

Valorization of Waste Printed Circuit Board using Pyrolysis and Metal Extraction

Thesis submitted in partial fulfilment of the requirement for the
degree of,

Doctor of Philosophy

by

Bibari Boro

(196107002)



**Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati-781039
Assam, India**



Department of Chemical Engineering

Indian Institute of Technology Guwahati

Guwahati-781039, Assam, India

STATEMENT

I do hereby declare that the content embodied in this thesis entitled “*Valorization of Waste Printed Circuit Board using Pyrolysis and Metal Extraction*”, is the result of investigation carried out by me in the Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India under the guidance of Prof. Pankaj Tiwari. In keeping with the general practice of reporting scientific observations and findings, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Date:

Bibari Boro



Department of Chemical Engineering

Indian Institute of Technology Guwahati

Guwahati-781039, Assam, India

CERTIFICATE

This is to certify that the thesis entitled “*Valorization of Waste Printed Circuit Board using Pyrolysis and Metal Extraction*”, submitted by Miss Bibari Boro (Roll no. 196107002), a research scholar in the Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India for the award of the degree of Doctor of Philosophy is a record of an original research work carried out by her under my supervision and guidance. The Thesis fulfilled all requirements as per the regulations of the institute and in my opinion has reached the standard needed for submission. The work documented in this thesis have not been submitted to any other university or institute for the award of any degree.

(Prof. Pankaj Tiwari)

Professor

Department of Chemical Engineering,

Indian Institute of Technology Guwahati,

Guwahati, Assam, India 781039



Dedicated to my Family Members...

Acknowledgement

First and foremost, I would like to express my deepest gratitude to my supervisor, Prof. Pankaj Tiwari, for his continuous guidance, encouragement, and invaluable support throughout my research journey. I would like to thank him for encouraging my research and for enabling me to develop as a research scientist. His advice on both my research and career has been priceless. His uncompromising approach to completing the experimental part, analyzing the data, and preparing the manuscripts has helped me a lot in achieving my research objectives.

I am sincerely thankful to the doctoral committee members, Prof. Vaibhav V. Goud (Chairperson) and Prof. G. Pugazhenthir from the Department of Chemical Engineering, and Prof. Ajay Kalamdhad from the Department of Civil Engineering at the Indian Institute of Technology Guwahati, for their constructive feedback and suggestions, which helped shape the work.

I am also thankful to all the faculty members and staff members (technical and non-technical) in the Department of Chemical Engineering for their cooperation in the Analytical Laboratory and others. I want to thank the Department of Chemical Engineering for providing the licensed version of Aspen Plus[®] software.

I am thankful to the Central Instruments Facility (CIF) of the Indian Institute of Technology Guwahati for allowing me to carry out the crucial analyses, which have been very important in this research work. In this regard, I would like to acknowledge all the members of CIF for their assistance. My special thanks to the ICP-MS team members, Dr. Babulal Das, senior technical officer, and the operators, Mr. Inamul Haque and Mr. Kishore Talukdar, under whose support I could successfully complete my duty as a teaching assistant (TA) for the instrument ICP-MS as well as run my own samples. My sincere appreciation to my fellow ICP-MS instrument TAs, Ajay, Vaishnavi, Madhusmita, Srijan, Jyothika, Nishan, Shanmugam, and Shilpa for their

consistent support and cooperative spirit, which greatly enriched the working environment and facilitated smooth analytical operations.

I would also like to thank all the members of the Energy Conversion Technology Laboratory (ECTL) for their help and support. Their motivation and cooperation created a positive research environment in the lab. I am indebted to the ECTL members Dr. Bhargav Baruah, Dr. Punampriya Borgohain, Mr. Govind Dubey, Mr. Sachin Kuriachan E, Mr. Vishal Dhar, Miss Shilpa Nandi and Mr. Onkar Choukekar; and members from other lab, Dr. Keshav Choudhary, Dr. Pravin G. Suryawanshi, Miss Priyanka P., and Miss Rebika Salam for their constant support and encouragement during highs and lows of my stay at IIT Guwahati. Special thanks to Samujjal Pal and Rupam Dutta for helping me prepare my feedstock. I would also like to thank my fellow batchmates Aviti, Janaki, Arti, Puja, Sayani, Kakoli, Sarmistha, and Silvia for their constant support in various forms.

Finally, I would like to thank my parents (Mr. Dinesh Chandra Boro and Mrs. Anjana Brahma) and my elder sisters (Ruprekha Kar and Dipika Boro) for their unconditional love, patience, and encouragement throughout the PhD and the journey of my life. Their love, care, and sacrifices have made it possible for me to come so far.

Abstract

Waste printed circuit board (WPCB) is one of the most vital components of any electrical and electronic equipment (EEE) and contributes about 4–7% of the total E-waste. WPCBs consist of a heterogeneous mixture of approximately 30% polymers, 30% metals and 40% ceramic materials. This thesis work explores viable routes to recover these materials from WPCB using a combination of pyrolysis and metal extraction using hydrometallurgy processing to produce valuable products and perform a techno-economic assessment of the proposed plant. Pyrolysis is a thermochemical technology that converts organic materials to valuable oil and gas fractions. However, the brominated flame retardants (BFRs) present in WPCB get transferred into the product fractions, thereby making these products unsuitable for use due to environmental concerns. The bromine content in gas can be controlled by means of scrubbing; however, removing it from the oil fraction is difficult. The performance of the embedded metals present in WPCB was explored to reduce the transfer of bromine in oil. The metal extraction was performed using acid leaching and cementation process. Finally, a plant containing comminution, pyrolysis and metal extraction sections was simulated using Aspen Plus[®] software, and its techno-economic assessment was performed.

Waste printed circuit boards from the computer system were reduced to $\sim 1 \times 1 \text{ cm}^2$ cut pieces (RW-cut) and a fraction of them was ground and sieved to $< 100 \text{ }\mu\text{m}$ (RW). The materials were characterized using proximate, CHNS, thermogravimetric-derivative (TG-DTG), Fourier transform infrared spectroscopy (FTIR), etc. Using the TG-DTG data, kinetic analysis for the RW sample was performed. Kinetic triplets (activation energy, reaction model and pre-exponential factor) and reconstruction of conversion profiles were determined according to the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendation guidelines. Reconstruction of conversion profiles showed that Starink is the best fit model

compared to the other isononversional methods Friedman, Ozawa-FlynnWall (OFW), and Kissinger–Akahira–Sunose (KAS). Comparison of the kinetic triplets among four different materials was performed to understand their effect on the kinetic parameters. The materials were: (i) RW, (ii) NM, (iii) RW-sox-T, and (iv) NM-sox-T, where NM is the non-metallic fraction of RW after acid leaching, RW-sox-T and NM-sox-T are the Soxhlet extracted versions of RW and NM using toluene as solvent. Characterization of pyrolytic product fractions produced via these routes has been studied, but before that, optimization of pyrolysis parameters for minimization of char yield and maximization of oil yield was performed using response surface methodology (RSM) in Design Expert (v13) software. For the optimization study, the RW-cut sample was subjected to lab-scale pyrolysis at experimental runs designed for the given ranges of temperature (300–600 °C), heating rate (5–30 °C/min) and hold time (60–180 min). The optimized condition obtained was approximately 500 °C, 30 °C/min and 156 min hold time. At the optimized condition, char yield of $76.39 \pm 1.53\%$ and oil yield of $6.93 \pm 0.45\%$ were obtained experimentally. Among the independent parameters, temperature was found to be the most significant parameter.

To study the reduction of bromine content in pyrolytic oil, lab-scale pyrolysis was performed at the previously optimized conditions using four different materials: (i) RW, (ii) NM, (iii) RW-sox-A, and (iv) NM-sox-A, where RW-sox-A and NM-sox-A are the Soxhlet extracted versions of RW and NM using acetone as solvent. It was found that more than 75% of the bromine gets transferred into the gas fraction irrespective of the feed preparation step(s). In the pyrolytic oil, the minimum bromine content was obtained when RW was the feed. Thus, the embedded metals acted as a catalyst in reducing the transfer of bromine in oil. Moreover, a change in the chemical composition of the oil was observed. A higher amount of phenol was present in NM than in RW. However, the Soxhlet extraction was less effective in lowering bromine content in oil. Thus, the suitable route is the pyrolysis of WPCB with intact metals and recovery of metals

and glass fibers from char. This way, the polymer fraction will be valorized into valuable oil and gas fractions, and metal-enriched char will be produced.

Waste printed circuit board is one of the richest sources of copper, and the E-waste contains about \$19 billion worth of copper. Thus, the recovery of copper was focused. Leaching of copper from WPCB using (a) H_2SO_4 and (b) $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ was explored for different materials (i) RW-cut, (ii) RW, and their pyrolyzed versions (iii) RW-cut-char and (iv) RW-char, respectively. A comparative study on the leaching efficiencies of these materials was performed to observe the effect of grinding and pyrolysis. The leaching efficiency increased with the introduction of H_2O_2 for all the samples. Due to grinding, the powder samples (RW) showed higher leaching efficiency than the cut pieces (RW-cut). However, the pyrolyzed version of the cut pieces (RW-cut-char) exhibited improved leaching efficiency. A maximum of 96% efficiency was obtained for RW-cut-char. Then the copper was precipitated out from the leachate using zinc cementation. The precipitate consisted of 97.4 wt% copper, obtained from EDX analysis.

A techno-economic assessment for a proposed plant to recover the materials, polymers, copper, and glass fibers from cut pieces of WPCB was performed. The plant containing comminution, pyrolysis, and metal extraction sections was simulated using Aspen Plus[®] with a capacity of 500 kg/h. Aspen Plus[®] provided the mass balance, energy balance, equipment sizing, and their costs. The proposed plant was found to be economically feasible with net present value (NPV) = \$2.87 M, discounted payback period = 5.4 years, internal rate of return = 29 % and profitability index = 2.25. The minimum selling price (MSP) of oil was calculated for different scenarios and found to be dependent on the revenue generation from copper and glass fibers. Thus, this thesis presents a comprehensive study of the recovery of materials from WPCB with minimum generation of secondary waste.

