappan, S., Bhosale, R.R., Nguyen, D.D., Chi, N.T.L., Ponnusamy, V.K., ... Kumar, G. 2021. Catalytic hydrothermal liquefaction of biomass into bio-oils and other value-added products – A review. *Fuel*. 285.
- Namias, J. 2013. The Future of Electronic Waste Recycling in the United States : Obstacles and Domestic Solutions. Columbia University, New York.
- Nassajfar, M.N., Deviatkin, I., Leminen, V. & Horttanainen, M. 2021. Alternative materials for printed circuit board production: An environmental perspective. *Sustainability (Switzerland)*. 13(21):12126.
- Nazari, L., Yuan, Z., Souzanchi, S., Ray, M.B. & Xu, C. 2015. Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils. *Fuel*. 162:74–83.
- Nizamuddin, S., Baloch, H.A., Griffin, G.J., Mubarak, N.M., Bhutto, A.W., ... Ali, B.S. 2017. An overview of effect of process parameters on hydrothermal carbonization of biomass. *Renewable and Sustainable Energy Reviews*. 73:1289–1299.
- Okajima, I., Yamada, K., Sugeta, T. & Sako, T. 2002. Decomposition of epoxy resin and recycling of CFRP with sub- and supercritical water. *Journal of Chemical Engineering of Japan*. 35(11):553–558.
- Otto, S., Kibbe, A., Henn, L., Hentschke, L. & Kaiser, F.G. 2018. The economy of E-waste collection at the individual level: A practice oriented approach of categorizing determinants of E-waste collection into behavioral costs and motivation. *Journal of Cleaner Production*. 204:33–40.
- Overend, R.P., Chornet, E. & Gascoigne, A. 1987. Fractionation of lignocellulosics by steam-aqueous pretreatments. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*. 321(1561):523–536.
- Özkan, İ. & Çokça, E. 2023. The Investigation of the Addition of Sodium Lignosulfonate to Lime Column Used for Improving the Expansive Soils. *Technical Journal of Turkish Chamber of Civil Engineers*. 34(1):135–152.
- Panisko, E., Wietsma, T., Lemmon, T., Albrecht, K. & Howe, D. 2015. Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks. *Biomass and Bioenergy*. 74:162–171.
- Pant, D., Joshi, D., Upreti, M.K. & Kotnala, R.K. 2012. Chemical and biological extraction of metals present in E waste: A hybrid technology. *Waste Management*. 32(5):979–990.
- dos Passos, J.S., Glasius, M. & Biller, P. 2020. Screening of common synthetic polymers for depolymerization by subcritical hydrothermal liquefaction. *Process Safety and Environmental Protection*. 139:371–379.
- Patil, R.A. & Ramakrishna, S. 2020. A comprehensive analysis of e-waste legislation worldwide. *Environmental Science and Pollution Research*. 27(13):14412–14431.
- Pedersen, T.H. & Conti, F. 2017. Improving the circular economy via hydrothermal processing of high-density waste plastics. *Waste Management*. 68:24–31.
- Perkins, D.N., Brune Drisse, M.N., Nxele, T. & Sly, P.D. 2014. E-waste: A global hazard. *Annals of Global Health*. 80(4):286–295.
- Ponnusamy, V.K., Nagappan, S., Bhosale, R.R., Lay, C.H., Duc Nguyen, D., ... Kumar, G. 2020. Review on sustainable production of biochar through hydrothermal liquefaction: Physico-chemical properties and applications. *Bioresource Technology*. 310.

- Poravou, C.A., Tsongidis, N.I., Lekkou, C., Zacharopoulou, V.A. & Konstandopoulos, A.G. 2022. Valorization of Plastic Waste: A Lab-Scale Approach with the Aid of Solar Hydrothermal Liquefaction Technology. *Waste and Biomass Valorization*. 13(9):3835–3844.
- Prestigiacomo, C., Scialdone, O. & Galia, A. 2022. Hydrothermal liquefaction of wet biomass in batch reactors: Critical assessment of the role of operating parameters as a function of the nature of the feedstock. *Journal of Supercritical Fluids*. 189.
- Priya, A. & Hait, S. 2020. Biometallurgical recovery of metals from waste printed circuit boards using pure and mixed strains of *Acidithiobacillus ferrooxidans* and *Acidiphilium acidophilum*. *Process Safety and Environmental Protection*. 143:262–272.
- Qian, L., Wang, S. & Savage, P.E. 2017. Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions. *Bioresource Technology*. 232:27–34.
- Qin, F., Wen, B., Shan, X.Q., Xie, Y.N., Liu, T., ... Khan, S.U. 2006. Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat. *Environmental Pollution*. 144(2):669–680.
- Raikova, S., Smith-Baedorf, H., Bransgrove, R., Barlow, O., Santomauro, F., ... Chuck, C.J. 2016. Assessing hydrothermal liquefaction for the production of bio-oil and enhanced metal recovery from microalgae cultivated on acid mine drainage. *Fuel Processing Technology*. 142:219–227.
- Rajagopal, R.R., Rajarao, R., Cholakke, S.T. & Sahajwalla, V. 2017. Sustainable composite panels from non-metallic waste printed circuit boards and automotive plastics. *Journal of Cleaner Production*. 144:470–481.
- Ratha, S.K., Renuka, N., Abunama, T., Rawat, I. & Bux, F. 2022. Hydrothermal liquefaction of algal feedstocks: The effect of biomass characteristics and extraction solvents. *Renewable and Sustainable Energy Reviews*. 156.
- Republic of South Africa (RSA). 2012. *National Environmental Management: National Waste Information Regulations*. Government Gazette No.35583, GNR 625. 13 August 2012. Pretoria.
- Republic of South Africa (RSA). 2014. *National Environment: Waste Amendment Act*. Government Gazette No.37083, GNR 581. 29 November 2013. Pretoria.
- Del Río, J.C., Rencoret, J., Gutiérrez, A., Elder, T., Kim, H. & Ralph, J. 2020. Lignin Monomers from beyond the Canonical Monolignol Biosynthetic Pathway: Another Brick in the Wall. *ACS Sustainable Chemistry and Engineering*. 8(13):4997–5012.
- Rudin, A. & Choi, P. 2013. Chapter 1 - Introductory Concepts and Definitions. In: A. Rudin & P. Choi, eds. Third Edit ed. *The Elements of Polymer Science & Engineering (Third Edition)*. Boston: Academic Press. pp. 1–62.
- Rudra, S. & Jayathilake, M. 2022. 5.08 - Hydrothermal Liquefaction of Biomass for Biofuel Production. In: T.M. Letcher, ed. Second Edi ed. *Comprehensive Renewable Energy (Second Edition)*. Oxford: Elsevier. pp. 165–186.
- Run Dong, L., Bing Shuo, L., Tian Hua, Y. & Ying Hui, X. 2013. Liquefaction of rice stalk in sub- and supercritical ethanol. *Ranliao Huaxue Xuebao/Journal of Fuel Chemistry and Technology*. 41(12):1459–1465.
- Saba, N., Jawaid, M., Alothman, O.Y., Paridah, M.T. & Hassan, A. 2016. Recent advances in epoxy resin, natural fiber-reinforced epoxy composites and their applications. *Journal of Reinforced Plastics and Composites*. 35(6):447–470.
- Sahajwalla, V. & Gaikwad, V. 2018. The present and future of e-waste plastics recycling. *Current Opinion in Green and Sustainable Chemistry*. 13:102–107.

- Seward, T.M. & Driesner, T. 2004. Hydrothermal solution structure: Experiments and computer simulations. *Aqueous Systems at Elevated Temperatures and Pressures: Physical Chemistry in Water, Steam and Hydrothermal Solutions*. 149–182.
- Shakya, R., Whelen, J., Adhikari, S., Mahadevan, R. & Neupane, S. 2015. Effect of temperature and Na₂CO₃ catalyst on hydrothermal liquefaction of algae. *Algal Research*. 12:80–90.
- Shin, S.R., Mai, V.D. & Lee, D.S. 2019. Chemical recycling of used printed circuit board scraps: Recovery and utilization of organic products. *Processes*. 7(1):22.
- Shuping, Z., Yulong, W., Mingde, Y., Kaleem, I., Chun, L. & Tong, J. 2010. Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. *Energy*. 35(12):5406–5411.
- Soler, A., Conesa, J.A. & Ortuño, N. 2017. Emissions of brominated compounds and polycyclic aromatic hydrocarbons during pyrolysis of E-waste debrominated in subcritical water. *Chemosphere*. 186:167–176.
- Stapleton, H.M., Allen, J.G. & Kelly, S.M. 2008. Alternate and new brominated flame retardants detected in U.S. house dust. *Environmental Science & Technology*. 42(18):6910–6916.
- Sthiannopkao, S. & Wong, M.H. 2013. Handling e-waste in developed and developing countries: Initiatives, practices, and consequences. *Science of the Total Environment*. 463–464:1147–1153.
- Sum, E.Y.L. 1991. The recovery of metals from electronic scrap. *Jom*. 43(4):53–61.
- Suzuki, A., Nakamura, T., Yokoyama, S. ya, Ogi, T. & Koguchi, K. 1988. Conversion of sewage sludge to heavy oil by direct thermochemical liquefaction. *Journal of Chemical Engineering of Japan*. 21(3):288–293.
- Takanori, H., Ryuichi, A., Youichi, M., Minoru, N., Yasuhiro, T. & Takao, A. 2009. Techniques to separate metal from waste printed circuit boards from discarded personal computers. *Journal of Material Cycles and Waste Management*. 11:42–54.
- Tekin, K., Karagöz, S. & Bektaş, S. 2012. Hydrothermal liquefaction of beech wood using a natural calcium borate mineral. *Journal of Supercritical Fluids*. 72:134–139.
- Tenorio, J.A.S., Menetti, R.P. & Chaves, A.P. 1997. Production of non-ferrous metallic concentrates from electronic scrap. *TMS Annual Meeting*. 505–509.
- Tesfaye, F., Lindberg, D. & Hamuyuni, J. 2017. Valuable metals and energy recovery from electronic waste streams. *Minerals, Metals and Materials Series*. 103–116.
- Thakur, P. & Kumar, S. 2022. Evaluation of e-waste status, management strategies, and legislations. *International Journal of Environmental Science and Technology*. 19(7):6957–6966.
- Tohka, A. & Lehto, H. 2005. Mechanical and Thermal Recycling of Waste from Electric and Electrical Equipment Mechanical and Thermal Recycling of Waste from Electric and Electrical Equipment. *Environmental Protection*.
- Toor, S.S., Rosendahl, L. & Rudolf, A. 2011. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy*. 36(5):2328–2342.
- Udayakumar, S., Razak, M.I.B.A. & Ismail, S. 2022. Recovering valuable metals from Waste Printed Circuit Boards (WPCB): A short review. *Materials Today: Proceedings*. 66:3062–3070.
- Usman, Y.M., Abubakar, S., Abdullahi, M.D. & Mohammed, A.B. 2022. Assessment of Heavy Metals Contamination in Rice At Dadinkowa Dam Basin Gombe State. *Journal of*

Chemical Society of Nigeria. 47(2).

- Vardon, D.R., Sharma, B.K., Scott, J., Yu, G., Wang, Z., ... Strathmann, T.J. 2011. Chemical properties of biocrude oil from the hydrothermal liquefaction of *Spirulina* algae, swine manure, and digested anaerobic sludge. *Bioresource Technology*. 102(17):8295–8303.
- Vermeşan, H., Tiuc, A.E. & Purcar, M. 2020. Advanced recovery techniques for waste materials from IT and telecommunication equipment printed circuit boards. *Sustainability (Switzerland)*. 12(1):1–23.
- Vernon, L.S., Rudolf, O. & Rosa, M.L.-R. 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagent. *Methods in Enzymology*. 299:152–178.
- Wadrzyk, M., Berdel, M., Janus, R. & Brilman, D.W.F. 2019. Hydrothermal processing of pine wood: Effect of process variables on bio-oil quality and yield. In: Vol. 108. *E3S Web of Conferences*.
- Wan, X., Kleemola, L., Klemettinen, L., O'Brien, H., Taskinen, P. & Jokilaakso, A. 2021. On the Kinetic Behavior of Recycling Precious Metals (Au, Ag, Pt, and Pd) Through Copper Smelting Process. *Journal of Sustainable Metallurgy*. 7(3):920–931.
- Wath, S.B., Dutt, P.S. & Chakrabarti, T. 2011. E-waste scenario in India, its management and implications. *Environmental Monitoring and Assessment*. 172(1–4):249–262.
- Watson, J., Wang, T., Si, B., Chen, W.T., Aierzhati, A. & Zhang, Y. 2020. Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability. *Progress in Energy and Combustion Science*. 77.
- Weil, E.D. & Levchik, S. 2004. A Review of Current Flame Retardant Systems for Epoxy Resins. *Journal of Fire Sciences*. 22(1):25–40.
- Wijitkosum, S. & Jiwnok, P. 2019. Elemental composition of biochar obtained from agricultural waste for soil amendment and carbon sequestration. *Applied Sciences (Switzerland)*. 9(19).
- Williams, P.T. & Slaney, E. 2007. Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures. *Resources, Conservation and Recycling*. 51(4):754–769.
- Wu, Q., Leung, J.Y.S., Geng, X., Chen, S., Huang, X., ... Lu, Y. 2015. Heavy metal contamination of soil and water in the vicinity of an abandoned e-waste recycling site: Implications for dissemination of heavy metals. *Science of The Total Environment*. 506–507:217–225.
- Xiang, D., Mou, P., Wang, J., Duan, G. & Zhang, H.C. 2007. Printed circuit board recycling process and its environmental impact assessment. *International Journal of Advanced Manufacturing Technology*. 34(9–10):1030–1036.
- Xing, M. & Zhang, F.S. 2013. Degradation of brominated epoxy resin and metal recovery from waste printed circuit boards through batch sub/supercritical water treatments. *Chemical Engineering Journal*. 219:131–136.
- Xiu, S., Shahbazi, A., Shirley, V. & Cheng, D. 2010. Hydrothermal pyrolysis of swine manure to bio-oil: Effects of operating parameters on products yield and characterization of bio-oil. *Journal of Analytical and Applied Pyrolysis*. 88(1):73–79.
- Xu, C. & Etcheverry, T. 2008. Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. *Fuel*. 87(3):335–345.
- Xu, Y.H. & Li, M.F. 2021. Hydrothermal liquefaction of lignocellulose for value-added products: Mechanism, parameter and production application. *Bioresource Technology*. 342.

