

The Use of Hydrothermal Liquefaction for the Recovery of Materials from E-Waste

Frans Waanders¹, Dian Swanepoel¹, Roelf Venter¹, Sanette Marx¹

Abstract— The generation of e-waste has increased in recent years due to a decrease in the lifespan of electronic equipment and a huge increase in supply and demand. Often, inadequate treatment and disposal practices lead to e-waste being used for landfill and pollution of the air, soil, and water, rather than being a valuable source of secondary materials.

Hydrothermal liquefaction (HTL) can be used as an alternative option to recover these valuable materials. This study aims to determine the suitability of the HTL process as a treatment method for locally obtained printed circuit board (PCB) e-waste, co-processed with lignosulphonate biomass in a 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, bio-oils, and aqueous phases obtained during the process.

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.

Low bio-oil yields were found at all process conditions, with the oils mostly consisting of phenolic compounds. The residue products consisted of inorganics, such as ceramics and metals, as well as unreacted epoxy resin and heavy carbon molecules. It was observed that temperature influenced the yields and composition of products more than the residence time. By increasing the waste loading, both the bio-oil and residue yields increased. Increasing the waste loadings resulted in a non-linear increase for most metal concentrations, with the metal concentrations at 90 and 100 wt.% waste loadings being significantly higher than the original feedstock, with less than 6 wt.% carbon in the residues.

HTL can thus be a suitable treatment method for waste PCBs.

Key words: Hydrothermal liquefaction, electronic waste, valuable metals

I. INTRODUCTION

The ever-growing reliance on technology and the constant demand for advancements in all sectors of life have become a norm in modern society. However, these advancements

continuously render countless electrical products redundant and significantly reduce their lifecycle [1].

Yearly e-waste generation is currently estimated at roughly 54 million tonnes, with only 17.4% documented and recycled [2], with forecasts of nearly 75 million tons per year by 2030 [3]. South Africa produced approximately 66.9 million tonnes of hazardous waste in 2017, with only 6% of this waste reused or recycled. Additionally, 360,000 tonnes of this hazardous waste was attributed to waste electrical and electronic equipment, otherwise known as e-waste. Only 9.7% of e-waste was recycled, with the remainder being landfilled [4]. As a result of more disposable income, industrialisation, and urbanisation in developing countries like South Africa, the generation of e-waste is set to rise considerably [5].

According to the E-waste Recycling Authority [6], the South African chain of recovery and recycling consists of collectors, refurbishers, pre-processors, and end-processors, where end-processing refers to processes that include biometallurgy, hydrometallurgy, and pyrometallurgy, capable of recovering valuable metals and/or organic fractions from pre-processed e-waste. Pyrolysis, a pyrometallurgical process, has been used for the recovery of metals from e-waste, where the waste is thermochemical treated for the decomposition of the organic materials at high temperatures (450°C-1100°C) in the absence of oxygen, to produce products that can be used as fuel or chemical feedstock, but produces brominated and other halogenic compounds, as well as dioxins, which are toxic to the environment [7]. Consequently, more studies into novel methods for e-waste treatment are necessary, of which HTL can be a feasible option.

HTL is a thermochemical depolymerisation process, similar to pyrolysis, but operates at lower temperatures and high pressures in the presence of a solvent, such as water, which serves as a hydrogen donor. It can convert organic materials into liquid biocrude oil and char, with lesser amounts of gas emissions [8]. Unfortunately, there is little information available related to the hydrothermal processing, of e-wastes, thus, HTL could be a potential option for the treatment of e-waste, especially when co-processing with biomass. In addition, PCBs form an estimated 3% to 6% of all e-waste and are central components in most electrical and electronic equipment with high concentrations of precious metals, heavy metals, and other polymer fractions, thus serving as an ideal feedstock for experimental treatment via HTL [9,10].