Table of contents

Acknowledgement.....	iv
Abstract.....	vi
List of Tables.....	xv
List of Figures.....	xx
List of Abbreviations.....	xxvii
Nomenclature.....	xxxi
1. Introduction.....	2
1.1. Defining E-waste.....	2
1.2. Categories and composition of E-waste	3
1.2.1. Categories of E-waste	3
1.2.2. Composition of E-waste	6
1.3. Global scenario of E-waste.....	7
1.3.1. E-waste generation	7
1.3.2. Illegal transboundary movement of E-waste	8
1.3.3. E-waste legislations	9
1.3.4. Environmental impact due to informal recycling	11
1.4. Indian scenario of E-waste.....	11
1.5. Waste printed circuit board: components and types.....	13
1.6. Material composition of WPCB.....	15
1.7. Brominated flame retardants in WPCB	16
1.8. Recycling processes: why it is necessary and types.....	17

1.9. Physical separation.....	19
1.10. Pyrometallurgical processing.....	20
1.11. Hydrometallurgical processing	20
1.11.1. Leaching of metals into leaching solution	21
1.11.2. Recovery of metals from leachate	24
1.11.3. Recovery of copper from WPCB using hydrometallurgy	26
1.12. Bio-metallurgical processing	28
1.13. Pyrolysis	28
1.13.1. Pyrolysis temperature	31
1.13.2. Heating rate of pyrolysis	31
1.13.3. Residence time	32
1.13.4. Thermal degradation kinetics of WPCB	32
1.13.5. Optimization of lab-scale WPCB pyrolysis parameters	36
1.14. Reduction of brominated compounds.....	36
1.15. Simulation of a WPCB recycling plant and techno-economic assessment	38
1.16. Research gap	39
1.17. Research objectives	40
1.18. Thesis outline	40
2. Materials and methodology.....	43
2.1. Feedstock preparation.....	44
2.2. Chemical reagents used	44
2.3. Characterization techniques for the feedstock and product fractions	45

2.3.1. Composition of polymer, metals and ceramic fraction in WPCB	45
2.3.2. Proximate and CHNSO analyses	45
2.3.3. Fourier transform infrared spectroscopy	46
2.3.4. Thermal degradation study	46
2.3.5. Inductively coupled plasma mass spectrometry analysis	47
2.3.6. X-ray fluorescence spectroscopy analysis	48
2.3.7. Oxygen bomb-Ion chromatography	49
2.3.8. Simulated distillation analysis	50
2.3.9. Gas chromatography-mass spectrometry	50
2.3.10. Nuclear magnetic resonance spectroscopy	51
2.3.11. Calorific value using bomb calorimeter	51
2.3.12. Gas chromatography	51
2.3.13. Field emission scanning electron microscope	52
2.3.14. Energy dispersive X-ray spectroscopy	52
2.4. Kinetic study of WPCB samples.....	53
2.4.1. Isoconversional methods for determination of activation energy	53
2.4.2. Reaction model	55
2.4.3. Pre-exponential factor	57
2.4.4. Reconstruction of conversion profile	58
2.5. Lab-scale pyrolysis experiments.....	59
2.6. Response surface methodology study	60
2.7. Soxhlet extraction for reduction of bromine content	61
2.8. Extraction of copper	63
2.9. Simulation using Aspen Plus®	63

2.10. Techno-economic assessment	67
2.10.1. Capital and operating expenses	67
2.10.2. Discounted cash flow analysis	70
2.10.3. Economic evaluation of the plant and Minimum selling price of oil	71
2.11. Summary	72
3. Thermal degradation kinetics of WPCB	74
3.1. Elemental analysis of the WPCB samples prepared using X-ray fluorescence spectroscopy	75
3.2. Thermal degradation behavior of the WPCB samples	76
3.3. Kinetic parameter determination.....	81
3.3.1. Activation energy	81
3.3.2. Reaction model and pre-exponential factor	87
3.3.3. Reconstruction of conversion profiles	91
3.4. Summary.....	94
4. Optimization of lab-scale pyrolysis of WPCB using RSM.....	96
4.1. Physical and chemical properties of raw WPCB sample	97
4.1.1. Material composition, proximate, and CHNSO analyses	97
4.1.2. Functional group determination of solid samples: feedstock and char	99
4.1.3. Metal concentration of WPCB feedstock	99
4.1.4. Thermal degradation study of WPCB feedstock	101
4.2. Design of experiment, ANOVA and RSM optimization	102
4.3. Characterization of pyrolytic products obtained at different temperatures	109
4.3.1. Oil characterization	109

4.3.2. Gas characterization	115
4.3.3. Char characterization	118
4.4. Summary.....	121
5. Reduction of bromine in pyrolytic oil produced from WPCB	124
5.1. Selection of solvent for Soxhlet extraction.....	125
5.2. Characterization of the feedstocks	126
5.2.1. Elemental composition of feedstocks using XRF analysis	126
5.2.2. Material composition, proximate and CHNSO analyses	128
5.2.3. Thermal degradation study	131
5.3. Lab-scale pyrolysis: product yield distribution.....	133
5.4. Characterization of pyrolytic oil and gas fraction.....	135
5.4.1. FTIR analysis of pyrolytic oil	135
5.4.2. ¹ H NMR of oil samples	135
5.4.3. GC-MS of oil samples	137
5.4.4. SimDist analysis of oil samples	138
5.4.5. Calorific values of the feedstock, pyrolytic char and oil	141
5.4.6. Gas chromatography of gas fraction	142
5.5. Characterization of char to examine the effect of pyrolysis	145
5.5.1. CHNS analysis of char	145
5.5.2. FTIR analysis of char	145
5.6. Distribution of bromine among pyrolysis product fractions using oxygen bomb-ion chromatography	148
5.7. Summary.....	149

6. Recovery of copper from WPCB using hydrometallurgy	152
6.1. Leaching of copper.....	153
6.1.1. Effect of addition of oxidant on copper leaching efficiency	154
6.1.2. Effect of grinding and pyrolysis on copper leaching efficiency	158
6.2. Cementation using zinc powder.....	160
6.3. Summary.....	163
7. Simulation using Aspen Plus® and techno-economic assessment	165
7.1. Simulation of an integrated comminution-pyrolysis-hydrometallurgy plant using Aspen Plus®	166
7.2. Techno-economic assessment of the proposed plant.....	170
7.2.1. Capital and operating expenses	170
7.2.2. Discounted cash flow analysis	173
7.2.3. Economic evaluation and minimum selling price of oil	175
7.3. Summary.....	177
8. Overall conclusion and future recommendations.....	179
8.1. Overall conclusion of the thesis	179
8.2. Future recommendations	183
Appendix A.....	186
Appendix B.....	188
Appendix C.....	196
Thesis output.....	198
References.....	206

List of Tables

Table no.	Title of Tables	Page no.
Chapter 1		
Table 1.1	Different categories of electrical and electronic equipment according to the European Union WEEE directive	5
Table 1.2	Permissible limit of hazardous substances to be used in EEE given by the Restriction of hazardous substances (RoHS) directive	10
Table 1.3	Material composition of a typical WPCB	16
Table 1.4	Relevant literature for the recovery of metals from pretreated WPCB using hydrometallurgy	27
Table 1.5	Types of pyrolysis based on its operating condition	30
Table 1.6	Kinetic parameters for thermal degradation of waste printed circuit board	35
Chapter 2		
Table 2.1	List of the solid-state kinetic models used for the determination of reaction mechanism using Criado master plot	57
Table 2.2	The range of independent factors chosen for the design of experiment	61
Table 2.3	CAPEX and OPEX components used for the economic assessment of the proposed plant	69

Table 2.4	Discounted cash flow analysis calculation	71
-----------	---	----

Chapter 3

Table 3.1	Elemental composition of RW, NM, RW-sox-T and NM-sox-T using XRF	78
Table 3.2	The values of onset, offset, and maximum degradation temperatures for RW, NM, RW-sox-T and NM-sox-T at heating rates of 5, 10, 20, and 50 °C/min	79
Table 3.3	Plots for determination of activation energy using isoconversional methods	83
Table 3.4	Average activation energies of the RW, NM, RW-sox-T, and NM-sox-T determined using isoconversional methods of Friedman, OFW, KAS, and Starink	85
Table 3.5	Kinetic triplets for the materials RW, NM, RW-sox-T, and NM-sox-T (using Starink)	93

Chapter 4

Table 4.1	Material composition, proximate and CHNSO analysis of the feed material	98
Table 4.2	ICP-MS analysis for metal concentration in the WPCB cut pieces (RW-cut) and powdered (RW) samples	100
Table 4.3	ANOVA table for the selection of a model for oil yield	103
Table 4.4	ANOVA table for the selection of a model for char yield	104
Table 4.5	Experimental runs based on the DoE formulated for the WPCB pyrolysis and the responses (char and oil yields) obtained	106

Table 4.6	^1H NMR chemical shift integral regions and area% for the oil fractions obtained at pyrolysis temperatures 300, 500 and 600 °C	112
Table 4.7	^{13}C NMR chemical shift integral regions and area% for the oil fractions obtained at pyrolysis temperatures 300, 500 and 600 °C	112
Table 4.8	Metal concentration in oil fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C using ICP-MS analysis	114
Table 4.9	Calorific value, viscosity and density of the oil fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C	115
Table 4.10	CHNS analysis of the WPCB pyrolysis char at 300, 500 and 600 °C	120

Chapter 5

Table 5.1	Inorganic elemental composition of the materials RW, NM, RW-sox-A (acetone) and NM-sox-A (acetone) using XRF analysis	127
Table 5.2	Proximate and CHNSO analyses of the feedstock materials RW, NM, RW-sox-A and NM-sox-A	130
Table 5.3	^1H NMR chemical shift integral regions and area% for the pyrolytic oil obtained from RW, NM, RW-sox-A and NM-sox-A materials	136
Table 5.4	List of compounds detected using GC-MS analysis in the pyrolytic oil obtained from feedstock materials RW, NM, RW-sox-A and NM-sox-A	139

Table 5.5	Calorific values of feedstock, pyrolytic oil and char fractions produced from the WPCB samples RW, NM, RW-sox-A and NM-sox-A	142
-----------	--	-----