- Yang, C., Wu, J., Deng, Z., Zhang, B., Cui, C. & Ding, Y. 2017. A Comparison of Energy Consumption in Hydrothermal Liquefaction and Pyrolysis of Microalgae. *Trends in Renewable Energy*. 3(1):76–85.
- Yang, C., Zhu, N., Shen, W., Zhang, T. & Wu, P. 2017. Bioleaching of copper from metal concentrates of waste printed circuit boards by a newly isolated *Acidithiobacillus ferrooxidans* strain Z1. *Journal of Material Cycles and Waste Management*. 19(1):247–255.
- Yang, C., Wang, S., Jiang, Z., Li, J., He, C., ... Xu, D. 2022. Catalytic hydrotreatment upgrading of biocrude oil derived from hydrothermal liquefaction of animal carcass. *Fuel*. 317.
- Yildirim, E., Onwudili, J.A. & Williams, P.T. 2015. Chemical Recycling of Printed Circuit Board Waste by Depolymerization in Sub- and Supercritical Solvents. *Waste and Biomass Valorization*. 6(6):959–965.
- Yin, J., Li, G., He, W., Huang, J. & Xu, M. 2011. Hydrothermal decomposition of brominated epoxy resin in waste printed circuit boards. *Journal of Analytical and Applied Pyrolysis*. 92(1):131–136.
- Van Yken, J., Cheng, K.Y., Boxall, N.J., Sheedy, C., Nikoloski, A.N., ... Kaksonen, A.H. 2021. A comparison of methods for the characterisation of waste-printed circuit boards. *Metals*. 11(12).
- Yu, S., Yang, S. & Cho, M. 2009. Multi-scale modeling of cross-linked epoxy nanocomposites. *Polymer*. 50(3):945–952.
- Zeng, X., Mathews, J.A. & Li, J. 2018. Urban Mining of E-Waste is Becoming More Cost-Effective Than Virgin Mining. *Environmental Science and Technology*. 52(8):4835–4841.
- Zhai, Y., Chen, H., Xu, B.B., Xiang, B., Chen, Z., ... Zeng, G. 2014. Influence of sewage sludge-based activated carbon and temperature on the liquefaction of sewage sludge: Yield and composition of bio-oil, immobilization and risk assessment of heavy metals. *Bioresource Technology*. 159:72–79.
- Zhan, L., Jiang, L., Zhang, Y., Gao, B. & Xu, Z. 2020. Reduction, detoxification and recycling of solid waste by hydrothermal technology: A review. *Chemical Engineering Journal*. 390:124651.
- Zhang, Y. & Chen, W.-T. 2018. 5 - Hydrothermal liquefaction of protein-containing feedstocks. In: L. Rosendahl, ed. *Direct Thermochemical Liquefaction for Energy Applications*. Woodhead Publishing. pp. 127–168.
- Zhang, J., Dong, H., Tong, L., Meng, L., Chen, Y. & Yue, G. 2012. Investigation of curing kinetics of sodium carboxymethyl cellulose/epoxy resin system by differential scanning calorimetry. *Thermochimica Acta*. 549:63–68.
- Zhang, Z., Zhao, X., Kwon, E. & Calstaldi, M.J. 2010. Experimental research on microwave induced thermal decomposition of printed circuit board wastes. In: *18th Annual North American Waste-to-Energy Conference, NAWTEC18-3536*. pp. 15–21.
- Zhao, J.J., Shen, X.J., Domene, X., Alcañiz, J.M., Liao, X. & Palet, C. 2019. Comparison of biochars derived from different types of feedstock and their potential for heavy metal removal in multiple-metal solutions. *Scientific Reports*. 9(1).
- Zhao, X., Xia, Y., Zhan, L., Xie, B., Gao, B. & Wang, J. 2019. Hydrothermal Treatment of E-Waste Plastics for Tertiary Recycling: Product Slate and Decomposition Mechanisms. *ACS Sustainable Chemistry and Engineering*. 7(1):1464–1473.
- Zheng, C.Y., Tao, H.X. & Xie, X.A. 2013. Distribution and characterizations of liquefaction of

celluloses in sub- and super-critical ethanol. *BioResources*. 8(1):648–662.

Zhou, H., Yang, D. & Zhu, J.Y. 2016. Molecular Structure of Sodium Lignosulfonate from Different Sources and their Properties as Dispersant of TiO₂ Slurry. *Journal of Dispersion Science and Technology*. 37(2):296–303.

Zhou, L., Liu, Y., Liu, S., Yin, Y., Zeng, G., ... Huang, X. 2016. Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures. *Bioresource Technology*. 218:351–359.

APPENDIX A: ADDITIONAL DATA

A.1 Temperature profiles for HTL experiments

The temperature of each HTL experiment was noted every five minutes to create representative temperature profiles, as illustrated in Figure 5-1 to Figure 5-5.

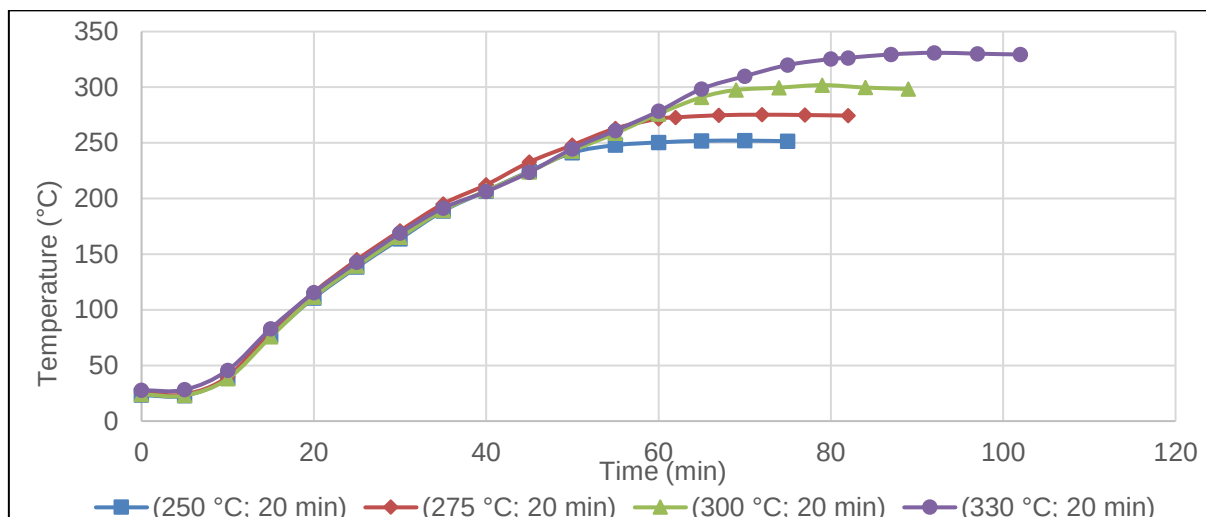


Figure 5-1: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 20 min at 250, 275, 300, and 330°C

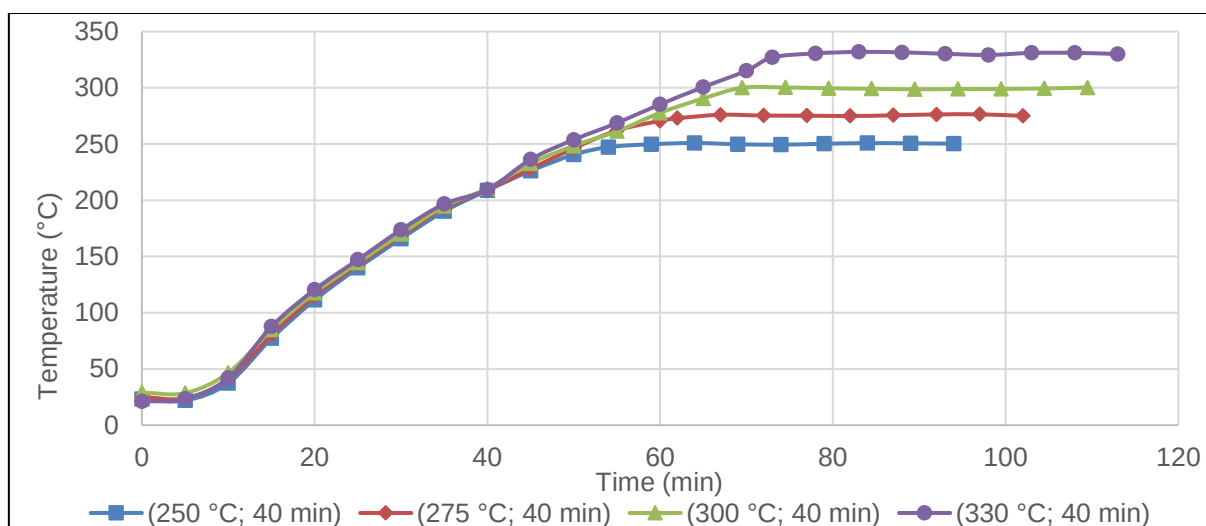


Figure 5-2: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 40 min at 250, 275, 300, and 330°C

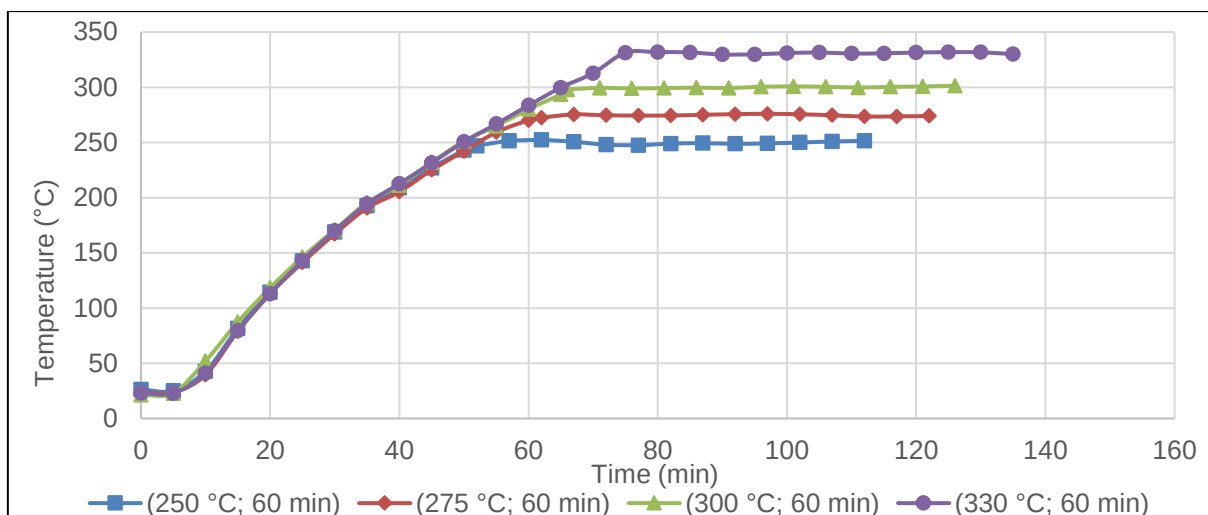


Figure 5-3: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 60 min at 250, 275, 300, and 330°C

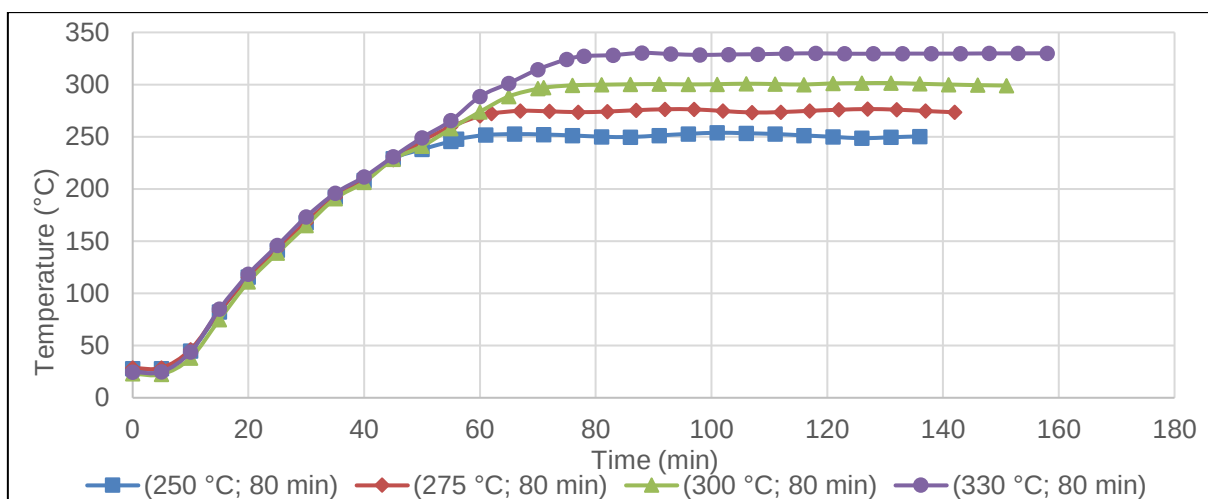


Figure 5-4: Reactor temperature profile for HTL of waste PCBs and lignosulphonate for 80 min at 250, 275, 300, and 330°C

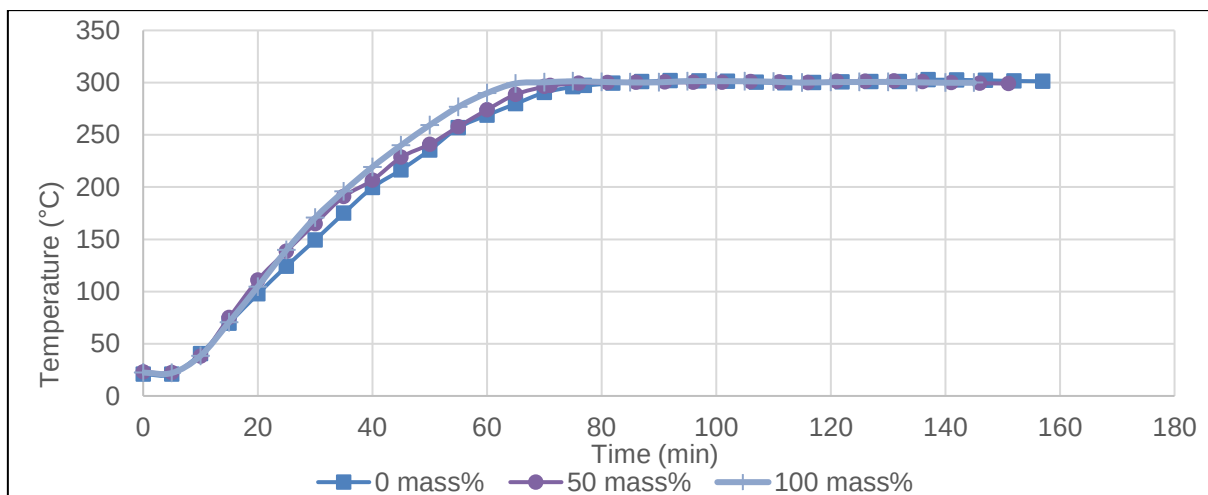


Figure 5-5: Reactor temperature profile for HTL of waste PCBs and lignosulphonate at 300°C for 80 min with 0, 50, and 100 wt.% waste PCB loading

A.2 Pressure profiles for HTL experiments

The pressure of each HTL experiment was noted every five minutes to create representative pressure profiles, as illustrated in Figure 5-6 to Figure 5-10.