The aim of this study is thus to determine the suitability of direct liquefaction as a treatment method for locally obtained

¹Frans Waanders, Dian Swanepoel, Roelf Venter and Sanette Marx, DSI/NRF Research Chair in Biofuels and Other Clean Alternative Fuels in the CoE in Carbon-based Fuels, School of Chemical and Mineral Engineering, NWU, South Africa

PCB e-waste co-processed with lignosulphonate biomass for the recovery of metals and organic compounds.

II. MATERIALS AND METHODS

Two primary raw materials were obtained, namely 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 and entailed the milling of whole PCBs to particle sizes smaller than 2.36 mm and manually sieving the milled sample to obtain a particle size smaller than 177 μm fit for HTL.

Sodium lignosulphonate, a byproduct of the sulphite pulping process, was obtained from the SAPPI paper mills in South Africa. The inclusion of this biomass was motivated by the potential immobilisation of metals during co-HTL with metal-containing materials.

To ensure representative results, subsamples were taken from both feedstocks, the cone-and-quartering method was employed, in accordance with the [11] standard, and the samples were stored in airtight containers.

The HTL experiments were conducted within a batch SS316 autoclave with maximum operational parameters of 450°C and 150 bar, and the schematic layout is depicted in Figure 1.

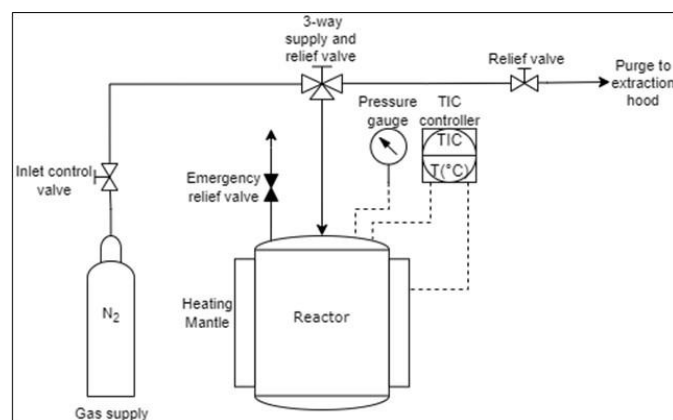


Fig. 1: Schematic diagram of reactor setup

The influence of operating temperature and residence time on the HTL products, as well as the repeatability and confidence levels for experiments were determined, using 250, 275, 300 and 330°C as operating temperatures and residence times that were varied between 20, 40, 60, and 80 min. A 43% volume loading and a 1:1 PCB to lignosulphonate loading were used for the latter. The solid and solvent mass loading was selected as 44 wt.% and 56 wt.%, respectively.

The influence of waste PCB loading on the HTL products was investigated 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 feedstock and final products were characterised and analysed using a CE-440 elemental analyser from Exeter Analytical Inc, a Shimadzu UVmini-240 UV-VIS spectrophotometer, an Agilent Technologies 7890GC instrument, coupled with a 5975C inert MS detector, a Shimadzu- IRAffinity-1 FTIR spectrometer, an Agilent Technologies 725-ES ICP-OES, and a Thermo Scientific ARL ADVANT'X IntelliPower XRF sequential spectrometer.

III. RESULTS AND DISCUSSION

3.1 EFFECT OF OPERATING PARAMETERS ON PRODUCT YIELDS

The elemental analysis of the milled and sieved waste PCBs, as well as lignosulphonate was conducted in triplicate, and the results are presented in Table I.

It was found that high concentrations of metals were present in the sieved waste PCBs, with Cu, Fe, Al, and Sn the most abundant, with other metals being Ag, Au, Ni, Pb, Ti, and Zn. The organic fraction was identified as the epoxy resin used to manufacture the PCB substrates. The majority of metals remained in a stable state within the residues, with only small concentrations detected in the bio-oils and aqueous phases

The lignosulphonate contained trace amounts of metals, with Al, Cu and Fe being the most notable. The S and Na are the predominant mineral elements in the lignosulphonate. The elevated S-concentration results from introducing sulphonic groups during the pulping process at the paper mill, while the high Na-content is attributed to the use of sodium as the salt in the pulping process[12].