Chapter 6

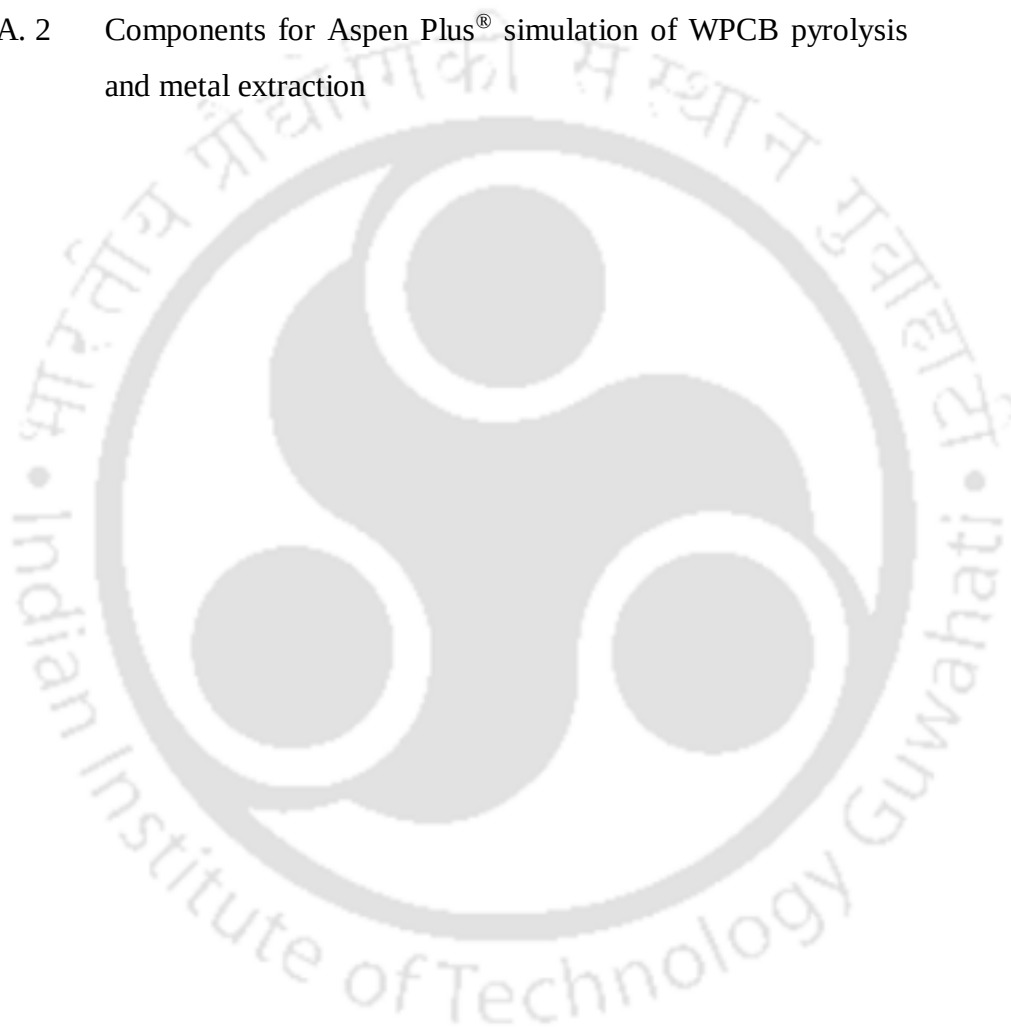
Table 6.1	Concentrations of copper and zinc in precipitate obtained and the remaining solution after the zinc cementation process	161
-----------	---	-----

Chapter 7

Table 7.1	Parameters assumed for the techno-economic assessment of the proposed plant	171
Table 7.2	Cost of equipment used in the proposed plant updated to year 2024	172
Table 7.3	Economic performance of the proposed plant	176

Appendix A

Table no.	Title of Table	Page no.
Table A. 1	GC-MS compound table for WPCB pyrolysis liquid fraction obtained at pyrolysis conditions of 500 °C	186
Table A. 2	Components for Aspen Plus [®] simulation of WPCB pyrolysis and metal extraction	187



List of Figures

Figure no.	Title of Figures	Page no.
Chapter 1		
Fig. 1.1	Contribution of different EEE categories in E-waste generated globally in 2022	4
Fig. 1.2	Contribution of materials to E-waste generated globally in 2022	7
Fig. 1.3	Amount of E-waste generated and collected based on different regions (Europe, Oceania, Americas, Asia and Africa) reported in Global E-waste Monitor 2024	8
Fig. 1.4	Country-wise distribution of E-waste generated in 2022 according to the Global E-waste Monitor 2024	12
Fig. 1.5	Schematic diagram showing the components of a WPCB (side-view)	14
Fig. 1.6	Broad classification of WPCB recycling methods	18
Fig. 1.7	Typical steps followed during physical separation method	19
Fig. 1.8	Schematic diagram showing the pyrolysis product fractions	29
Chapter 2		
Fig. 2.1	Determination of T_{onset} , T_{max} and T_{offset} temperatures in a TG-DTG profile of WPCB	47
Fig. 2.2	Schematic diagram of the lab-scale pyrolysis experimental set-up	60

Fig. 2.3	Schematic diagram for the experimental setup of Soxhlet extraction of WPCB samples using various organic solvents	62
----------	---	----

Fig. 2.4	Schematic diagram for the experimental setup of acid leaching of WPCB samples	63
----------	---	----

Chapter 3

Fig. 3.1	TG-DTG plot for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T from 30 to 1000 °C at heating rates of 5, 10, 20, and 50 °C/min	80
----------	--	----

Fig. 3.2	Temperature degradation window ($T_{\text{onset}} - T_{\text{offset}}$) for RW, RW-sox-T, NM and NM-sox-T at 5 °C/min	81
----------	---	----

Fig. 3.3	Activation energy distribution with conversion determined by isoconversional methods of Friedman, OFW, KAS and Starink for the materials (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T	84
----------	---	----

Fig. 3.4	Variation of activation energy with conversion ($\alpha = 0.05$ to 1.00) determined using the Starink method for the effect of (a) metals (RW versus NM) and (b) reduced bromine content (NM versus NM-sox-T)	86
----------	--	----

Fig. 3.5	Criado master plot at 5 °C/min for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T	89
----------	---	----

Fig. 3.6	Constable plots for RW determined using Starink method and (a) F1, (b) A2, (c) A3, (d) A4 reaction models	90
----------	---	----

Fig. 3.7	Experimental and simulated conversion profiles for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T for heating rates of 5, 10, 20, and 50 °C/min	92
----------	---	----

Fig. 3.8	Average R^2 values obtained for the isoconversional methods Friedman, OFW, KAS, and Starink for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T	93
----------	--	----

Chapter 4

Fig. 4.1	TG-DTG curve for WPCB cut piece (RW-cut) at 5 °C/min from 30 to 700 °C to determine the thermal degradation stages	102
Fig. 4.2	Actual versus predicted plots for product yields obtained for the (a) char, (b) oil yields	107
Fig. 4.3	3D Response surface plots for the WPCB pyrolysis char yield (wt%) with varying (a) A and B, (b) A and C, and (c) B and C, and oil yield (wt%) with varying (d) A and B, (e) B and C and (f) B and C	108
Fig. 4.4	FTIR analysis for the liquid fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C to determine the type of functional groups	110
Fig. 4.5	(a) ^1H NMR and (b) ^{13}C NMR spectra for the oil fraction obtained at pyrolysis temperature 600 °C	111
Fig. 4.6	Gas composition analysis at pyrolytic temperature 300, 500 and 600 °C using GC-TCD	116
Fig. 4.7	Gas composition analysis at pyrolytic temperatures 300, 500 and 600 °C using GC-FID	117
Fig. 4.8	FESEM images (top view) of (a) raw WPCB, (b) char at 300 °C (c) char at 500 °C and (d) char at 600 °C	119
Fig. 4.9	FTIR spectra for the raw WPCB and char obtained at pyrolysis temperatures of 300, 500 and 600 °C	120

Chapter 5

Fig. 5.1	Bromine reduction efficiency obtained after 24 h Soxhlet extraction using different solvents: toluene, DCM, acetone, and 2-propanol	126
Fig. 5.2	Compositional analysis (wt%) of the materials RW, NM, RW-sox-A and NM-sox-A in terms of polymer, metal and ceramic fractions	129
Fig. 5.3	TG-DTG study of (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A at 10 °C/min from 30 to 1000 °C under N ₂ environment	132
Fig. 5.4	Pyrolytic product yield distribution obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A materials based on (a) total feed and (b) organic fraction	134
Fig. 5.5	GC-MS chromatograms for the retention time (a) 4 to 6 min, and (b) 6 to 8 min, to show the presence of brominated compounds in the pyrolytic oil from the feedstocks RW, NM, RW-sox-A and NM-sox-A	140
Fig. 5.6	SimDist analysis of the pyrolytic oil samples obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A materials	141
Fig. 5.7	Compositional analysis of pyrolytic gas using GC-TCD, produced at 500 °C for the materials RW, NM, RW-sox-A and NM-sox-A	143
Fig. 5.8	Compositional analysis of pyrolytic gas using GC-FID, produced at 500 °C for the materials RW, NM, RW-sox-A and NM-sox-A	144
Fig. 5.9	Comparison of CHNS values in feed and char of the materials RW, NM, RW-sox-A and NM-sox-A	146

Fig. 5.10	FTIR comparison for the feedstock and char produced from pyrolysis of (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A	147
Fig. 5.11	Distribution of bromine into pyrolytic products produced from different feedstock materials (RW, NM, RW-sox-A and NM-sox-A) using oxygen bomb-ion chromatography method	149
Chapter 6		
Fig. 6.1	Copper leaching efficiencies at increasing H_2SO_4 concentrations and time depending on cut pieces (RW-cut) and powder (RW) form of WPCBs and their pyrolyzed versions (RW-cut-char and RW-char)	156
Fig. 6.2	Copper leaching efficiencies at 1 M H_2SO_4 and increasing H_2O_2 concentrations (5 vol% and 10 vol%) and time depending on cut pieces (RW-cut) and powder (RW) form of WPCBs and their pyrolyzed versions (RW-cut-char and RW-char)	157
Fig. 6.3	Side-view microscopic images of a WPCB cut piece (a) before pyrolysis, (b) after pyrolysis showing delamination of the glass fiber layers in substrate, and their respective FESEM-EDX mapping images (c) and (d)	159
Fig. 6.4	Photographs showing (a) leachate (blue color) after acid leaching, (b) solution (colorless) after zinc cementation and separation of the precipitate, and (c) precipitate obtained after zinc cementation	161
Fig. 6.5	EDX area analysis for the precipitate showing (a) selection of area and (b) composition (average wt%) of selected area	162

of the precipitate and mapping analysis showing (c) overall mapping, (d) mapping for copper and (e) mapping for zinc