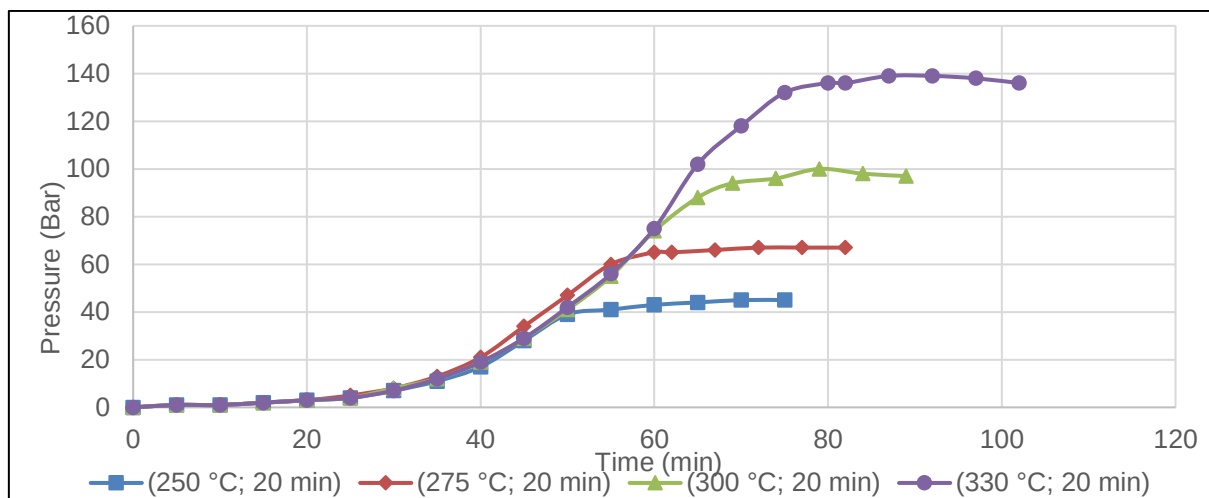


Figure 5-6: Reactor pressure profile for HTL of waste PCBs and liginosulphonate for 20 min at 250, 275, 300, and 330°C

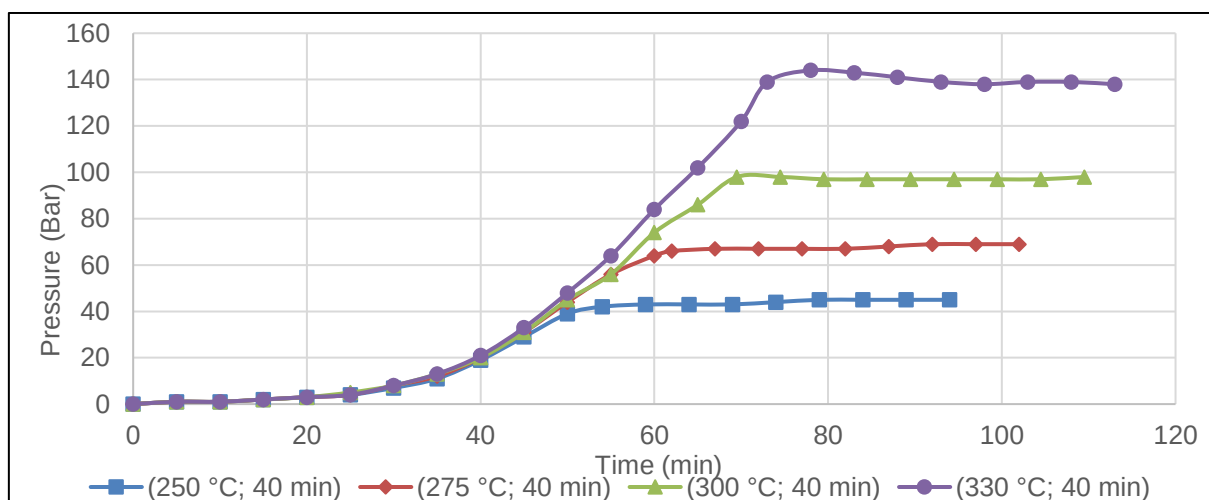


Figure 5-7: Reactor pressure profile for HTL of waste PCBs and liginosulphonate for 40 min at 250, 275, 300, and 330°C

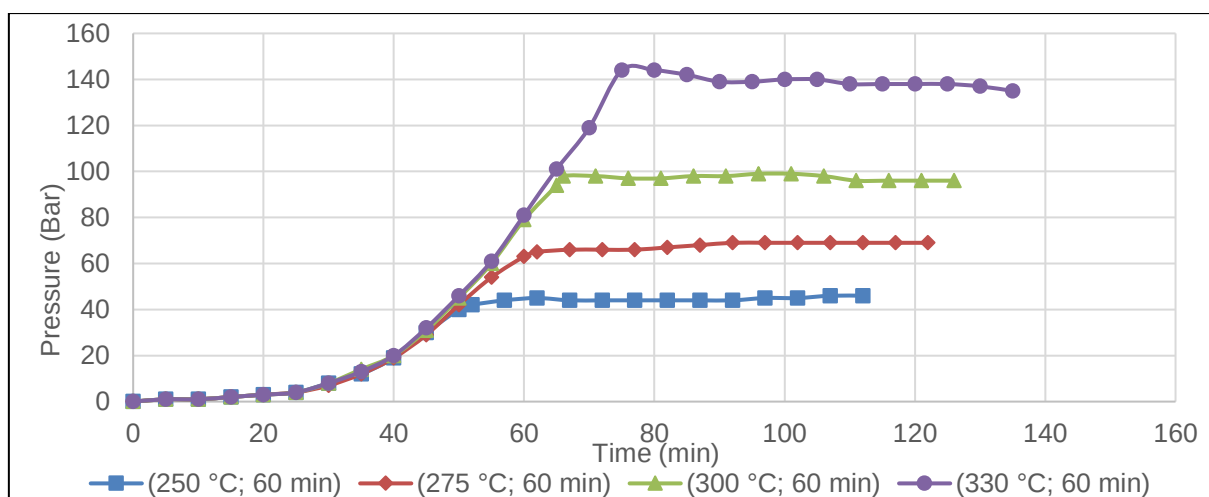


Figure 5-8: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 60 min at 250, 275, 300, and 330°C

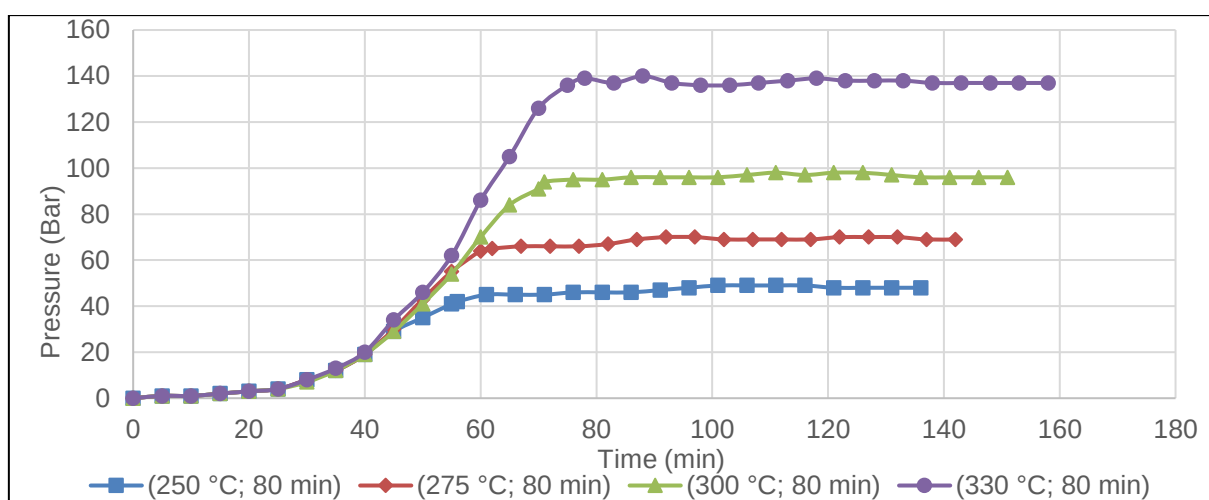


Figure 5-9: Reactor pressure profile for HTL of waste PCBs and lignosulphonate for 80 min at 250, 275, 300, and 330°C

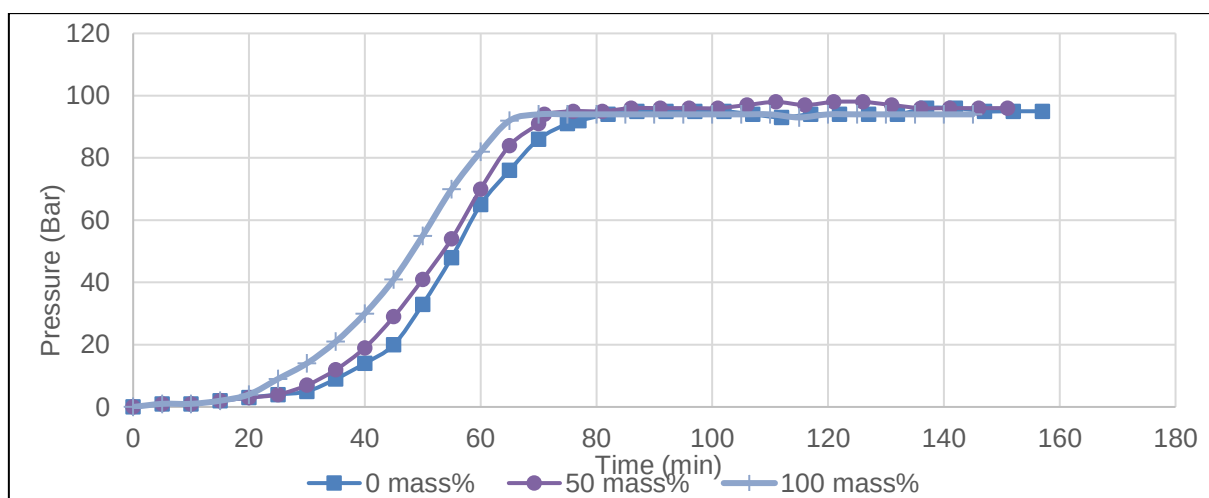


Figure 5-10: Reactor pressure profile for HTL of waste PCBs and lignosulphonate at 300°C for 80 min with 0, 50, and 100 wt.% waste PCB loading

A.3 HTL product yields

The mass yields for all HTL experiments with varying operating temperatures and residence times are presented in Table 5-1. The mass yields for HTL experiments with varying PCB waste loadings are illustrated in

Table 5-2.

Table 5-1: Product mass yields for HTL experiments at all operating temperatures and residence times

Operating parameters		Aqueous phase (wt.%) (± 2.22)	Residue (wt.%) (± 0.65)	Bio-oil (wt.%) (± 0.23)	Gas (wt.%) (± 1.68)	Total (wt.%)
Temperature (°C)	Residence time (min)					
250	20	49.14	28.16	1.01	21.7	100
	40	50.29	29.02	1.15	19.54	100
	60	53.74	28.74	1.44	16.09	100
	80	51.36	29.41	1.43	17.79	100
275	20	50.86	28.88	1.44	18.82	100
	40	51.01	28.45	2.01	18.53	100
	60	48.35	28.69	1.87	21.09	100
	80	50.57	28.65	1.86	18.91	100
300	20	45.62	27.83	2.30	24.25	100
	40	51.29	27.87	2.30	18.53	100
	60	48.85	27.73	2.44	20.98	100
	80	51.04	27.21	1.97	19.78	100
330	20	49.43	28.02	1.87	20.69	100
	40	54.45	26.58	2.16	16.81	100
	60	49.14	27.16	1.87	21.84	100
	80	51.15	27.08	2.01	19.77	100

Table 5-2: Product mass yields for HTL experiments at all waste PCB mass loadings

PCB mass loading (wt.%)	Aqueous phase (wt.%) (± 2.22)	Residue (wt.%) (± 0.65)	Bio-oil (wt.%) (± 0.23)	Gas (wt.%) (± 1.68)	Total (wt.%)
0	60.11	18.36	0.57	20.95	100
10	56.32	19.68	0.43	23.56	100
30	54.74	23.56	1.44	20.26	100
50	50.45	27.58	2.37	19.61	100
70	44.11	29.31	4.74	21.84	100
90	44.97	30.6	7.18	17.24	100

A.4 Severity factors

The severity factors compared to the residue, aqueous phase, bio-oil, and gas yields for HTL experiments with varying operating temperatures and residence times. SFs with constant residence times of 40 min and 60 min are illustrated in Figure 5-11 and Figure 5-12, respectively. Furthermore, severity factors with constant temperatures of 275°C and 300°C are shown in Figure 5-13 and Figure 5-14, respectively.