TABLE I. CONCENTRATIONS OF ELEMENTAL MINERALS AND METALS IN SIEVED WASTE PCB AND LIGNOSULPHONATE FEEDSTOCK

Element	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	-	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	-	0.00
Ti	2.84	0.31	4.49E-04	1.37E-04
Zn	6.45	0.46	8.22E-04	3.07E-03

The aqueous phases, residues, bio-oils, and gas products for all HTL experiments were measured and yields were calculated in terms of mass fractions and shown in Figure 2 illustrating the product yields obtained from HTL experiments conducted with varying residence times ranging from 20 to 80 min and operating temperatures spanning from 250 to 330°C.

The predominant product fraction obtained was the aqueous phase, but the yields were below the input mass fraction of

water, which was 59.60 wt.%. The yields were similar to those of dos Passos *et al* [13]. The aqueous phase typically consists of water and small polar organic products, indicating that various reactions, such as hydrolysis of the water solvent, occurred during the HTL process.

A notable quantity of gas was produced which can be expected since both waste PCBs and lignosulphonate contain significant amounts of volatiles. The gas production was favoured by cracking of bio-oils and gasification of residues, also similar with those documented by Williams & Slaney, [14].

The solid residue also constituted a substantial fraction of the product yields, due to reactions like repolymerisation of intermediates, cracking and condensation of the bio-oils, the formation of biochar structures in the residue, as well as gasification of the residues.

The bio-oil yields were very low due to the reference for biochar formation from the lignin, as reported by Gollakota *et al.*, [15] and Nizamuddin *et al.*, [16].

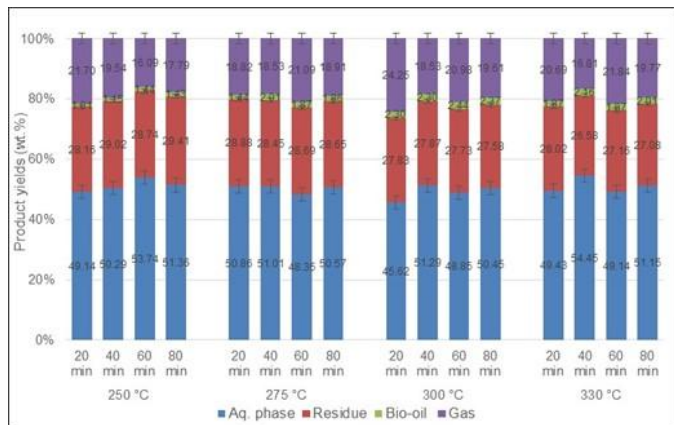


Fig. 2 : Aqueous phase, residue, bio-oil, and gas yields for the HTL experiments conducted at varying temperatures of 250°C-330°C and residence times of 20-80 min.

The reaction temperature influenced the product yields and composition of the HTL products as the bio-oil yield increased with rising temperatures, reaching a max at 300°C for both a short and long residence time, but still optimal at 80 min reaction time, after which cracking overtook repolymerisation reactions.

3.2 EFFECT OF WASTE LOADING ON PRODUCT YIELDS

The optimal reaction conditions at 300°C and 80 min were fixed, with the combined total solid loading of lignosulphonate and waste PCBs remaining constant, while the mass loading of waste PCBs ranged from 0 to 100 wt.% of the input. Figure 3 presents a visual representation of the product yield distributions.

No clear trend was observed in the gas yields, suggesting that both lignosulphonate and epoxy resin produce comparable amounts of volatile products, irrespective of the loading. In terms of the aqueous phase, an evident reduction is observed with increasing waste loadings, primarily attributed

to the dissolution of lignosulphonate in the water, leading to an increased aqueous phase yield.

On the contrary, for the bio-oil and the solid residue or char, a clear trend of increasing yields with increasing waste loading is observed. 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 bio-oil production.