Chapter 7

Fig. 7.1	Aspen Plus® simulation flowsheet of WPCB pyrolysis and metal extraction considering three different steps: comminution, pyrolysis and metal extraction	167
Fig. 7.2	Material balance for the (a) pyrolysis and (b) metal extraction processes	169
Fig. 7.3	Comparison of simulated and experimental pyrolytic product yields	170
Fig. 7.4	Contribution of the comminution, pyrolysis and metal extraction sections towards (a) CAPEX and (b) OPEX (fixed)	172
Fig. 7.5	Discounted cash flow analysis for the recovery of polymer, copper and glass fibers from WPCB using an integrated comminution-pyrolysis-hydrometallurgical processes	174
Fig. 7.6	Discounted cash flow analysis for the recovery of copper from WPCB using comminution-hydrometallurgical processes	174

Appendix B

Figure no.	Title of Figures	Page no.
Fig. A. 1	3D response surface plots for the WPCB pyrolysis gas yield (wt%) with varying (a) A and B, (b) A and C, and (c) B and C	188
Fig. A. 2	FTIR analysis of pyrolytic oil obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A	189
Fig. A. 3	¹ H NMR analysis of the pyrolytic oil produced using materials (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A	190
Fig. A. 4	Material balance for the comminution section	191
Fig. A. 5	Stream results showing the total and component mass flow around the equipment SSPLIT in the pyrolysis section	192
Fig. A. 6	Stream results showing the total and component mass flow around the equipment FLASH in the pyrolysis section	193
Fig. A. 7	Stream results showing the total and component mass flow around the equipment SEP-I in the metal extraction section	194
Fig. A. 8	Stream results showing the total and component mass flow around the equipment SEP-II in the metal extraction section	195

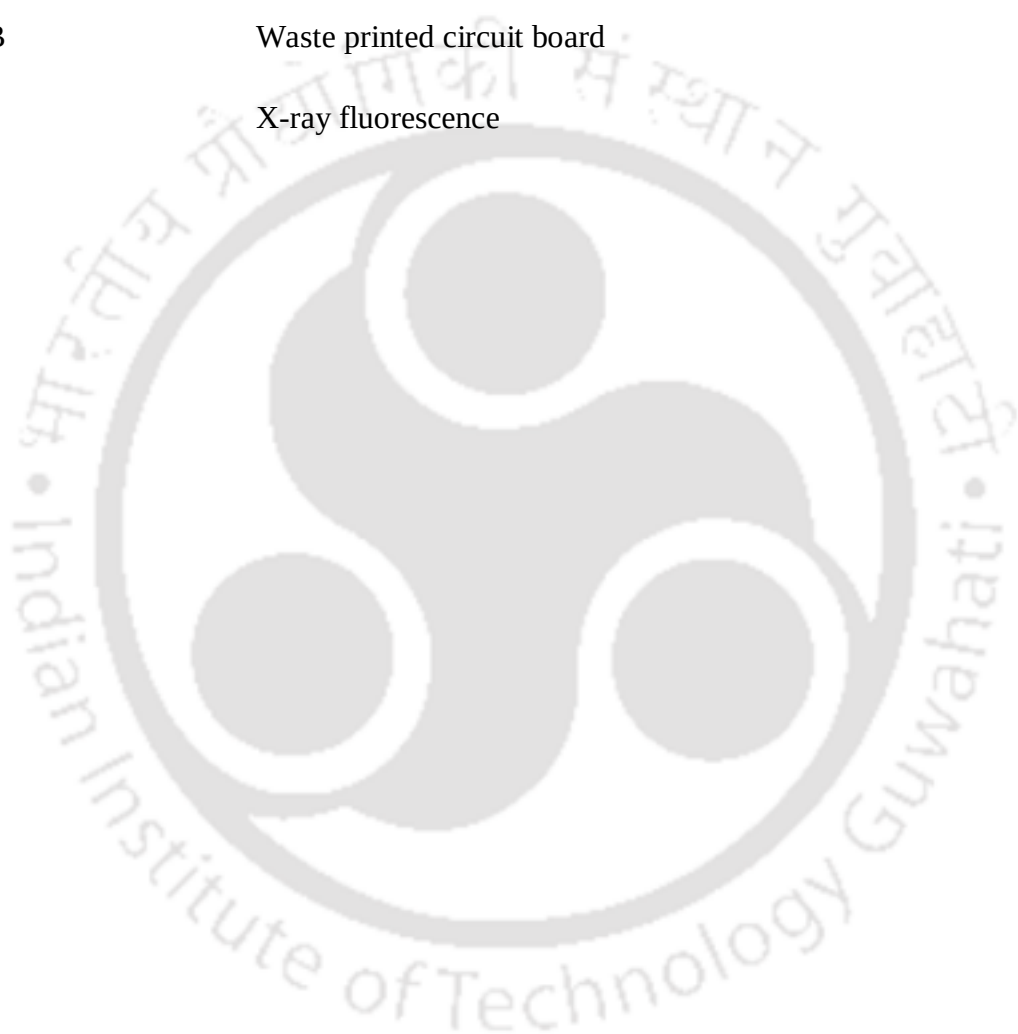
List of Abbreviations

Abbreviations	Full form
^1H NMR	Proton NMR
AC	Ash content
APEA	Aspen Plus Economic Analyzer
BBP	Butyl benzyl phthalate
BFR	Brominated flame retardant
BSS	British standard sieve
CAPEX	Capital expenditure
CCD	Central composite design
CDCl_3	deuterated chloroform
CEPCI	Chemical Engineering Plant Cost Index
DAEM	Distributed activation energy model
DBP	Dibutyl phthalate
DCF	Discounted cash flow
DCM	Dichloromethane
DEHP	Bis(2-ethylhexyl) phthalate
DI	de-ionized
DIBP	Diisobutyl phthalate
EC	Electronic component
EDX	Energy dispersive X-ray
EEE	Electrical and electronic equipment

EoL	End-of-life
EPR	Extended producer responsibility
EU	European Union
FC	Fixed carbon
FESEM	Field emission scanning electron microscope
FID	Flame ionization detector
FR	Flame retardant
FTIR	Fourier transform infrared spectroscopy
FV	Future value
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GF	Glass fibers
HBCCD	Hexabromocyclododecane
ICP-MS	Inductively coupled plasma mass spectrometry
IRR	Internal rate of return
KAS	Kissinger-Akahira-Sunose
LCA	Life cycle assessment
MC	Moisture content
MoEFCC	Ministry of Environment, Forest and Climate Change
MSP	Minimum selling price
NIST	National Institute of Standards and Technology
NPV	Net present value
OECD	Organization for economic cooperation and development

OFW	Ozawa, and/or Flynn and Wall
OPEX	Operating expenditure
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBP	Payback period
PCB	Printed circuit board
PI	Profitability index
PID	Proportional-Integral-Derivative
POP	Persistent organic pollutant
PV	Present value
RoHS	Restricted of Hazardous Substances
RSI	Reverse search index
RSM	Response surface methodology
RSS	Sum of the residual square
RT	Retention time
S/L	Solid to liquid
SI	Search index
SimDist	Simulated distillation
TBBPA	Tetrabromobisphenol A
TCD	Thermal conductivity detector
TEA	Techno-economic assessment
TGA	Thermogravimetric analysis
TG-DTG	Thermogravimetric-derivative thermogravimetric

TG-FTIR	Thermogravimetric-fourier transform infrared
US	United States
VM	Volatile matter content
WC	Working capital
WEEE	Waste electrical and electronic equipment
WPCB	Waste printed circuit board
XRF	X-ray fluorescence



Nomenclature

Notation	Description of the notation	Unit
A	pre-exponential factor	1/s
A	code for 'temperature'	-
B	code for 'heating rate'	-
C	code for 'hold time'	-
C_{Br}	concentration of bromine in the sample	$\mu\text{g/g}$
C_{com}	concentration of bromine in the combustate	$\mu\text{g/mL}$
$CEPCI_{ref}$	Chemical engineering plant cost index for the reference year	\$
$CEPCI_{2024}$	Chemical engineering plant cost index for the year 2024	\$
C_{ICP}	concentration of analyte in final solution obtained from ICP-MS	mg/L
$Cost_{ref}$	cost of equipment in reference year	\$
$Cost_{2024}$	cost of equipment in the year 2024	\$
Cu_L	copper concentration in leachate	mg/L
Cu_o	copper concentration in the material RW-cut, RW, RW-cut-char, or RW-char	wt%
DF	dilution factor	fraction
E	activation energy	kJ/mol
E°_{anode}	standard electrode potential of anode	V
$E^{\circ}_{cathode}$	standard electrode potential of cathode	V
E°_{cell}	standard electrode potential of cell	V