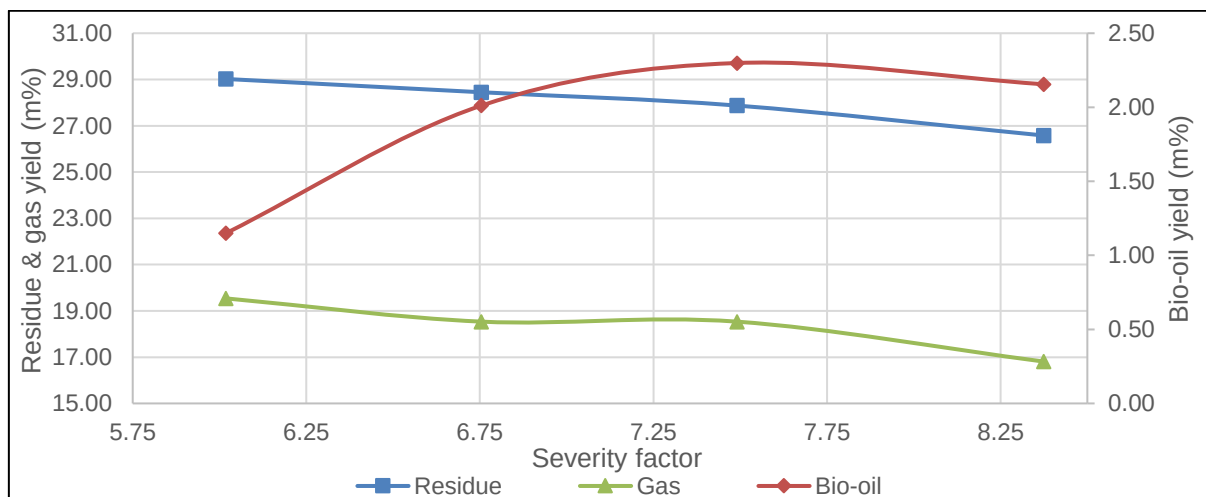


Figure 5-11: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 40 min at 250, 275, 300, and 330°C

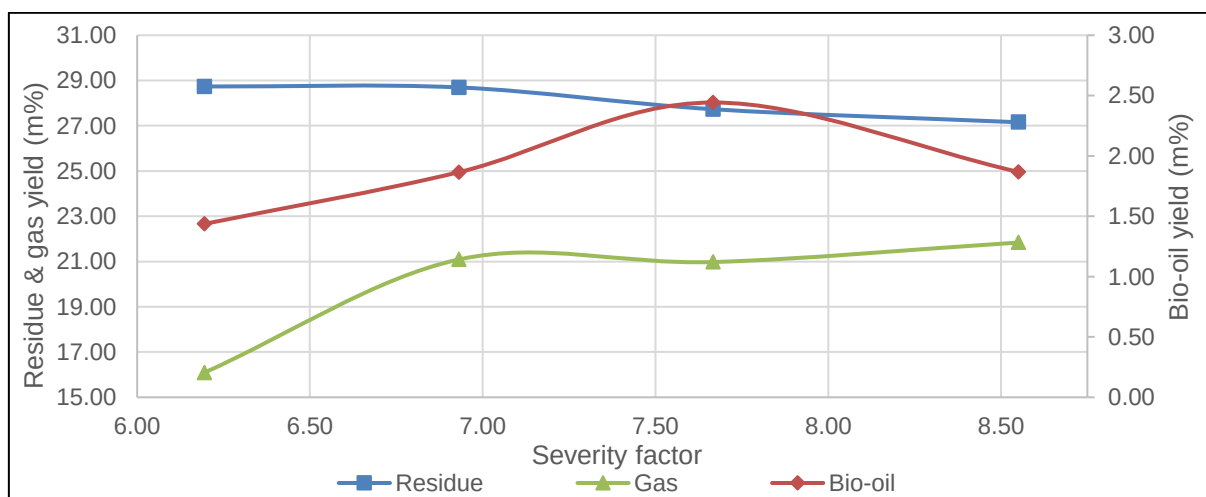


Figure 5-12: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 60 min at 250, 275, 300, and 330°C

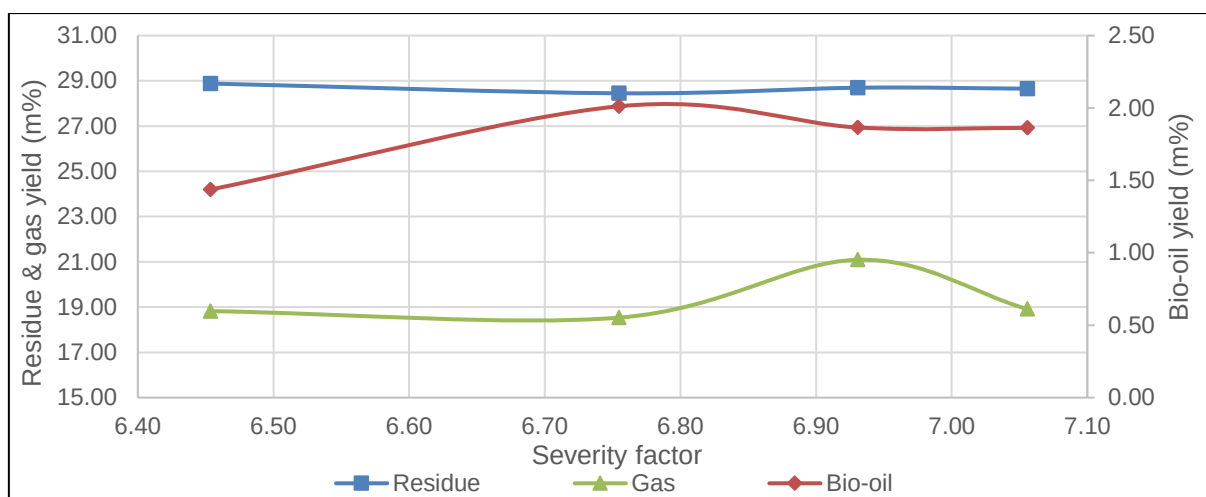


Figure 5-13: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 275°C at 20, 40, 60 and 80 min

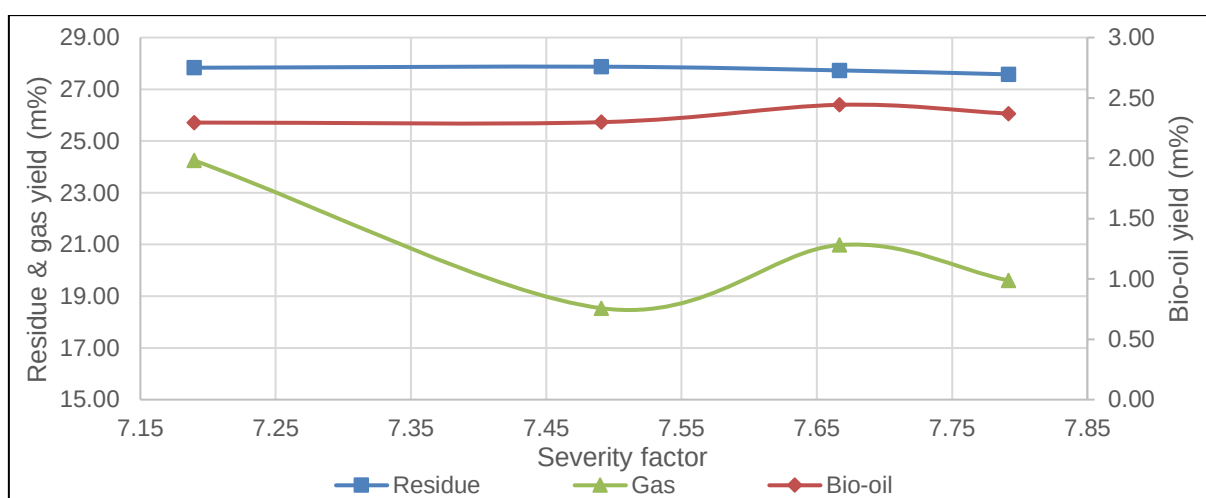


Figure 5-14: Residue, bio-oil, and gas products obtained from the HTL of waste PCBs and lignosulphonate at severity factors calculated for 300°C at 20, 40, 60, and 80 min

A.5 Elemental analysis

The carbon, nitrogen, and hydrogen contents obtained through elemental analysis of residues and bio-oils produced through HTL of sieved waste PCBs and lignosulphonate at various residence times and temperatures are presented in Table 5-3. Figure 5-15 presents the van Krevelen plot for bio-oils at all temperatures and times, with Figure 5-16 illustrating the van Krevelen plot for all PCB loadings.

Table 5-3: Elemental analysis of bio-oils and residues at all temperatures and residence times

Product	Operating parameters		C (wt.%) (±1.45)	H (wt.%) (±0.45)	N (wt.%) (±0.25)	R (wt.%) (±2.12)
	Temperature (°C)	Residence time (min)				
Bio-oil	250	20	54.47	5.88	0.61	39.04
		40	57.35	5.66	0.52	36.47
		60	56.05	6.09	0.67	37.19
		80	61.18	6.47	0.82	31.54
	275	20	65.04	6.84	0.88	27.24
		40	65.60	6.80	0.88	26.73
		60	66.45	6.51	0.65	26.38
		80	66.75	6.69	0.84	25.73
	300	20	67.15	6.75	0.85	25.25
		40	68.44	6.89	0.90	23.76
		60	68.83	7.00	0.91	23.32
		80	69.38	6.82	0.88	22.91
	330	20	70.95	7.10	0.85	21.10
		40	71.73	7.03	0.78	20.46
		60	72.96	7.15	0.87	19.03
		80	72.48	7.28	0.80	19.44
Product	Operating parameters		C (wt.%) (±0.86)	H (wt.%) (±0.05)	N (wt.%) (±0.03)	R (wt.%) (±0.90)
Residue	250	20	22.06	1.84	0.85	75.25
		40	22.19	1.80	1.07	74.94
		60	23.07	2.02	0.40	74.51
		80	22.26	1.90	0.41	75.43
	275	20	22.42	1.83	0.36	75.39
		40	22.31	1.73	0.32	75.65
		60	19.85	1.55	0.30	78.29
		80	21.51	1.64	0.31	76.54
	300	20	20.38	1.45	0.21	77.96
		40	20.47	1.40	0.24	77.89
		60	22.09	1.44	0.21	76.25
		80	20.56	1.32	0.16	77.96
	330	20	21.15	1.40	0.48	76.97
		40	18.57	1.21	0.51	79.71
		60	19.64	1.26	0.68	78.41
		80	21.75	1.41	0.42	76.46

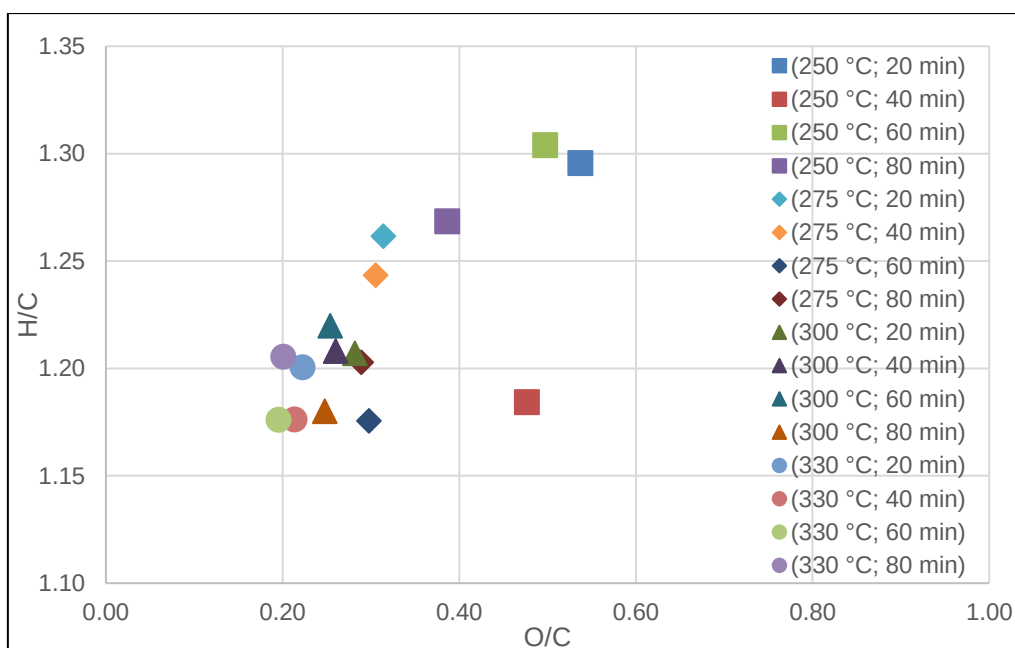


Figure 5-15: The van Krevelen plot for bio-oils produced at all temperatures and residence times

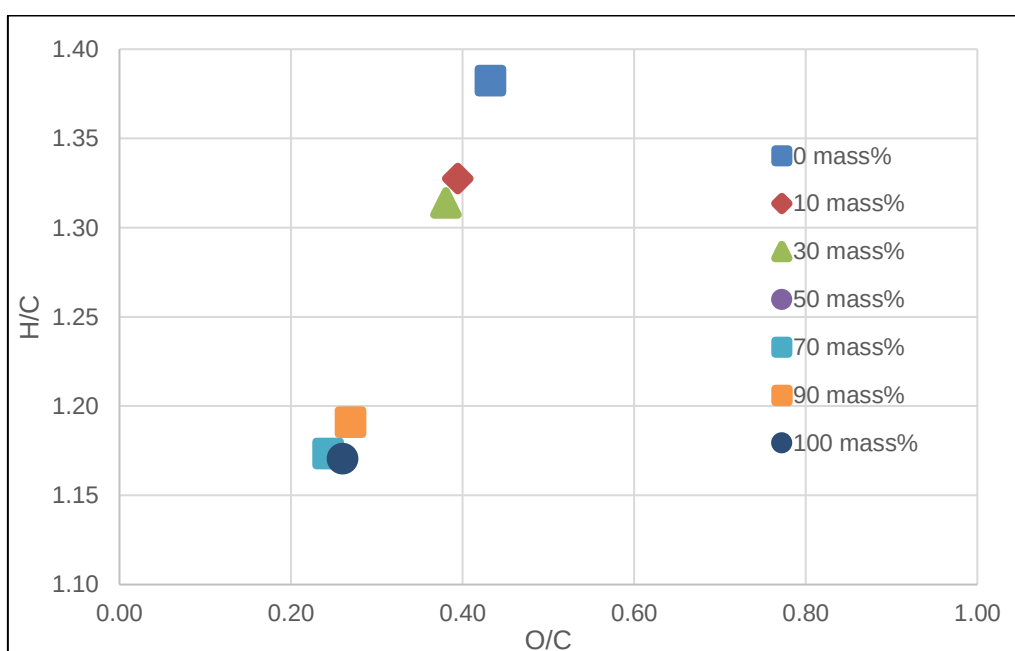


Figure 5-16: The van Krevelen plot for bio-oils produced at all waste PCB loadings

A.6 Energy content

The HHV calculated with Equation 5 through the carbon, nitrogen and hydrogen contents of bio-oils produced through HTL of sieved waste PCBs and lignosulphonate at various residence times and temperatures are presented in Table 5-4.