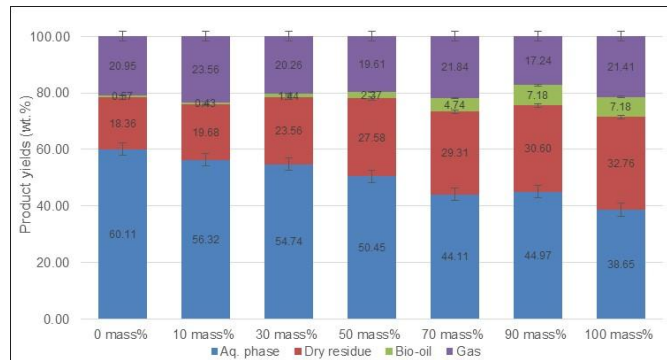


Fig. 3: Aqueous phase, residue, bio-oil, and gas yields for HTL experiments with waste PCB mass loadings between 0 and 100 wt.%

At 0 wt.% waste loading, approximately 18 wt.% of carbon-rich biochar is produced which could be desirable for metal adsorption. The residue yield obtained from a 100 wt.% PCB loading is approximately 33 wt.%, signifying a step towards the valorisation of e-waste and furthermore confirms the decomposition of the organic material.

IV. CONCLUSIONS

This study aimed 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. From these results it was proven that HTL is a suitable treatment method for waste PCBs through converting waste organics to valuable phenolic compounds and the producing of metal-rich residues, with temperature, residence time, and waste loading influencing the HTL products significantly.

V. ACKNOWLEDGEMENTS

The North-West University (NWU) is recognized for giving assistance with funding, and construction of the experimental equipment, and data analysis. The authors also show appreciation to the SARChI chair in Biofuels and other alternatives for provided funding and support for the project.

REFERENCES

[1] 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. <https://doi.org/10.1016/j.jclepro.2019.118815>

[2] 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).

- [3] 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.
<https://doi.org/10.1016/j.jenvman.2022.116181>
- [4] 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. 2022
- [5] 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).
- [6] eWaste Recycling Authority (ERA). 2018. *South African E-waste Industry Waste Management Plan (V.1) 2019-2024*. Cape Town.
- [7] Arun, J. & Gopinath, K.P. 2020. Chemical Recycling of Electronic-Waste for Clean Fuel Production. In: Springer, Cham. pp. 111–126.
- [8] 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.
<https://doi.org/10.1016/B978-0-08-101029-7.00004-7>
- [9] 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.
<https://doi.org/10.1016/j.jclepro.2015.02.024>
- [10] 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.
<https://doi.org/10.3390/su12010074>
- [11] STANDARD GUIDE FOR LABORATORY SUBSAMPLING OF MEDIA RELATED TO WASTE MANAGEMENT ACTIVITIES. BOOK OF STANDARDS VOLUME:11.04. DEVELOPED BY SUBCOMMITTEE: D34.01.01. PP 11. DOI: 10.1520/D6323-19. ICS CODE: 13.030.01
<https://doi.org/10.1520/D6323-19>
- [12] Aro, T. & Fatehi, P. 2017. Production and Application of Lignosulfonates and Sulfonated Lignin. *ChemSusChem*. 10(9):1861–1877.
<https://doi.org/10.1002/cssc.201700082>
- [13] dos Passo 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.
<https://doi.org/10.1016/j.psep.2020.04.040>
- [14] 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.
<https://doi.org/10.1016/j.resconrec.2006.12.002>
- [15] Gollakota, A.R.K., Kishore, N. & Gu, S. 2018. A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 81:1378–1392.
<https://doi.org/10.1016/j.rser.2017.05.178>
- [16] 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.
<https://doi.org/10.1016/j.rser.2016.12.122>

Author Contributions

Conceptualization, S.M., R.V., writing—original draft preparation, D.S.; writing—review and initial editing, F.W.; supervision, S.M.,R.V.; F.W.; project administration, S.M. F.W.; funding acquisition, S.M.; F.W. All authors have read and agreed to the published version of the manuscript.