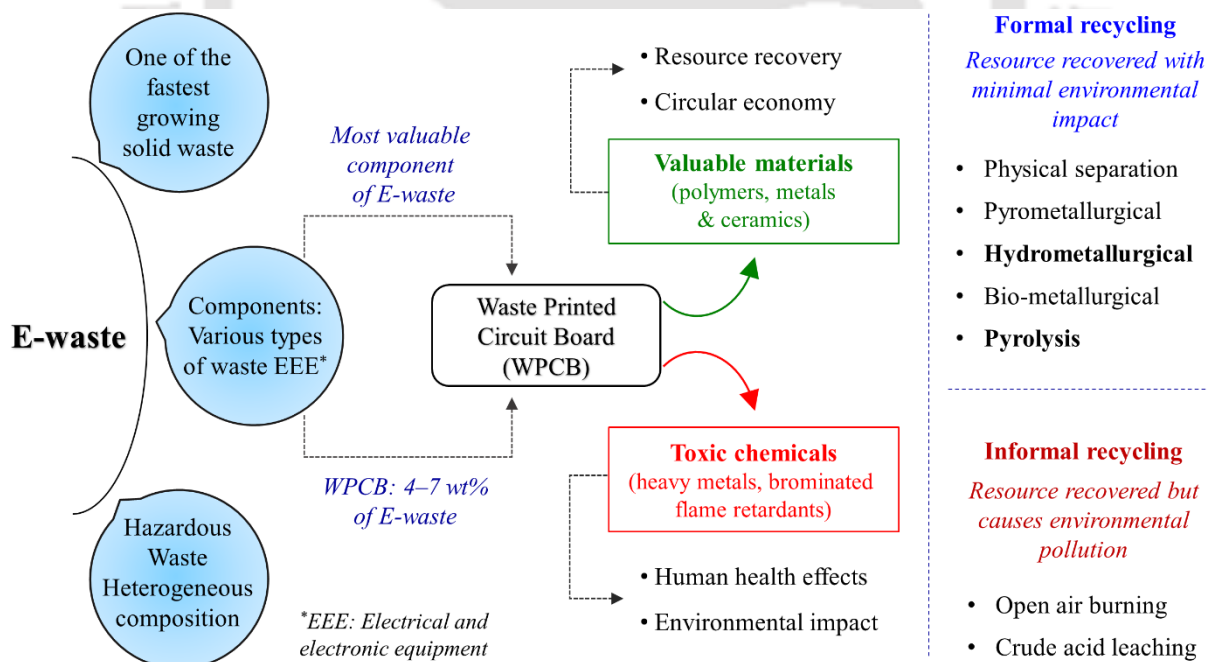
E_{α}	Apparent activation energy	kJ/mol
$f(\alpha)$	reaction model	-
$g(\alpha)$	integral form of reaction model	-
i	temperature program	-
m_f	final mass of the sample	g
m_o	initial mass of the sample	g
MSP_i	minimum selling price of pyrolytic oil when copper and GF were also sold	\$/kg
MSP_{ii}	Minimum selling price of pyrolytic oil when only GF was also sold	\$/kg
MSP_{iii}	Minimum selling price of pyrolytic oil when only copper was sold	\$/kg
MSP_{iv}	Minimum selling price of pyrolytic oil when neither copper nor GF were sold	\$/kg
m_t	mass of the sample at time t	g
N	number of non-particulate processing steps (mixing, heating, cooling, and compression)	-
N_L	number of labors	-
n	no. of years	years
OF	organic fraction	-
P	number of solid handling steps	-
r	discount rate	fraction
t	time	min
T	temperature	°C
T_{max}	maximum degradation temperature	°C

T_{offset}	offset temperature	$^{\circ}\text{C}$
T_{onset}	onset temperature	$^{\circ}\text{C}$
V_{com}	total volume of combustate	mL
V_{final}	total volume of the final solution in which the sample is dissolved	L
W_i	weight of material taken for leaching	mg
W_o	weight of sample combustate	g
W_{sample}	mass of the original sample digested	g
X	weight of RW-cut	g
Y	weight of RW-cut after ignition	g
Z	weight of RW-cut after ignition + acid leaching	g
$z(\alpha)$	$f(\alpha) \times g(\alpha)$	-
α	extent of conversion	fraction
β	heating rate	$^{\circ}\text{C}/\text{min}$
β_i	heating rate at the temperature program ' i '	$^{\circ}\text{C}/\text{min}$
η	leaching efficiency	%

Chapter 1

Introduction

- Electronic waste
- Waste printed circuit board
- Pyrolysis
- Hydrometallurgy
- Thesis outline



1. Introduction

Electrical and electronic equipment (EEE) has become an indispensable part of our lives. The change in lifestyle and dependency on EEE to fulfil daily tasks have made it mandatory for the people to pursue these items. For example, starting from using an electric toothbrush early morning to the present work-from-home scenario, and then using a microwave oven to reheat dinner, the demand for EEE have boomed. Advancement in technology and competition among the manufacturers have led to the frequent launch of upgraded products in the market. Old products become obsolete, and thus the consumers are compelled to buy new products and discard the old ones even before their end-of-life (EoL). These discarded EEE are known as electronic waste (E-waste) or waste electrical and electronic equipment (WEEE). The inadequate public awareness regarding the end-life management of these obsolete devices, combined with limited recycling infrastructure, often results in their indiscriminate disposal alongside municipal solid waste in landfills [1]. Consequently, a substantial increase in global E-waste generation has been observed, establishing it as one of the fastest growing categories of solid waste worldwide [2].

1.1. Defining E-waste

Globally, the term ‘E-waste’ lacks a uniform definition, leading to ambiguity in understanding the associated environmental and management challenges. Few representative definitions are summarized below:

- I. Definition 1: Solving the E-waste problem (StEP) initiative White paper (2014) has defined EEE as “Any household or business item with circuitry or electrical components with power or battery supply” [3]. If the owner of the EEE decides to discard it without the intent to re-use, then the EEE will be termed as an ‘E-waste’. But if the owner decides to donate the EEE to someone else to be used for the same purpose for which it was

designed, then that EEE will not be termed as an E-waste. Depending on the circumstance and the region, E-waste can also be referred to as electronic waste, e-scrap, or WEEE [4, 5].

- II. Definition 2: According to the E-waste (Management) Rule 2022, E-waste is, “Electrical and electronic equipment, including solar photo-voltaic modules or panels or cells, whole or in part discarded as well as rejects from manufacturing, refurbishment and repair processes” [6]. This document defined the EEE as “Equipment which are dependent on electric current or electro-magnetic field in order to become functional and also the equipment for the generation, transfer and measurements of the electricity”.

1.2. Categories and composition of E-waste

1.2.1. Categories of E-waste

E-waste comprises a diverse range of components, including mobile phones, laptops, refrigerators, and other electrical and electronic items, each characterized by variation in size, material composition, and hazardous constituents. The European Union WEEE directive 2012/19/EU classifies 56 types of EEE into six general categories [4]. The contribution of these six EEE categories to the global E-waste generated in 2022 is shown in Fig. 1.1, and a detailed list of these categories is presented in Table 1.1 [7]. In India, the categorization of EEE is different. The E-waste (Management) Rules 2022, and its revised version (2023), have listed EEE considered under the rule in Schedule I [5, 6]. The EEE have been categorized into the following seven general categories:

- I. Information technology and telecommunication equipment
- II. Consumer electrical and electronics and photovoltaic panels
- III. Large and small electrical and electronic equipment
- IV. Electrical and electronic tools (exception: large-scale stationary industrial tools)

- V. Toys, leisure and sports equipment
- VI. Medical devices (with the exception of all implanted and infrared products)
- VII. Laboratory instruments

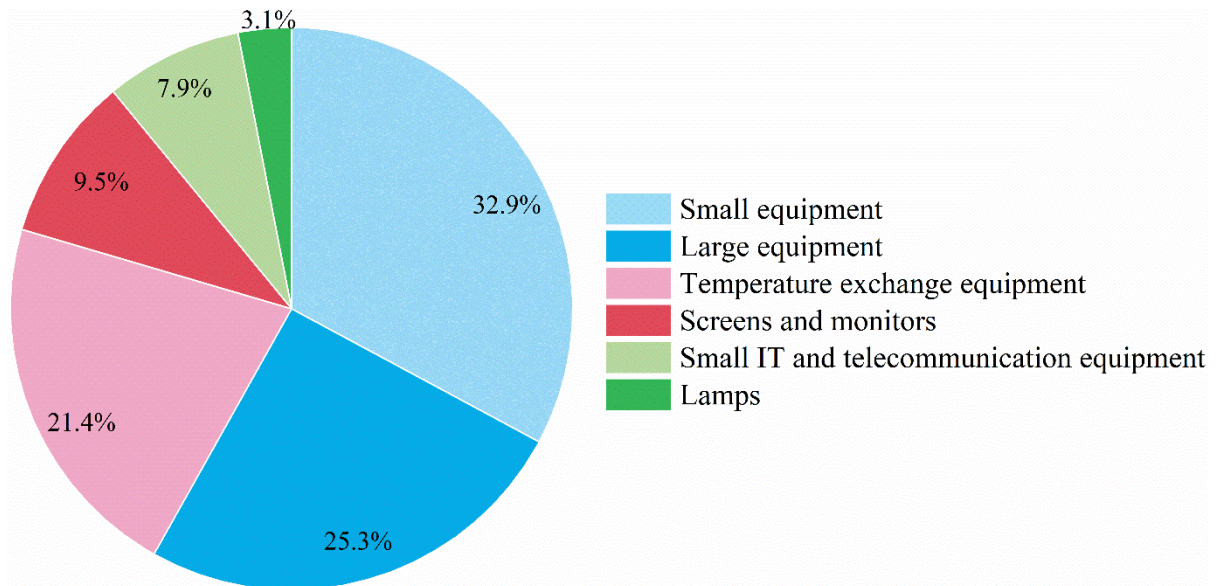


Fig. 1.1 Contribution of different EEE categories in E-waste generated globally in 2022 [8]

Table 1.1 Different categories of electrical and electronic equipment according to the European Union WEEE directive [9]

Sl. No.	General category of EEE	EEE under the category
1	Temperature Exchange Equipment	Refrigerators, Freezers, Equipment which automatically delivers cold products, Air conditioning equipment, Dehumidifying equipment, Heat pumps, Radiators containing oil and other temperature exchange equipment using fluids other than water for the temperature exchange.
2	Screens, monitors, and equipment containing screens having a surface greater than 100 cm ²	Screens, Televisions, LCD photo frames, Monitors, Laptops, Notebooks.
3	Lamps	Straight fluorescent lamps, Compact fluorescent lamps, fluorescent lamps, High intensity discharge lamps – including pressure sodium lamps and metal halide lamps, Low pressure sodium lamps, LED.
4	Large Equipment (any external dimension more than 50 cm)	Washing machines, Clothes dryers, Dish washing machines, Cookers, Electric stoves, Electric hot plates, Luminaires, Equipment reproducing sound or images, Musical equipment (excluding pipe organs installed in churches), Appliances for knitting and weaving, Large computer-mainframes, Large printing machines, Copying equipment, Large coin slot machines, Large medical devices, Large monitoring and control instruments, Large appliances which automatically deliver products and money, Photovoltaic panels.
5	Small Equipment (no external dimension more than 50 cm)	Vacuum cleaners, Carpet sweepers, Appliances for sewing, Luminaires, Microwaves, Ventilation equipment, Irons, Toasters, Electric knives, Electric kettles, Clocks and Watches, Electric shavers, Scales, Appliances for hair and body care, Calculators, Radio sets, Video cameras, Video recorders, Hi-fi equipment, Musical instruments, Equipment reproducing sound or images, Electrical and electronic toys, Sports equipment, Computers for biking, diving, running, rowing, etc., Smoke detectors, Heating regulators, Thermostats, Small Electrical and electronic tools, Small medical devices, Small Monitoring and control instruments, Small Appliances which automatically deliver products, Small equipment with integrated photovoltaic panels.
6	Small IT and Telecommunication Equipment (no external dimension more than 50 cm)	Mobile phones, GPS, Pocket calculators, Routers, Personal computers, Printers, Telephones.