Table 5-4: HHV of bio-oils at all temperatures and residence times

Operating parameters		HHV (MJ/kg) (± 1.49)
Temperature ($^{\circ}\text{C}$)	Residence time (min)	
250	20	21.86
	40	23.04
	60	22.73
	80	25.64
275	20	28.16
	40	28.44
	60	28.58
	80	28.98
300	20	29.30
	40	30.25
	60	30.62
	80	30.74
330	20	32.07
	40	32.47
	60	33.45
	80	33.32

A.7 Proximate analysis

The moisture, volatile, fixed carbon, and ash contents obtained through proximate analysis of residues produced through HTL of sieved waste PCBs and lignosulphonate at various residence times and temperatures are presented in Table 5-5.

Table 5-5: Proximate analysis of residues at all temperatures and residence times

Operating parameters		Moisture (wt.%) (±0.45)	Volatile (wt.%) (±2.00)	Fixed carbon (wt.%) (±2.94)	Ash (wt.%) (±2.01)
Temperature (°C)	Residence time (min)				
250	20	3.75	26.39	3.94	65.92
	40	3.90	25.81	4.78	65.51
	60	5.17	23.57	4.23	67.04
	80	5.31	24.14	4.85	65.71
275	20	4.20	25.51	3.49	66.79
	40	4.57	23.08	4.02	68.33
	60	4.74	23.32	4.05	67.89
	80	4.17	23.25	3.90	68.67
300	20	3.95	22.88	3.74	69.43
	40	4.51	20.66	4.25	70.58
	60	4.27	20.86	3.95	70.93
	80	4.07	21.82	3.65	70.45
330	20	4.45	19.53	3.87	72.16
	40	3.80	19.03	3.32	73.84
	60	3.70	19.43	2.18	74.69
	80	4.09	18.38	3.05	74.47

A.8 GPC analysis

The weight and number molecular averages, as well as the PDI, obtained through GPC analysis of bio-oils through HTL of sieved waste PCBs and lignosulphonate at various residence times and temperatures are presented in Table 5-6.

Table 5-6: GPC analysis of bio-oils at all temperatures and residence times

Operating parameters		Mw (g/mol) (± 77.58)	Mn (g/mol) (± 2.87)	PDI (± 0.54)
Temperature ($^{\circ}\text{C}$)	Residence time (min)			
250	20	1420.16	249.49	5.69
	40	1395.26	256.22	5.46
	60	1451.85	251.26	5.78
	80	1330.89	237.75	5.59
275	20	1404.67	219.54	6.40
	40	1402.87	195.95	7.67
	60	1297.15	173.36	7.49
	80	1295.42	171.33	7.56
300	20	1134.55	153.39	7.40
	40	1150.30	146.19	7.86
	60	873.02	126.39	6.90
	80	976.90	134.27	7.27
330	20	690.39	123.45	5.59
	40	645.76	115.70	5.58
	60	636.07	121.89	5.22
	80	512.43	112.27	4.56

A.9 FTIR analysis

The FTIR spectrum of the waste PCBs used as feedstock is compared to the epoxy resin used in EEE in Figure 5-17. Furthermore, the FTIR spectrums obtained from the analysis of bio-oils and residues at various reaction temperatures and residence times are presented in Figure 5-18 to Figure 5-21. Figure 5-22 presents the residue of HTL from 100 wt.% waste PCB feed compared to glass. Comparing the relevant size of peaks on each FTIR spectrum allows for the qualitative deduction of functional group prominence in each sample. The wavenumber groupings corresponding to the notations of each peak are presented in Table 5-20.

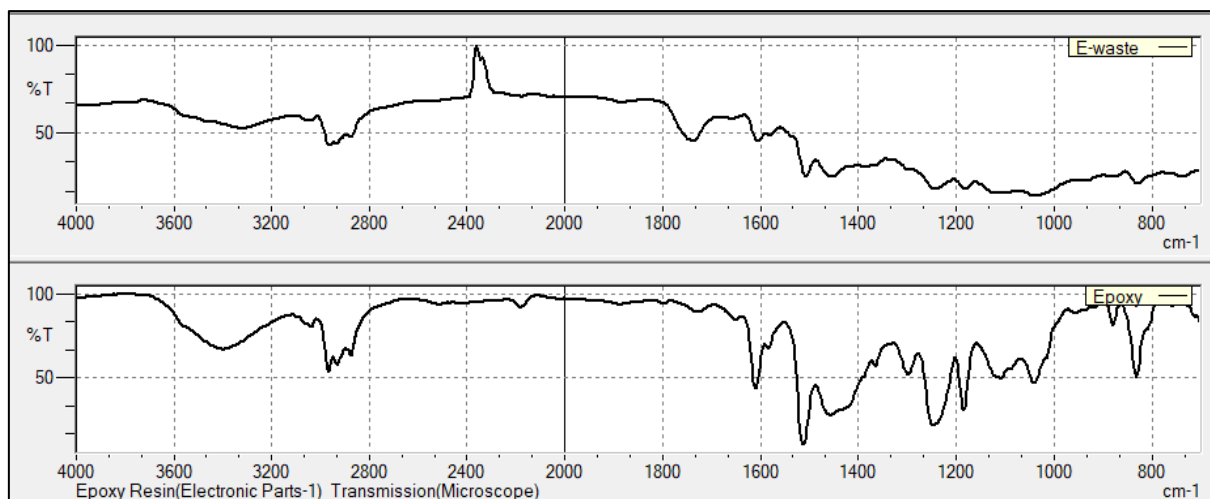


Figure 5-17: FTIR spectrum of sieved waste PCB feedstock compared to conventional epoxy resin used in EEE

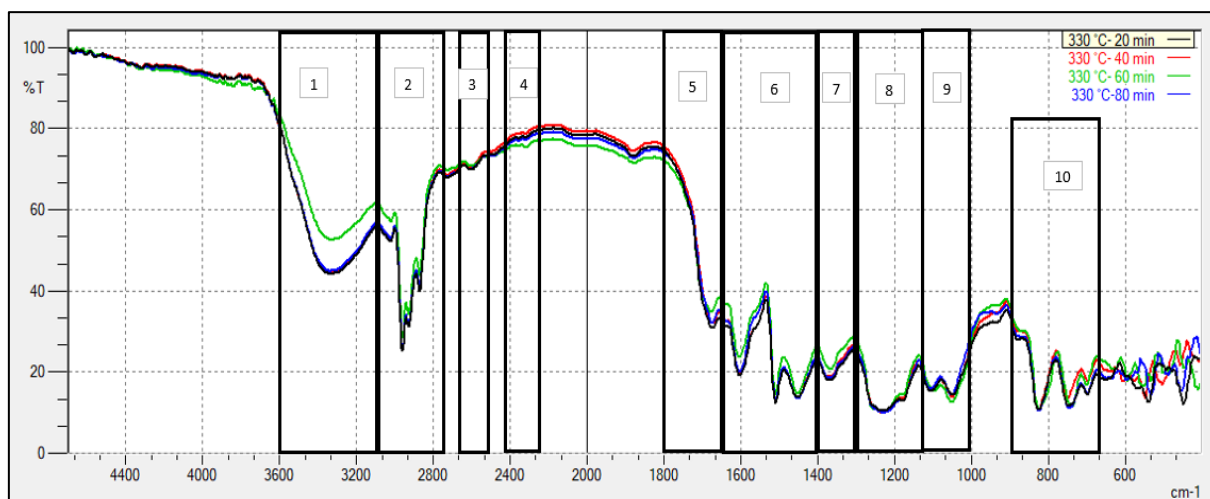


Figure 5-18: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 330°C for 20, 40, 60, and 80 min

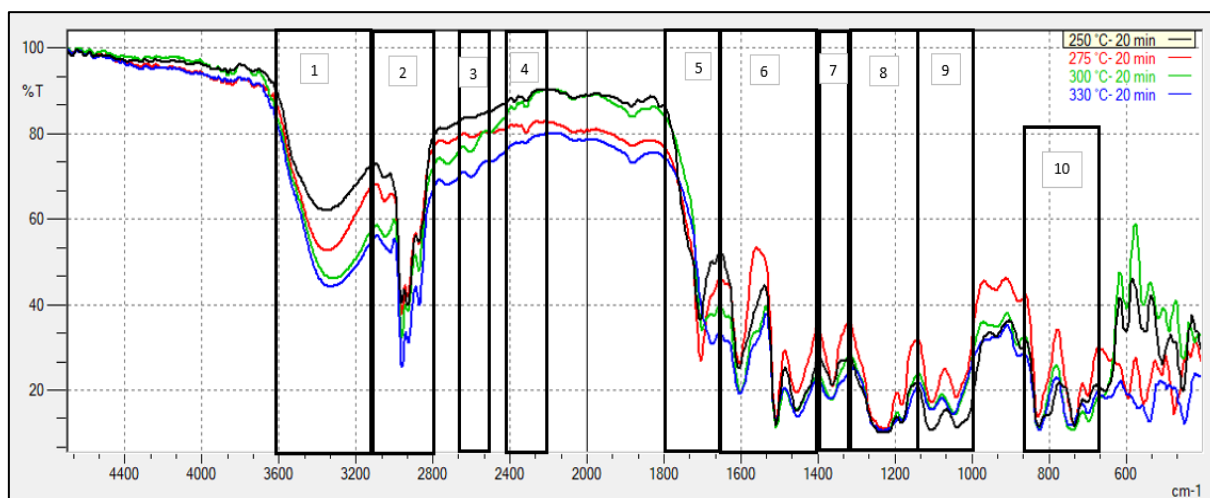


Figure 5-19: FTIR spectrum of bio-oils from the HTL of waste PCBs and lignosulphonate at 20 min for 250, 275, 300, and 330°C

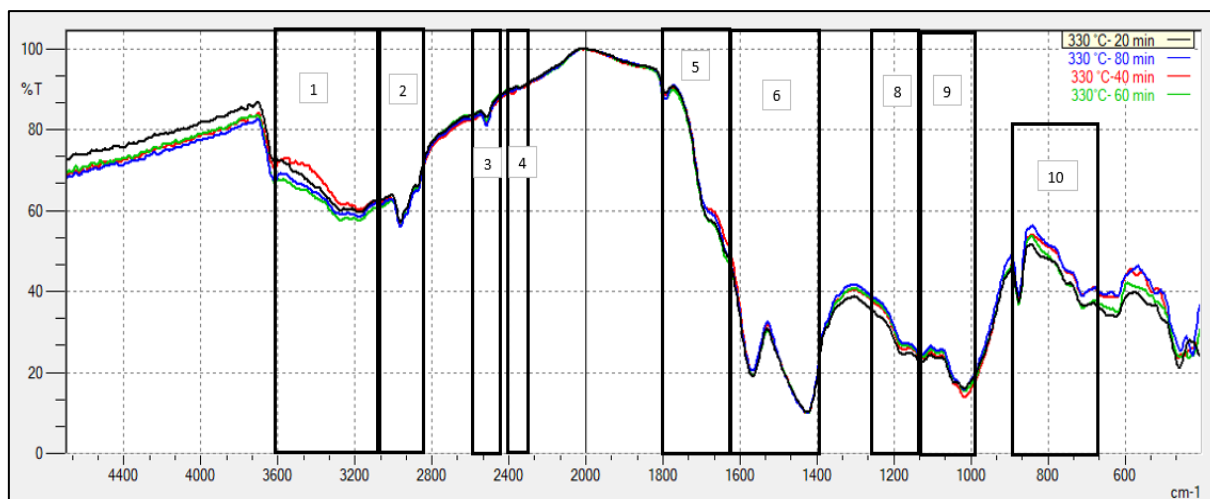


Figure 5-20: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 330°C for 20, 40, 60, and 80 min

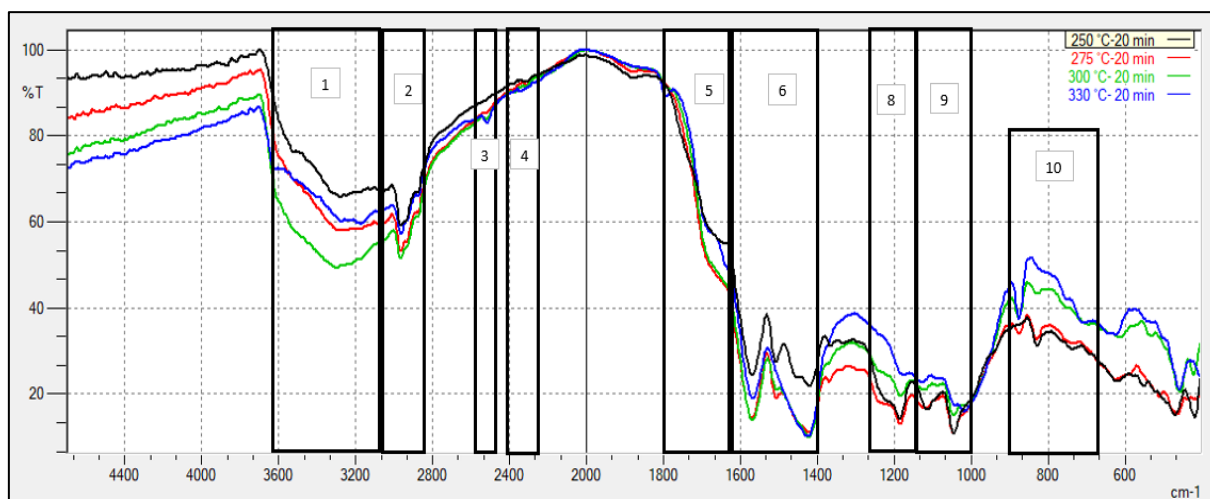


Figure 5-21: FTIR spectrum of residues from the HTL of waste PCBs and lignosulphonate at 20 min for 250, 275, 300, and 330°C