1.2.2. Composition of E-waste

Electronic waste comprises numerous components with diverse sizes and material compositions. A total of 60 elements from the periodic table can be found in E-waste [10]. It is noteworthy that metals contribute 50% to the composition of E-waste which includes, precious metals (gold, silver, platinum, palladium, etc.), base metals (copper, aluminum, zinc, iron, cobalt, etc.), critical metals (indium, germanium, antimony, etc.), and heavy metals (lead, mercury, cadmium, arsenic, etc.). Thus, E-waste is a potential secondary source of many metals or, a suitable candidate for urban mining. The concentration of metals varies depending on the E-waste component. For instance, waste printed circuit board is the richest source of precious metals. Apart from metals, plastics contribution (27%) is also high in E-waste (Fig. 1.2) [8]. Plastics are used in EEE for the purpose of insulation, covering/casing, noise reduction, etc. Chemical feedstock and fuel can be produced with the thermochemical treatment of the non-metallic fraction (plastics). The characteristics of the products generated will be dependent on the composition of the polymer feed. However, the plastics contain mostly flame retardants which was originally used for safety purposes but affects the usability of the products obtained from the thermal degradation processes. Thus, unlike conventional solid wastes such as household waste, E-waste has the dual attributes of hazardousness and resourcefulness.

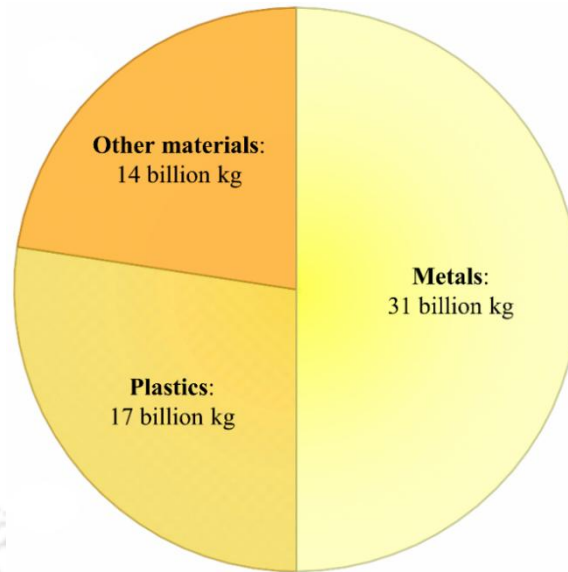


Fig. 1.2 Contribution of materials to E-waste generated globally in 2022 [8]

1.3. Global scenario of E-waste

1.3.1. E-waste generation

The data estimation reported in the Global E-waste Monitor 2024 shows that 62 billion kg of E-waste was generated in 2022. This is equivalent to about 7.8 kg per capita per year. Out of this, only 22.3% is reported to be properly collected and recycled [8]. This recycling rate has increased over the years but, the matter of concern is that, generated data outpaced the recycling rate by a factor of five (since 2010). The distribution of E-waste generated, collected and recycled can be grouped based on different regions as shown below (Fig. 1.3). In European region, the per capita E-waste generation in kg is the highest, but the formal collection and recycling rate is also the highest (42.8%), whereas Asian and African regions have the lowest recycling rate values of 11.8% and 0.7%, respectively. The reason behind less recycling rate in these regions is the less stringent laws for E-waste regulation and because of which illegal transboundary movement is happening without any difficulty.

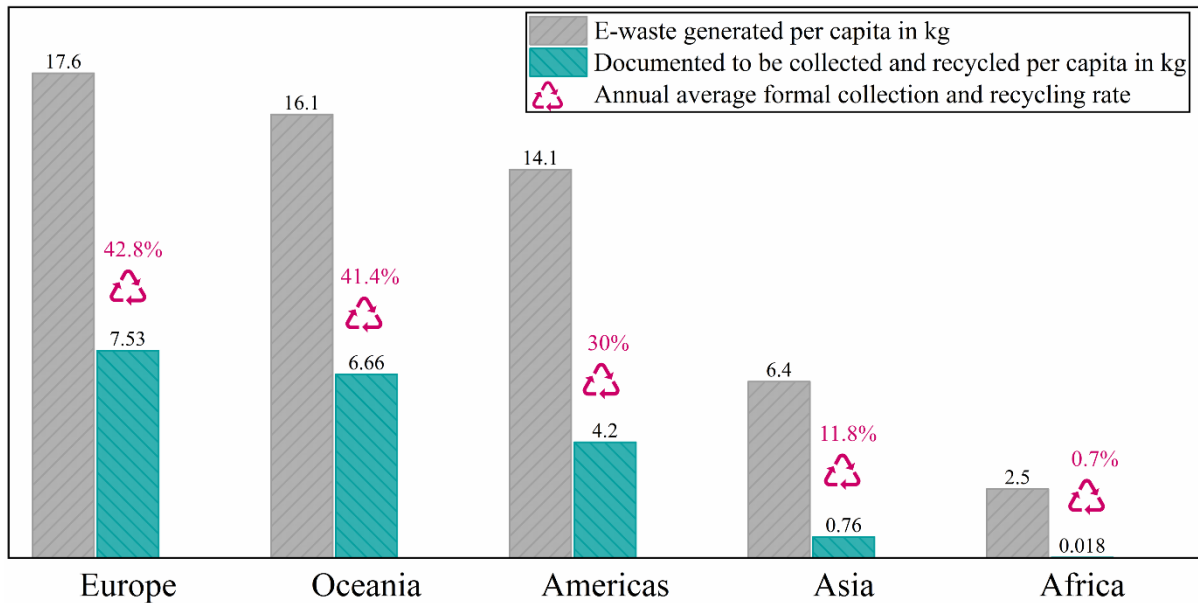


Fig. 1.3 Amount of E-waste generated and collected based on different regions (Europe, Oceania, Americas, Asia and Africa) reported in Global E-waste Monitor 2024 [8]

1.3.2. Illegal transboundary movement of E-waste

Another issue in E-waste is the illegal transboundary movement of EEE from developed countries to developing countries where there are less stringent laws. One of the primary challenges in controlling the transboundary movement of E-waste is distinguishing between waste and used EEE (which is not waste) [1]. Often non-working/waste EEE are transferred in place of the used EEE. This transboundary movement has resulted in increased E-waste in these developing countries, having less stringent laws and lack recycling facilities. In 2022, a total of 5.1 billion kg of E-waste were shipped across international borders. Out of this, 65% of the shipment occurred from high-income to middle- and low-income countries through informal and unregulated channels [8]. It leads to an environmental burden in the developing countries with minimal awareness and recycling facilities. However, awareness has increased over the years and E-waste legislations are also coming up in developing nations.

1.3.3. E-waste legislations

The massive generation of E-waste, unprofessional recycling practices and lack of awareness of its impact on the environment and human health is posing a challenge in dealing with the problem of E-waste. The awareness level of E-waste generation and its processing practices are deficient [11]. To tackle this problem, many countries have adopted E-waste regulations. The need for an E-waste regulation has been realized from the two incidents in 1986 and 1988; the Khian sea case and the Koko case, respectively [12]. The Basel Convention in 1989 was held to discuss these issues where 186 countries were brought together to sign the treaty titled “Transboundary Movement of Hazardous Waste and Disposal.”

The European Union (EU) has been very active in managing the E-waste problem. The convention of 1989 came into force on May 5, 1992 [13]. The following year, “Waste Shipment Regulation” was proposed, which prohibited the export of hazardous E-waste to the non-OECD (Organization for Economic Cooperation and Development) countries. For shipment to the non-OECD countries, prior permission from the concerned officials is required. Around a decade later, the “Restriction of Hazardous Substances (RoHS) directive” was passed in 2003. In this directive, a concentration limit was put on the use of some hazardous substances in the manufacturing of EEE. The list of chemicals and their permissible limit is given in Table 1.2. Later in 2012, the WEEE Directive (2012/19/EU) was passed by the commission of EU that focused on the regulation of the collection, recycling, and recovery of E-waste in the member nations from disposal to reuse.

Table 1.2 Permissible limit of hazardous substances to be used in EEE given by the Restriction of hazardous substances (RoHS) directive [9]

Toxic elements	Permissible limit (wt%)
Lead	0.10
Mercury	0.10
Cadmium	0.01
Hexavalent chromium (Cr^{6+})	0.10
Polybrominated biphenyl (PBB)	0.10
Polybrominated diphenyl ether (PBDE)	0.10
Bis(2-ethylhexyl) phthalate (DEHP)	0.10
Butyl benzyl phthalate (BBP)	0.10
Dibutyl phthalate (DBP)	0.10
Diisobutyl phthalate (DIBP)	0.10

1.3.4. Environmental impact due to informal recycling

Electronic waste is categorized as hazardous waste because of the presence of toxic elements such as heavy metals and halogenated flame retardants. Thus, E-waste should be treated properly to avoid the transfer of these toxic elements into the environment or the ecosystem. In an informal recycling site, the E-waste components are treated by untrained professionals, without any personal protective equipment, who tend to focus on the recovery of valuables, but ignoring the effect of toxic components present in E-waste. It often starts from the ragpickers that collect the obsolete EEE from households, then treat them by means of open burning, or crude acid baths to recover the valuable metals. The residues are directly dumped in water bodies or in landfills, which contaminate the environment [14]. Effect on human health can take place by direct or indirect pathway. Due to the unregulated working conditions, the workers are subjected to have direct effect during recycling and the nearby residents indirectly, from inhalation of polluted air or through the food chain. Many authors have reported contamination of soil, water bodies, and air. Guo et al. [15] reported the release of particulate matter and volatile organic compounds from thermal treatment of waste PCB (printed circuit board) of a television and suggested using personal protective equipment for the workers. Most contaminations are reported to be concentrated in dumping sites and informal recycling sites [16]. However, the contamination can even be migrated from the dumpsite to downstream places, as reported by Wong et al. [17] in Guiyu, China, which is a matter of concern.