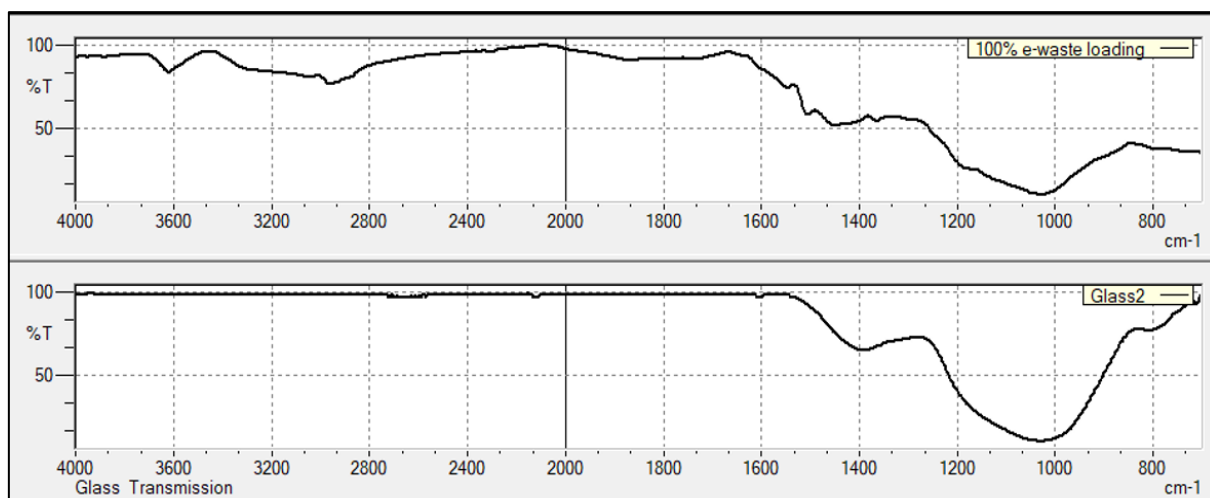


Figure 5-22: FTIR spectrum of residue from the HTL of waste PCBs at 100 wt.% PCB mass loading compared to glass

A.10 GC-MS analysis

The GC-MS analysis of bio-oils obtained through HTL of sieved waste PCBs and lignosulphonate at various temperatures and residence times are presented in Table 5-7 and Table 5-8. All identified compounds with a purity of 80 or more are categorised into several chemical groups and normalized to 100%.

Table 5-7: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min

Compound groups (area%)	275°C				300°C			
	20 min	40 min	60 min	80 min	20 min	40 min	60 min	80 min
Acids (± 1.25)	3.03	6.20	3.29	3.61	2.85	1.70	1.88	3.42
Alkenes (± 0.60)	0.00	0.75	0.39	0.19	0.33	0.05	0.86	0.40
Benzene derivatives (± 1.04)	0.13	0.98	0.00	0.00	0.59	0.00	3.51	0.55
Fatty acids (± 0.27)	2.51	1.15	1.34	0.80	1.04	0.44	0.23	0.71
Nitrogen compounds (± 1.64)	0.00	0.00	0.00	0.00	2.20	1.00	1.23	0.72
Ketones (± 2.17)	4.82	1.96	1.98	1.71	2.30	2.55	0.22	2.20
Phenolic compounds (± 4.50)	73.88	83.44	87.49	89.02	87.23	89.77	90.12	84.96
Sulphur compounds (± 0.09)	1.17	0.00	0.00	0.19	0.00	0.03	0.00	0.04
Others (± 4.35)	14.45	5.52	5.50	4.48	3.45	4.46	1.96	7.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Phenol (% of phenolics) (± 2.94)	14.99	26.30	25.16	22.54	26.02	20.48	21.34	19.11
Cresols (% of phenolics) (± 0.70)	0.91	2.43	1.26	2.79	3.73	6.54	7.68	7.57

Table 5-8: GC-MS analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C

Compound groups (area%)	40 min				60 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Acids (± 1.25)	11.08	6.20	1.70	1.75	13.96	3.29	1.88	2.17
Alkenes (± 0.60)	2.72	0.75	0.05	0.89	1.21	0.39	0.86	1.47
Benzene derivatives (± 1.04)	0.01	0.98	0.00	4.91	0.00	0.00	3.51	0.00
Fatty acids (± 0.27)	3.13	1.15	0.44	0.00	2.66	1.34	0.23	0.93
Nitrogen compounds (± 1.64)	0.92	0.00	1.00	0.55	0.82	0.00	1.23	0.28
Ketones (± 2.17)	1.42	1.96	2.55	1.99	0.79	1.98	0.22	2.47
Phenolic compounds (± 4.50)	61.73	83.44	89.77	83.45	58.35	87.49	90.12	86.52
Sulphur compounds (± 0.09)	0.67	0.00	0.03	0.28	0.17	0.00	0.00	0.26
Others (± 4.35)	18.32	5.52	4.46	6.18	22.05	5.50	1.96	5.88
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Phenol (% of phenolics) (± 2.94)	6.79	26.30	20.48	13.22	7.71	25.16	21.34	5.50
Cresols (% of phenolics) (± 0.70)	0.00	2.43	6.54	10.13	0.00	1.26	7.68	7.25

A.11 Total phenolic analysis

The total phenolic analysis of aqueous phases obtained through HTL of sieved waste PCBs and lignosulphonate at various temperatures and residence times are presented in Table 5-9.

Table 5-9: Total phenolic analysis of aqueous phases at all temperatures and residence times

Operating parameters		g/l as phenol (± 0.11)
Temperature ($^{\circ}\text{C}$)	Residence time (min)	
250	20	16.66
	40	12.89
	60	10.78
	80	6.88
275	20	6.45
	40	6.43
	60	6.47
	80	5.80
300	20	6.45
	40	7.00
	60	6.53
	80	5.93
330	20	5.45
	40	5.45
	60	4.98
	80	5.03

A.12 ICP-OES analysis

The ICP-OES analysis of all products obtained through HTL of sieved waste PCBs and lignosulphonate at various temperatures and residence times are presented in Table 5-10 to Table 5-15. All minerals and metals are presented in mg element per gram of product to accurately identify the distribution and trends of all elements. Table 5-16 compares the results from the ICP-OES analysis of sieved waste PCBs to the results from the XRF analysis.

Table 5-10: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min

Element (mg/g)	275°C				300°C			
	20 min	40 min	60min	80 min	20 min	40 min	60 min	80 min
Ca (±1.41)	42.72	40.77	42.76	42.26	44.05	43.36	45.63	43.55
K (±0.03)	1.21	1.20	1.24	1.30	1.36	1.44	1.38	1.75
Mg (±0.16)	2.32	2.35	2.34	2.34	2.42	2.44	2.39	2.22
Na (±2.28)	36.76	37.74	45.31	43.87	44.74	47.70	44.37	45.42
S (±1.34)	31.94	34.31	33.72	35.63	38.11	33.39	34.00	34.40
P (±0.07)	0.68	0.66	0.68	0.68	0.68	0.73	0.69	0.79
Al (±1.95)	43.61	45.14	45.59	46.10	46.88	45.10	49.02	44.93
Ag (±0.10)	0.36	0.57	0.59	0.82	0.49	0.41	0.48	0.71
Au (±0.04)	0.16	0.23	0.19	0.20	0.18	0.24	0.22	0.19
Cu (±6.12)	47.85	58.13	55.64	56.99	51.76	52.87	64.00	58.74
Fe (±4.11)	37.11	43.38	42.51	42.33	38.78	41.82	45.42	44.37
Ni (±0.46)	3.04	3.83	3.46	3.53	3.08	3.77	3.84	3.73
Pb (±0.30)	3.43	3.58	3.49	3.55	3.49	3.58	3.82	3.85
Sb (±0.01)	0.43	0.41	0.47	0.43	0.46	0.46	0.42	0.35
Sn (±0.69)	25.32	26.10	26.25	25.16	25.54	26.09	28.16	25.80
Ti (±0.30)	1.77	2.03	2.03	2.08	1.66	1.84	1.91	1.99
Zn (±0.29)	3.94	4.78	4.25	4.17	3.98	4.31	4.31	4.29

Table 5-11: ICP-OES analysis of residues from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C

Element (mg/g)	40 min				60 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (±1.41)	41.24	40.77	43.36	47.20	42.38	42.76	45.63	46.06
K (±0.03)	1.05	1.20	1.44	1.46	1.16	1.24	1.38	1.46
Mg (±0.16)	2.26	2.35	2.44	2.65	2.38	2.34	2.39	2.54
Na (±2.28)	33.28	37.74	47.70	53.00	33.93	45.31	44.37	57.00
S (±1.34)	30.31	34.31	33.39	38.44	32.07	33.72	34.00	39.63
P (±0.07)	0.56	0.66	0.73	0.82	0.65	0.68	0.69	0.62
Al (±1.95)	45.97	45.14	45.10	49.08	45.13	45.59	49.02	46.28
Ag (±0.10)	0.49	0.57	0.41	0.51	0.29	0.59	0.48	0.66
Au (±0.04)	0.20	0.23	0.24	0.33	0.23	0.19	0.22	0.21
Cu (±6.12)	63.91	58.13	52.87	63.11	62.33	55.64	64.00	59.52
Fe (±4.11)	44.99	43.38	41.82	51.68	47.08	42.51	45.42	45.11
Ni (±0.46)	3.73	3.83	3.77	4.45	4.05	3.46	3.84	3.94
Pb (±0.30)	3.73	3.58	3.58	3.96	3.67	3.49	3.82	3.65

Sb (± 0.01)	0.44	0.41	0.46	0.41	0.45	0.47	0.42	0.42
Sn (± 0.69)	26.21	26.10	26.09	29.24	26.20	26.25	28.16	34.26
Ti (± 0.30)	2.20	2.03	1.84	2.53	2.16	2.03	1.91	2.10
Zn (± 0.29)	4.80	4.78	4.31	5.22	5.06	4.25	4.31	4.68

Table 5-12: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min

Element (mg/g)	275°C				300°C			
	20 min	40 min	60min	80 min	20 min	40 min	60 min	80 min
Ca (± 0.63)	0.94	1.08	0.70	0.90	0.69	1.15	0.63	1.19
K (± 0.10)	0.17	0.19	0.15	0.17	0.21	0.19	0.25	0.19
Mg (± 0.07)	0.14	0.13	0.11	0.11	0.10	0.13	0.13	0.12
Na (± 2.70)	11.37	11.11	11.40	18.24	15.58	17.79	17.01	15.62
S (± 4.73)	21.02	18.92	16.43	17.91	12.72	20.07	16.65	14.22
P (± 0.02)	0.05	0.05	1.16E-03	0.02	3.11E-03	0.02	8.45E-03	8.51E-03
Al (± 0.08)	0.43	0.42	0.21	0.32	0.19	0.31	0.08	0.10
Ag (± 0.01)	5.04E-03	1.05E-02	1.08E-02	7.51E-03	9.50E-03	3.68E-03	ND	9.34E-03
Au ($\pm 3.81E-03$)	ND	5.35E-03	BDL	6.92E-03	4.32E-03	8.39E-03	6.13E-03	6.75E-03
Cu (± 0.09)	0.33	0.39	0.27	0.37	0.27	0.36	0.10	0.24
Fe (± 0.05)	0.06	0.07	0.06	0.08	0.10	0.13	0.09	0.12
Ni (± 0.01)	1.06E-02	9.69E-03	3.98E-03	3.47E-03	7.96E-03	1.22E-02	1.30E-02	1.39E-02
Pb (± 0.04)	3.33E-03	2.00E-03	3.75E-03	6.32E-03	3.63E-03	7.52E-03	1.63E-03	1.47E-02
Sb (± 0.05)	0.07	0.04	0.03	0.09	0.05	0.04	0.07	0.07
Sn (± 0.58)	1.09	2.14	2.03	1.64	1.87	1.52	2.93	1.53
Ti (± 0.05)	0.04	0.54	9.64E-03	1.45E-02	1.32E-02	0.02	0.03	0.05
Zn (± 0.02)	ND	2.13E-03	ND	ND	1.39E-02	0.02	0.02	1.24E-02

*BDL=Below detection limit, ND=No detection

Table 5-13: ICP-OES analysis of bio-oils from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C

Element (mg/g)	40 min				60 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (±0.63)	1.31	1.08	1.15	1.01	1.21	0.70	0.63	0.60
K (±0.10)	0.22	0.19	0.19	0.26	0.18	0.15	0.25	0.18
Mg (±0.07)	0.13	0.13	0.13	0.17	0.10	0.11	0.13	0.15
Na (±2.70)	13.25	11.11	17.79	15.91	12.17	11.40	17.01	13.85
S (±4.73)	15.18	18.92	20.07	17.70	14.53	16.43	16.65	12.19
P (±0.02)	0.04	0.05	0.02	0.03	0.04	1.16E-03	8.45E-03	1.30E-02
Al (±0.08)	0.43	0.42	0.31	0.10	0.41	0.21	0.08	0.07
Ag (±0.01)	7.66E-03	1.05E-02	3.68E-03	6.51E-03	8.24E-03	1.08E-02	ND	7.69E-03
Au (±3.81E-03)	ND	5.35E-03	8.39E-03	1.11E-02	7.07E-04	BDL	6.13E-03	6.91E-03
Cu (±0.09)	0.43	0.39	0.36	0.29	0.51	0.27	0.10	0.43
Fe (±0.05)	0.07	0.07	0.13	0.19	0.09	0.06	0.09	0.22
Ni (±0.01)	2.62E-03	9.69E-03	1.22E-02	1.32E-02	5.88E-03	3.98E-03	1.30E-02	6.82E-03
Pb (±0.04)	BDL	2.00E-03	7.52E-03	1.23E-02	3.83E-03	3.75E-03	1.63E-03	1.02E-02
Sb (±0.05)	0.05	0.04	0.04	0.16	0.06	0.03	0.07	0.17
Sn (±0.58)	1.55	2.14	1.52	0.92	1.49	2.03	2.93	0.36
Ti (±0.05)	0.02	0.54	0.02	0.20	4.31E-03	9.64E-03	0.03	0.08
Zn (±0.02)	9.54E-03	2.13E-03	0.02	0.05	ND	ND	0.02	0.02