1.4. Indian scenario of E-waste

India ranks third in E-waste generating countries producing 4100 million kg in 2022, after China and the United States (US) (Fig. 1.4). Rapid urbanization, digitalization and increasing population have significantly contributed to the consumption of the EEE and the lack of awareness, collection and recycling facilities have put India among the top generators of E-waste. Majority of the E-waste is generated by a few cities/states in India. Total 65 cities

contribute 60% and 10 states contribute 70% of the total E-waste generated [18]. Among the cities, Mumbai generates the highest amount of E-waste, followed by Delhi and Bangalore, and among the states, Maharashtra is the highest contributor, followed by Tamil Nadu and Andhra Pradesh.

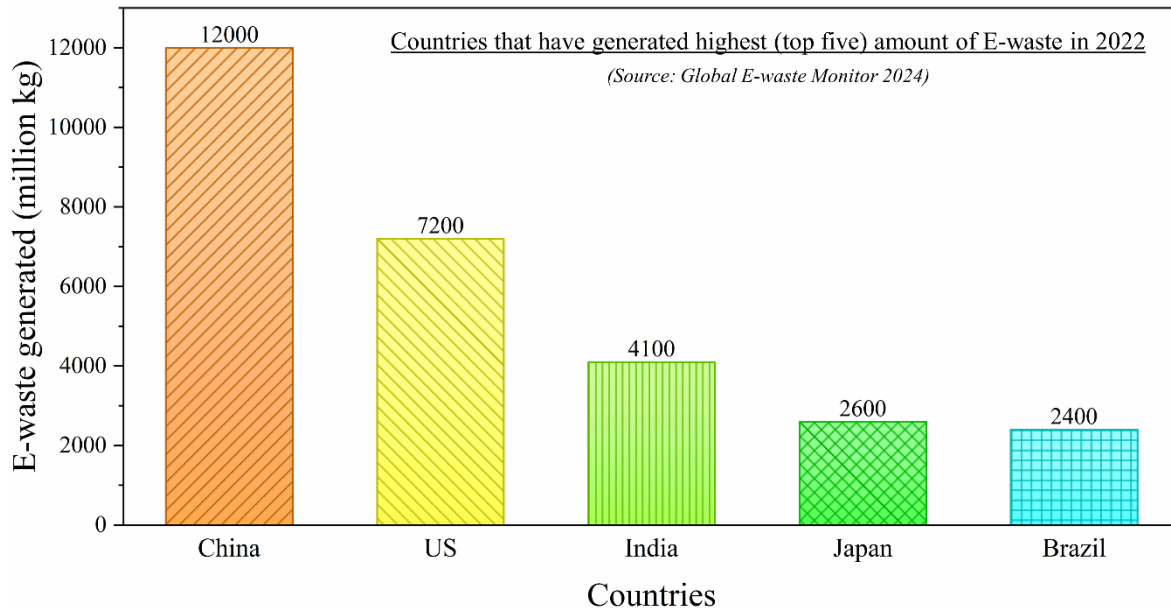


Fig. 1.4 Country-wise distribution of E-waste generated in 2022 according to the Global E-waste Monitor 2024 [8]

India's E-waste recycling scenario represents a mixture of formal and informal sector, while the latter being the dominating one. According to the Annual report 2023–2024 published by the Ministry of Environment, Forest and Climate Change (MoEFCC), Govt. of India, there are 569 authorized dismantlers/recyclers of E-waste in India, having annual processing capacity of about 1790 million kg per annum [19]. The infrastructure of formal E-waste recycling in India has expanded following the implementation of the E-waste (Management) Rules, 2016, and their subsequent revisions under the E-waste (Management) Rules 2022. These regulations introduced a comprehensive framework for Extended Producer Responsibility (EPR), through a centralized online platform where the producers and recyclers are required to register for tracking the flow of E-waste, setting annual collection and recycling targets, and verifying

compliance through EPR credits. There are 3430 producers and 124 recyclers, who have been granted registration at E-waste EPR portal under E-waste (Management) Rules, 2022 [19]. Moreover, 106 types of EEE were considered in comparison to 21 EEE categories regulated under the E-waste (Management) Rules, 2016 [20].

The formal recycling infrastructure is improving in India; however, informal recycling facility still dominates the industry. It starts from the '*kabariwalas*' who collect WEEE along with other solid waste (dry) from household in exchange for money which end up in informal recycling units [21]. Over 90% of the E-waste generated in India is handled by the informal recyclers [22]. These informal recyclers practice manual dismantling, open burning and use of toxic chemicals without any safety measures. Children and pregnant women are also reported to be working in such firms or in their own backyard, risking the lives of themselves as well as the neighborhood [23, 24]. The concentrations of hazardous substances were found to be higher in the vicinity of the recycling centers. Moreover, these toxic chemicals are also reported to have travelled to the downstream areas. [25]

1.5. Waste printed circuit board: components and types

Waste printed circuit board (WPCB) is a vital component in any WEEE. Typically, non-working PCBs are termed as WPCB. It contributes about 4–7 wt% in E-waste and consists of about 30–50% metals and 50–70% non-metals. Its weight contribution and material composition depend on the type, source of EEE and period of manufacture [26]. Typically, a WPCB consists of a layer of components, such as; substrate, copper foil, solder mask and silkscreen (Fig. 1.5). The substrate provides the mechanical support, typically made of woven glass fibers reinforced with epoxy resin. The layer of copper foil provides the electrical connection between the electronic components (ECs) such as the resistors, capacitors, thermistors, inductors, etc. that are mounted on top of the board. These are essential for the functioning of the EEE. To protect the board against oxidation and environmental

contamination, the solder mask is used. Silkscreens are used to provide crucial visual information for manufacturing, assembly, and testing of the ECs.

Depending on the grade of substrate used in the manufacture of a PCB, it can be classified into FR-4 and FR-2. Notably, FR stands for flame retardant and denotes the flammability safety of the woven fiberglass-reinforced epoxy laminates. For computers and communication equipment, FR-4 is the most common grade, while for home electronics and television, FR-2 is predominantly used. Today, high-value equipment increasingly contains FR-4 boards due to the high thermal resistance and infinitesimal water absorption. PCBs are exposed to high temperatures during soldering and potential electric energy impacts; therefore, low-flammability materials are essential for PCB fabrication [27]. Traditionally, brominated fire retardants have been the most important and popular fire retardants in this sector. Although less toxic alternatives such as, phosphorous or nitrogen-based fire retardants are available however, brominated fire retardants are still predominantly used because of their better efficiency and compatibility with a wide range of polymers [28, 29]. PCBs can also be classified into several other categories. For instance, based on the Au content also, PCBs are categorized as: low grade (<100 ppm), medium-grade (100–400 ppm) and high-grade (>400 ppm). Similarly, depending on the substrate type, PCBs are classified as single-layer, multi-layer, rigid, or flexible.

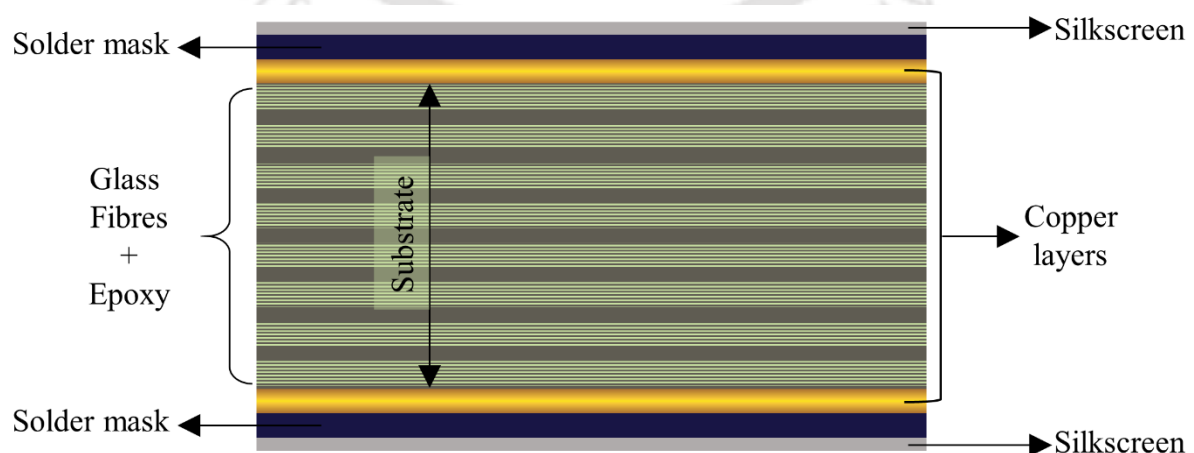


Fig. 1.5 Schematic diagram showing the components of a WPCB (side-view)

1.6. Material composition of WPCB

Waste printed circuit boards primarily consist of polymers, metals and ceramics. Their composition varies depending on the type, manufacturing period, source, etc. For example, a WPCB obtained from a mobile phone has a different material composition than that from a computer system. The general chemical composition of a WPCB with the ECs intact is listed in Table 1.3 [30]. Thus, WPCB is a rich source of valuable materials. Most importantly, the gold and copper concentrations are 40–800, and 30–40 times higher than the amount of gold and copper present in the respective ores found in the United States [27]. Thus, WPCB is one of the most valuable components in WEEE. Apart from these valuable metals, WPCB also consists of heavy metals such as lead, and toxic chemicals such as brominated flame retardants (BFRs). The low melting behavior of lead makes it suitable to be used in solders and the BFRs are used as a preventive measure to avoid fire hazards during manufacturing as well as usage by the owner of the device. Thus, from economic as well as environmental perspectives, WPCBs should be treated properly.