*BDL=Below detection limit, ND=No detection

Table 5-14: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 275°C and 300°C for 20, 40, 60, and 80 min

Element (mg/g)	275°C				300°C			
	20 min	40 min	60min	80 min	20 min	40 min	60 min	80 min
Ca (±0.10)	0.13	0.35	0.33	0.41	0.32	0.28	0.18	0.28
K (±0.05)	0.36	0.39	0.32	0.28	0.39	0.23	0.32	0.24
Mg (±2.38E-03)	8.16E-03	7.61E-03	7.46E-03	1.14E-02	7.21E-03	5.71E-03	3.39E-03	6.19E-03
Na (±0.64)	35.98	32.05	30.55	31.75	33.54	30.39	32.48	29.54
S (±0.29)	9.32	7.45	6.95	6.80	7.45	3.99	3.73	3.42
P (±8.89E-05)	5.40E-04	5.32E-04	6.28E-04	3.27E-04	ND	2.97E-04	4.23E-04	5.79E-05
Al (±9.64E-04)	0.10	0.04	0.02	0.02	5.17E-03	1.05E-03	2.01E-04	7.35E-04
Ag (±0.00)	ND	ND	ND	ND	ND	ND	ND	ND
Au (±2.51E-04)	6.32E-04	4.24E-04	5.75E-04	4.41E-04	9.50E-04	7.21E-04	7.10E-04	5.40E-04
Cu (±1.99E-03)	1.03E-02	7.59E-03	8.36E-03	5.92E-03	7.25E-03	8.14E-03	1.11E-02	9.69E-03
Fe (±3.84E-05)	1.54E-03	8.86E-04	9.08E-04	5.42E-04	5.36E-04	1.41E-04	1.91E-04	1.73E-04

Ni ($\pm 2.21\text{E-}04$)	1.04E-03	5.40E-04	6.28E-04	6.42E-04	4.82E-04	6.44E-04	8.23E-04	5.40E-04
Pb ($\pm 6.93\text{E-}05$)	1.27E-04	1.57E-04	2.59E-04	3.10E-05	5.67E-05	ND	1.72E-04	2.49E-05
Sb ($\pm 2.23\text{E-}03$)	2.81E-03	5.52E-03	3.20E-03	2.34E-03	6.78E-03	3.93E-03	1.37E-02	5.02E-03
Sn (± 0.01)	0.03	0.08	0.07	0.03	0.03	0.02	0.02	0.02
Ti ($\pm 2.15\text{E-}05$)	2.72E-04	3.29E-04	2.21E-04	1.21E-04	9.51E-05	2.45E-05	1.60E-05	2.88E-05
Zn (± 0.00)	ND	ND	ND	ND	ND	ND	ND	ND

*ND=No detection

Table 5-15: ICP-OES analysis of aqueous phases from the HTL of waste PCBs and lignosulphonate at 40 min and 60 min for 250, 275, 300, and 330°C

Element (mg/g)	40 min				60 min			
	250°C	275°C	300°C	330°C	250°C	275°C	300°C	330°C
Ca (± 0.10)	0.76	0.35	0.28	0.22	0.64	0.33	0.18	0.26
K (± 0.05)	0.49	0.39	0.23	0.25	0.40	0.32	0.32	0.27
Mg ($\pm 2.38\text{E-}03$)	0.02	7.61E-03	5.71E-03	4.85E-03	1.39E-02	7.46E-03	3.39E-03	7.36E-03
Na (± 0.64)	34.57	32.05	30.39	27.73	34.06	30.55	32.48	26.21
S (± 0.29)	12.68	7.45	3.99	2.50	12.34	6.95	3.73	2.62
P ($\pm 8.89\text{E-}05$)	2.03E-03	5.32E-04	2.97E-04	2.59E-04	1.11E-03	6.28E-04	4.23E-04	ND
Al ($\pm 9.64\text{E-}04$)	0.20	0.04	1.05E-03	ND	0.17	0.02	2.01E-04	2.83E-05
Ag (± 0.00)	ND	ND	ND	ND	ND	ND	ND	ND
Au ($\pm 2.51\text{E-}04$)	1.03E-03	4.24E-04	7.21E-04	8.41E-04	8.52E-04	5.75E-04	7.10E-04	4.44E-04
Cu ($\pm 1.99\text{E-}03$)	9.84E-03	7.59E-03	8.14E-03	8.43E-03	9.77E-03	8.36E-03	1.11E-02	7.97E-03
Fe ($\pm 3.84\text{E-}05$)	4.99E-03	8.86E-04	1.41E-04	5.89E-05	4.77E-03	9.08E-04	1.91E-04	ND
Ni ($\pm 2.21\text{E-}04$)	1.08E-03	5.40E-04	6.44E-04	5.02E-04	9.88E-04	6.28E-04	8.23E-04	6.48E-04
Pb ($\pm 6.93\text{E-}05$)	3.29E-04	1.57E-04	ND	ND	8.66E-04	2.59E-04	1.72E-04	1.38E-04
Sb ($\pm 2.23\text{E-}03$)	4.06E-03	5.52E-03	3.93E-03	7.14E-03	4.10E-03	3.20E-03	1.37E-02	3.26E-03
Sn (± 0.01)	0.39	0.08	0.02	8.97E-03	0.34	0.07	0.02	9.05E-03
Ti ($\pm 2.15\text{E-}05$)	2.16E-03	3.29E-04	2.45E-05	1.47E-05	1.62E-03	2.21E-04	1.60E-05	2.88E-05
Zn (± 0.00)	ND	ND	ND	ND	ND	ND	ND	ND

*ND=No detection

Table 5-16: ICP-OES and XRF analysis of sieved waste PCBs

Element	XRF analysis		Digestion & ICP-OES analysis	
	Sieved waste PCBs (wt.%)	Confidence level ($\pm$) (wt.%)	Sieved waste PCBs (wt.%)	Confidence level ($\pm$) (wt.%)
Ca	8.33	0.38	5.50	0.56
K	0.02	0.00	0.04	2.76E-03
Mg	0.68	0.04	0.26	0.01
Na	Not analysed	-	0.10	0.01
S	0.13	0.02	0.22	0.02
P	0.04	0.02	0.11	3.84E-03
Al	12.43	0.32	6.12	0.34
Ag	Not analysed	-	0.06	0.01
Au	Not analysed	-	0.03	4.05E-03
Cu	7.97	0.73	8.30	0.17
Fe	6.28	0.06	6.21	0.24
Ni	0.49	0.04	0.51	0.04
Pb	0.53	0.04	0.48	0.04
Sb	Not analysed	-	0.06	0.01
Sn	Not analysed	-	4.20	0.11
Ti	0.70	0.03	0.28	0.03
Zn	0.64	0.01	0.64	0.04

APPENDIX B: ADDITIONAL INFORMATION

B.1 Hazardous materials in e-waste

Table 5-17: List of potentially hazardous materials and elements in e-waste with examples of EEE, sources, and routes to human exposure (adapted from Perkins *et al.*, 2014)

Persistent organic pollutants (POPs)	Examples of EEE component	Source of human exposure	Route of human exposure
BFRs, polybrominated diphenyl ethers, and polybrominated biphenyls (PBBs)	Flame retardants	Soil, water, food, dust, and air	Transplacental, inhalation, and ingestion
Polychlorinated biphenyls (PCBs)	Coolants, lubricants, and dielectric fluids	Food (accumulative in marine life), soil, dust, and air	Transplacental, inhalation, ingestion, and dermal contact
Dioxins	Examples of EEE component	Source of human exposure	Route of human exposure
Polychlorinated dibenzodioxins and dibenzofurans	Combustion product	Air, food, vapour, water, soil, and dust	Transplacental, dermal contact inhalation and ingestion
Dioxin-like polychlorinated biphenyls	Combustion products, Coolants, lubricants, and dielectric fluids	Food, soil, dust, and air	Dermal contact inhalation and ingestion
Polyaromatic hydrocarbons	Combustion product	Food, soil, dust, and air	Dermal contact inhalation and ingestion
Metals	Examples of EEE component	Source of human exposure	Route of human exposure
Lead (Pb)	Batteries, solder, televisions, light bulbs, cathode ray tubes, and PCBs	Soil, dust, water, and air	Inhalation, ingestion, and dermal contact
Zinc (Zn)	Cathode ray tubes and metal coatings	Soil, water, and air	Inhalation and ingestion
Nickel (Ni)	Batteries	Food, water, soil, and air	Transplacental, inhalation, ingestion, and dermal contact

B.2 Metal content in waste PCBs and metal ores

Table 5-18: Metal contents of ores compared to the waste PCBs (adapted from Bizzo *et al.*, 2014)

Metal	Ores (%)	PCBs (%)
Ag	0.0005	0.01-0.52
Au	0.0005	0.0029-0.112
Cu	0.5-3.0	12.0-29.0
Fe	30-60	0.1-11.4
Ni	0.7-2.0	0.3-1.6
Pb	0.3-7.5	1.3-3.9
Sn	0.2-0.85	1.1-4.8
Zn	1.7-6.4	0.1-2.7

B.3 Molecular structure of lignin

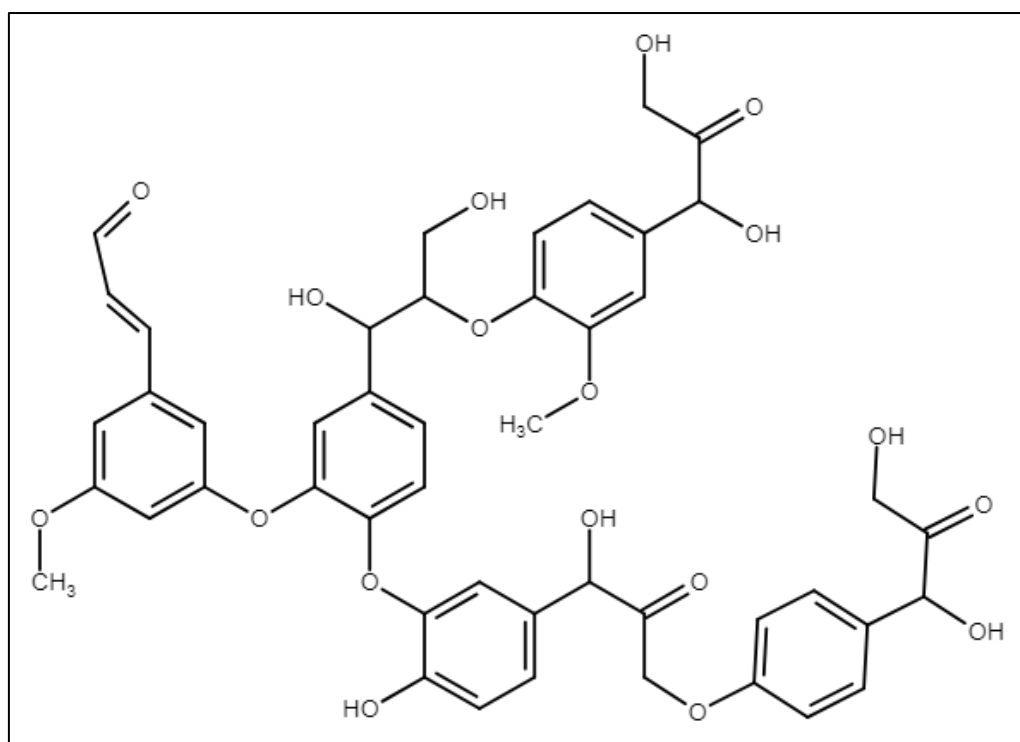


Figure 5-23: The structure of a lignin molecule

B.4 Calibration curve for total phenolic analysis

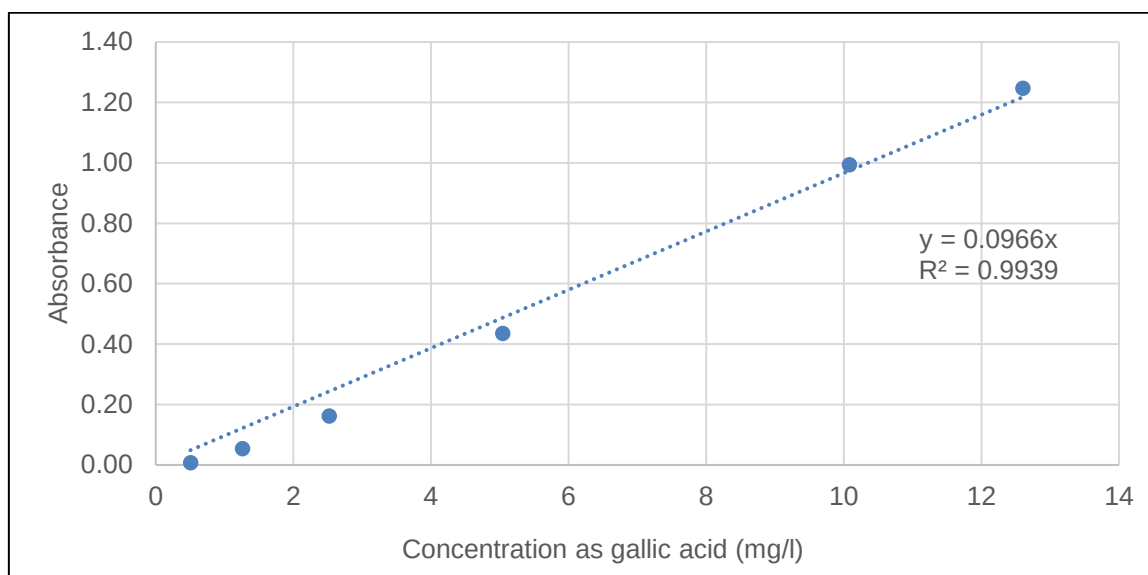


Figure 5-24: Gallic acid calibration curve for total phenolic analysis

B.5 List of metals detected by ICP-OES analysis

Table 5-19: List of categories and elements analysed by ICP-OES

Category	Element	Detection limit of ICP-OES (mg/l)	Detection limits (mg/g)		
			Residue	Bio-oil	Aqueous phase
Minerals	P	5.00E-03	5.00E-04	1.00E-03	5.00E-06
	Mg	4.00E-05	4.00E-06	8.00E-06	4.00E-08
	Ca	6.00E-05	6.00E-06	1.20E-05	6.00E-08
	K	4.00E-03	4.00E-04	8.00E-04	4.00E-06
	S	9.00E-03	9.00E-04	1.80E-03	9.00E-06
	Na	2.00E-03	2.00E-04	4.00E-04	2.00E-06
Metals	Ag	1.00E-03	1.00E-04	2.00E-04	1.00E-06
	Al	9.00E-04	9.00E-05	1.80E-04	9.00E-07
	Au	2.50E-03	2.50E-04	5.00E-04	2.50E-06
	Cu	1.00E-03	1.00E-04	2.00E-04	1.00E-06
	Fe	8.00E-04	8.00E-05	1.60E-04	8.00E-07
	Ni	1.40E-03	1.40E-04	2.80E-04	1.40E-06
	Pb	5.00E-03	5.00E-04	1.00E-03	5.00E-06
	Sb	5.00E-03	5.00E-04	1.00E-03	5.00E-06
	Sn	7.00E-03	7.00E-04	1.40E-03	7.00E-06
	Ti	6.00E-03	6.00E-04	1.20E-03	6.00E-06
	Zn	5.00E-04	5.00E-05	1.00E-04	5.00E-07

B.6 FTIR spectrum functional group ranges

Table 5-20: Notations, wavenumbers, and functional groups used for the assignment of FTIR spectrum peaks

Notation	Wavenumber (cm ⁻¹)	Functional group
1	3600-3100	-OH stretch
2	3100-2850	sp ² & sp ³ C-H stretch
3	≈2550	S-H thiol
4	≈2250	C≡N nitrile
5	1800-1650	C=O stretch
6	1650-1400	C=C aromatic stretch (aromatic ring structures)
7	≈1380	sp ³ C-H bend
8	1350-1150	C-O phenol & acyl
9	1150-1000	C-O aliphatic & aromatic alkoxy (ether)
10	900-700	sp ² C-H aromatic bend

APPENDIX C: EXPERIMENTAL ERRORS

C.1 Experimental error calculations

The experimental errors were determined using a standard t-distribution suitable for estimating errors and confidence levels within a small sample size. Four identical HTL runs at 300°C for 80 minutes were repeated over a period of 2 months to calculate the uncertainty at a 95% confidence interval. A limited feedstock supply resulted in a small sample size. The mean, $\bar{x}$, of these samples can be calculated with equation 6:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (6)$$

Where the sample size is illustrated by n and the data point for each experiment is expressed by x_i . The degrees of freedom, DOF , can be expressed by Equation 7:

$$DOF = n - 1 \quad (7)$$

Therefore, the standard deviation, STD , can be calculated. The Excel function STDEV.S was used to calculate all standard deviations according to Equation 8:

$$STD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{DOF}} \quad (8)$$

The standard error, SE , of the mean is expressed by Equation 9:

$$SE = \frac{STD}{\sqrt{n}} \quad (9)$$

The critical t-values, t , for a two-tailed test were obtained from a standard critical t-value distribution table for varying degrees of freedom (Devore *et al.*, 2013). Thus, the confidence levels can be estimated with Equation 10:

$$Confidence\ level = \bar{x} \pm (SE \times t) \quad (10)$$

Where the variable $(SE \times t)$ is used to illustrate the experimental error. All results of the relevant experimental error calculations for product yields and analyses are illustrated in Table 5-21 to Table 5-39.

C.2 Experimental errors of product yields

Table 5-21: Experimental errors on HTL product yields

	Aqueous phase (wt.%)	Residue (wt.%)	Bio-oil (wt.%)	Gas (wt.%)
Average	50.45	27.58	2.37	19.61
STD	1.39	0.41	0.15	1.06
Standard error	0.70	0.20	0.07	0.53
T-critical value	3.18	3.18	3.18	3.18
Confidence level ($\pm$)	2.22	0.65	0.23	1.68

C.3 Experimental errors of elemental analysis

Table 5-22: Experimental errors for the elemental analysis on bio-oils

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Remainder (wt.%)
Average	69.38	6.82	0.88	22.91
STD	0.91	0.28	0.16	1.34
Standard error	0.45	0.14	0.08	0.67
T-critical value	3.18	3.18	3.18	3.18
Confidence level ($\pm$)	1.45	0.45	0.25	2.12

Table 5-23: Experimental errors for the elemental analysis on residues

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Remainder (wt.%)
Average	20.56	1.32	0.16	77.96
STD	0.54	0.03	0.02	0.57
Standard error	0.27	0.02	0.01	0.28
T-critical value	3.18	3.18	3.18	3.18
Confidence level ($\pm$)	0.86	0.05	0.03	0.90

Table 5-24: Experimental errors for the elemental analysis on milled waste PCB feedstock

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Remainder (wt.%)
Average	21.07	1.71	0.56	76.40
STD	3.02	0.59	0.02	3.28
Standard error	1.75	0.34	0.01	1.89
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	7.51	1.46	0.04	8.14

Table 5-25: Experimental errors for the elemental analysis on sieved waste PCB feedstock

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Remainder (wt.%)
Average	17.56	1.46	0.44	80.54
STD	0.19	0.02	0.11	0.10
Standard error	0.11	0.01	0.06	0.06
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	0.48	0.05	0.28	0.25

Table 5-26: Experimental errors for the elemental analysis on lignosulphonate feedstock

	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Remainder (wt.%)
Average	32.76	3.63	0.19	63.42
STD	0.32	0.03	0.02	0.33
Standard error	0.19	0.01	0.01	0.19
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	0.80	0.06	0.05	0.81

C.4 Experimental errors of proximate analysis

Table 5-27: Experimental errors for the proximate analysis on residues

	Moisture (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
Average	4.07	21.82	3.65	70.45
STD	0.28	1.26	1.85	1.27
Standard error	0.14	0.63	0.93	0.63
T-critical value	3.18	3.18	3.18	3.18
Confidence level ($\pm$)	0.45	2.00	2.94	2.01

Table 5-28: Experimental errors for the proximate analysis on milled waste PCB feedstock

	Moisture (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
Average	1.08	20.88	-0.37	78.41
STD	0.02	0.71	1.33	1.91
Standard error	0.01	0.41	0.77	1.10
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	0.05	1.76	3.31	4.75

Table 5-29: Experimental errors for the proximate analysis on sieved waste PCB feedstock

	Moisture (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
Average	1.12	22.84	0.97	75.07
STD	0.01	0.31	0.24	0.15
Standard error	0.00	0.18	0.14	0.09
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	0.01	0.77	0.59	0.38

Table 5-30: Experimental errors for the proximate analysis on lignosulphonate feedstock

	Moisture (wt.%)	Volatile (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
Average	3.84	53.91	16.91	25.33
STD	0.04	0.14	0.21	0.11
Standard error	0.01	0.41	0.77	1.10
T-critical value	4.30	4.30	4.30	4.30
Confidence level ($\pm$)	0.05	1.76	3.31	4.75

C.5 Experimental errors of HHV

Table 5-31: Experimental error for the HHV on bio-oils

	HHV (MJ/kg)
Average	30.74
STD	0.93
Standard error	0.47
T-critical value	3.18
Confidence level ($\pm$)	1.49

C.6 Experimental errors of GPC analysis

Table 5-32: Experimental errors for the GPC analysis on bio-oils

	Mw (g/mol)	Mn (g/mol)	PDI
Average	976.90	134.27	7.27
STD	48.76	1.81	0.34
Standard error	24.38	0.90	0.17
T-critical value	3.18	3.18	3.18
Confidence level ($\pm$)	77.58	2.87	0.54

C.7 Experimental errors of total phenolic analysis

Table 5-33: Experimental error for the total phenolic analysis on Aqueous phases

	Total phenols (g/l)
Average	5.93
STD	0.07
Standard error	0.04
T-critical value	3.18
Confidence level ($\pm$)	0.11

C.8 Experimental errors of GC-MS analysis

Table 5-34: Experimental error for the GC-MS analysis on bio-oils

Category (Area-%)	Average	STD	Standard error	T-critical value	Confidence level ($\pm$)
Acids	3.42	0.79	0.39	3.18	1.25
Alkenes	0.40	0.37	0.19	3.18	0.60
Benzene derivatives	0.55	0.65	0.33	3.18	1.04
Fatty acids	0.71	0.17	0.08	3.18	0.27
Heterocyclic nitrogen compounds	0.72	1.03	0.52	3.18	1.64
Ketones	2.20	1.36	0.68	3.18	2.17
Phenolics	84.96	4.08	2.04	3.18	6.50
Phenol (Area-% of phenolics)	19.11	1.85	0.92	3.18	2.94
Cresol (Area-% of phenolics)	7.57	0.44	0.22	3.18	0.70
Sulphur compounds	0.04	0.06	0.03	3.18	0.09
Others	7.00	2.73	1.37	3.18	4.35

C.9 Experimental errors of ICP-OES analysis

Table 5-35: Experimental error for the ICP-OES analysis on residues

Element (Mg/g)	Average	STD	Standard error	T-critical value	Confidence level ($\pm$)
Ca	43.55	0.89	0.44	3.18	1.41
K	1.75	0.02	0.01	3.18	0.03
Mg	2.22	0.10	0.05	3.18	0.16
Na	45.42	1.44	0.72	3.18	2.28
S	34.40	0.84	0.42	3.18	1.34
P	0.79	0.04	0.02	3.18	0.07

Al	44.93	1.22	0.61	3.18	1.95
Ag	0.71	0.06	0.03	3.18	0.10
Au	0.19	0.03	0.01	3.18	0.04
Cu	58.74	3.85	1.92	3.18	6.12
Fe	44.37	2.58	1.29	3.18	4.11
Ni	3.73	0.29	0.15	3.18	0.46
Pb	3.85	0.19	0.09	3.18	0.30
Sb	0.35	0.01	0.00	3.18	0.01
Sn	25.80	0.30	0.15	3.18	0.48
Ti	1.99	0.19	0.09	3.18	0.30
Zn	4.29	0.18	0.09	3.18	0.29

Table 5-36: Experimental error for the ICP-OES analysis on bio-oils

Element (Mg/g)	Average	STD	Standard error	T-critical value	Confidence level (±)
Ca	1.19	0.40	0.20	3.18	0.63
K	0.19	0.06	0.03	3.18	0.10
Mg	0.12	0.05	0.02	3.18	0.07
Na	15.62	1.70	0.85	3.18	2.70
S	14.22	2.97	1.49	3.18	4.73
P	0.01	0.01	0.01	3.18	0.02
Al	0.10	0.04	0.02	4.30	0.08
Ag	0.01	0.01	0.00	3.18	0.01
Au	0.01	0.00	0.00	3.18	0.00
Cu	0.24	0.04	0.02	4.30	0.09
Fe	0.12	0.02	0.01	4.30	0.05
Ni	0.01	0.01	0.00	3.18	0.01
Pb	0.01	0.02	0.01	3.18	0.04
Sb	0.07	0.03	0.02	3.18	0.05
Sn	1.53	0.37	0.18	3.18	0.58
Ti	0.05	0.03	0.02	3.18	0.05
Zn	0.01	0.01	0.01	3.18	0.02

Table 5-37: Experimental error for the ICP-OES analysis on aqueous phases

Element (Mg/g)	Average	STD	Standard error	T-critical value	Confidence level (±)
Ca	0.28	0.06	0.03	3.18	0.1
K	0.24	0.03	0.02	3.18	0.05

Mg	0.01	0.00	0.00	3.18	0.00
Na	29.54	0.4	0.2	3.18	0.64
S	3.42	0.18	0.09	3.18	0.29
P	0.00	0.00	0.00	3.18	0.00
Al	0.00	0.00	0.00	3.18	0.00
Ag	0.00	0.00	0.00	3.18	0.00
Au	0.00	0.00	0.00	3.18	0.00
Cu	0.01	0.00	0.00	3.18	0.00
Fe	0.00	0.00	0.00	3.18	0.00
Ni	0.00	0.00	0.00	3.18	0.00
Pb	0.00	0.00	0.00	3.18	0.00
Sb	0.01	0.00	0.00	3.18	0.00
Sn	0.02	0.01	0.00	3.18	0.01
Ti	0.00	0.00	0.00	3.18	0.00
Zn	0.00	0.00	0.00	3.18	0.00

Table 5-38: Experimental error for the ICP-OES analysis on sieved waste PCB feedstock

Element (Mg/g)	Average	STD	Standard error	T-critical value	Confidence level (±)
Ca	55.18	2.11	1.22	4.30	5.23
K	0.38	0.01	0.01	4.30	0.02
Mg	2.62	0.04	0.02	4.30	0.10
Na	0.95	0.02	0.01	4.30	0.06
S	2.24	0.05	0.03	4.30	0.14
P	1.10	0.02	0.01	4.30	0.05
Al	61.42	1.30	0.75	4.30	3.23
Ag	0.62	0.03	0.02	4.30	0.07
Au	0.31	0.02	0.01	4.30	0.04
Cu	83.31	0.63	0.37	4.30	1.57
Fe	62.33	1.14	0.66	4.30	2.84
Ni	5.08	0.16	0.09	4.30	0.40
Pb	4.86	0.15	0.09	4.30	0.37
Sb	0.57	0.03	0.01	4.30	0.06
Sn	42.20	0.62	0.36	4.30	1.55
Ti	2.84	0.13	0.07	4.30	0.31
Zn	6.45	0.19	0.11	4.30	0.46

Table 5-39: Experimental error for the ICP-OES analysis on lignosulphonate feedstock

Element (Mg/g)	Average	STD	Standard error	T-critical value	Confidence level (±)
Ca	0.35	0.03	0.02	4.30	0.09
K	2.68	0.09	0.05	4.30	0.22
Mg	0.55	0.05	0.03	4.30	0.13
Na	139.43	4.36	2.52	4.30	10.83
S	200.02	6.50	3.75	4.30	16.15
P	0.36	0.03	0.02	4.30	0.07
Al	0.01	0.00	0.00	4.30	0.00
Ag	0.00	0.00	0.00	4.30	0.00
Au	0.00	0.00	0.00	4.30	0.00
Cu	0.01	0.00	0.00	4.30	0.01
Fe	0.02	0.00	0.00	4.30	0.01
Ni	0.00	0.00	0.00	4.30	0.00
Pb	0.00	0.00	0.00	4.30	0.00
Sb	0.00	0.00	0.00	4.30	0.00
Sn	0.00	0.00	0.00	4.30	0.00
Ti	0.00	0.00	0.00	4.30	0.00
Zn	0.00	0.00	0.00	4.30	0.00