Table 1.3 Material composition of a typical WPCB [30]

Metals	wt%	Ceramics	wt%	Plastics	wt%
Cu	6.0–27.0	SiO ₂	15.0–30.0	PE	10.0–16.0
Fe	1.2–8.0	Al ₂ O ₃	6.0–9.4	PP	4.8
Al	2.0–7.2	Alkali-earthoxides	6.0	PS	4.8
Sn	1.0–5.6	Titanates-micas	3.0	Epoxy	4.8
Pb	1.0–4.2			PVC	2.4
Ni	0.3–5.4			PTPE	2.4
Zn	0.2–2.2			Nylon	0.9
Sb	0.1–0.4				
Au (ppm)	250–2050				
Ag (ppm)	110–4500				
Pd (ppm)	50–4000				
Pt (ppm)	5–30				
Co (ppm)	1–4000				

1.7. Brominated flame retardants in WPCB

Flame retardants are used in a wide range of WEEE components, including WPCB, to avoid fire hazards. Although the halogenated flame retardants have severe environmental impacts, it is essential to use them from the safety point of view. For example, in case of PCB, the board encounters high temperature during soldering. This may lead to fire hazards; thus, flame retardants are added in the board [31]. Among the halogenated flame retardants, mostly BFRs are used because of its lower cost and its compatibility with a lot of polymers. The most commonly used BFRs in WEEE are: Polybrominated diphenyl ethers (PBDEs),

Hexabromocyclododecane (HBCD), Tetrabromobisphenol A (TBBPA) and Polybrominated biphenyls (PBBs). These flame retardants are used in a variety of products, such as PBDEs are used in computer monitors, television sets, computer cases, wire and cable insulation, and electrical/ electronic connectors; HBCDs in foams and expanded polystyrene; TBBPA in electronic circuit boards; and PBBs are found in home electrical appliances, textiles, etc. BFRs like PBDEs, PBBs, and HBCDs are mixed with polymers as additives; whereas, TBBPAs are chemically bound to the polymer matrix. Knowledge about some of these substances is very limited and hinders environmental authorities from carrying out adequate risk assessments. All these BFRs appear to be persistent and bio-accumulative, resulting in food chain contamination, including human milk, producing adverse human health effects. Some of the health risks associated with BFRs include impact on the thyroid system, brain development, etc. Five BFRs have been listed among the twenty-eight persistent organic pollutants (POPs) by the Stockholm Convention 2009. BFRs damage the endocrine system, reproductive health, neurodevelopment impairment, immune system damage and cancer [32].

The source of brominated compounds in pyrolysis products is the BFRs present in the feed. On undergoing thermal treatment, these compounds lead to toxic gases, dioxins, and furans [33]. Thus, removing BFRs is a crucial step to protect its leaching into the environment and avoid the production of brominated compounds in pyrolysis. BFRs are studied to be removed using pre-treatment methods or simultaneous treatment during the pyrolysis process.

1.8. Recycling processes: why it is necessary and types

Although strategies such as reuse, repair and refurbish can extend the lifespan of electronic products, they cannot eliminate the need for proper EoL management. After several product lifecycles, recycling becomes essential to recover valuable materials and prevent environmental harm. Furthermore, E-waste comprises approximately 50% metallic components, with an estimated global value of around \$91 billion, highlighting its significant

potential for resource recovery and economic value generation [34]. Advancing recycling technologies is, therefore, an essential component of sustainable E-waste management. However, E-waste consists of a wide range of products containing different components/composition. Thus, the recycling processes cannot be generalized for E-waste, however it can be broadly categorized based on the target component of E-waste, or the target material. The recycling techniques for WPCB are: physical treatment, pyrometallurgical, hydrometallurgical, bio-metallurgical, and pyrolysis (Fig. 1.6). Each of these techniques have certain target of materials, advantages and disadvantages, which are discussed in the subsequent sections.

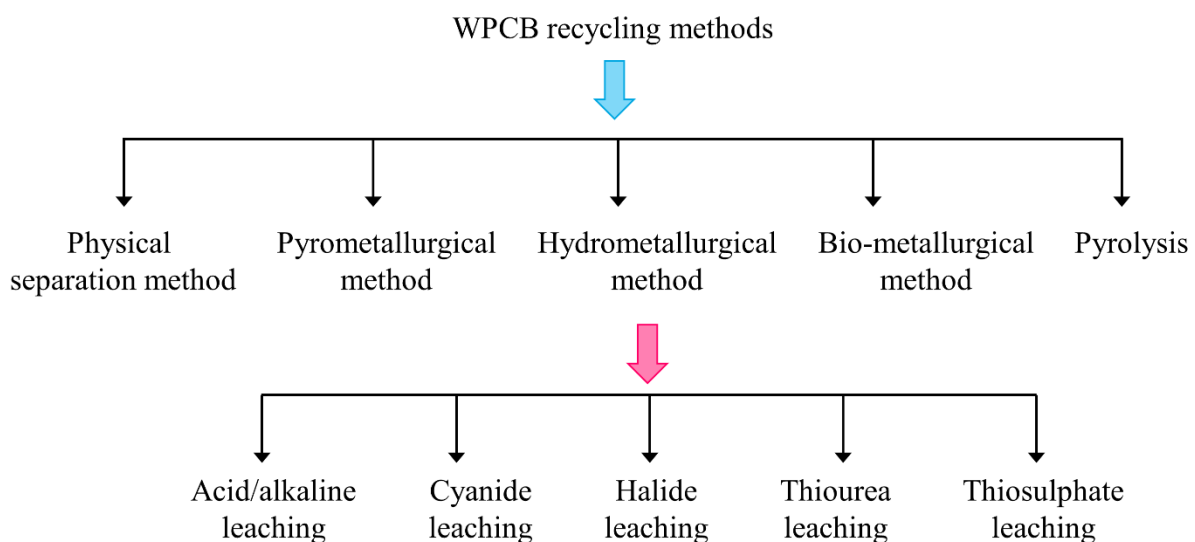


Fig. 1.6 Broad classification of WPCB recycling methods

1.9. Physical separation

This is a primary method that includes dismantling, sorting and size reduction operations. The ECs such as capacitors, resistors are removed in the first step so that these can be treated separately or reused. Manual dismantling is commonly done, however for large scale it becomes cumbersome [35]. Automatic separation of the ECs need to be performed [36]. This technique allows separation of the valuable components which can be reused. It is one of the most commonly used and cheapest means of recycling WPCB, however, the recovery of materials is crude resulting into the loss of resourceful materials [37]. After the size reduction operations, the WPCBs are sent for electro-magnetic separations to separate out the magnetic and ferromagnetic components (Fig. 1.7). This technique does not enable the recovery of materials/metals in its pure form. However, it serves as a prerequisite step to enhance efficiency prior to advanced recycling processes, such as size reduction in hydrometallurgical treatment.

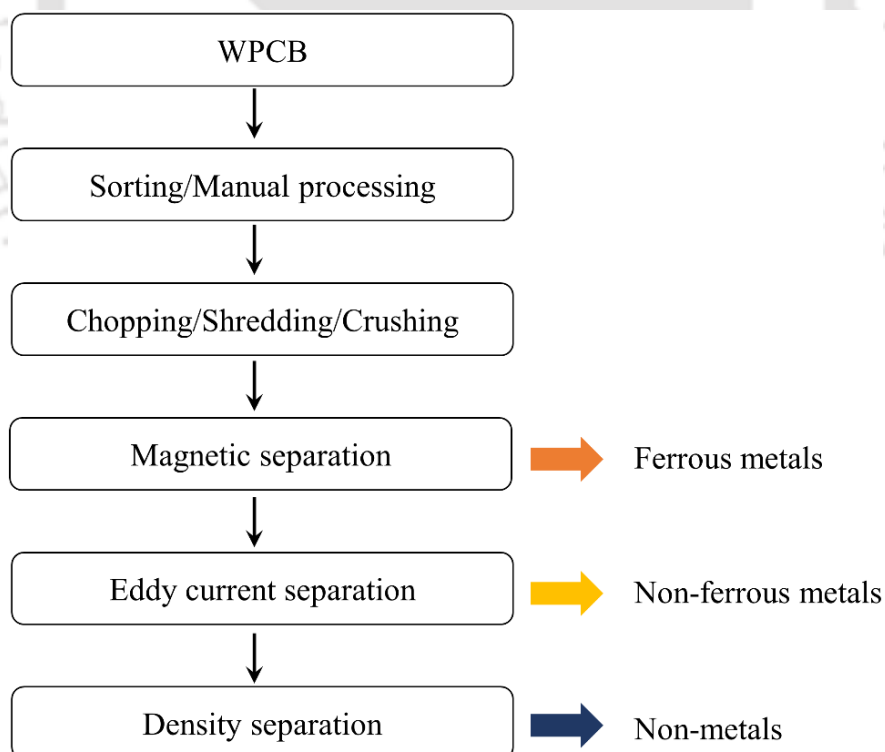


Fig. 1.7 Typical steps followed during physical separation method

1.10. Pyrometallurgical processing

The pyrometallurgical method uses high temperature treatment to recover metals, such as copper in the pure form from WPCBs. It is a well-established technology used in mining industry. In a typical pyrometallurgical method, firstly, the sample is pretreated and fed to the furnace. Melted copper is obtained from the furnace, which is converted to bullion for selling. The remaining metals are upgraded in a converter and finally electro-refined using electrolysis. The Umicore smelting (Belgium), Noranda smelting (Canada) and Rönnskär smelter (Boliden) are well-known metal recovery processes from WPCB using pyrometallurgy in a commercial scale [38]. The main disadvantage of the pyrometallurgical method is that iron and aluminum cannot be recovered as metals as they get oxidized and are collected in slag [39]. Moreover, the presence of about 30–40% glass fibers (ceramics) in WPCB is converted into slag, resulting in huge amount of slag production. The polymers present in WPCB are used for heat generation in this process. However, since it contains flame retardants, the burning leads to the formation of toxic gases, dioxins and furans, and metal vapors. This demands special measures to be taken so that the toxic gases are not released into the environment. Precious metals are recovered only after additional treatment at the end of the process. Metals like lead and zinc having high vapor pressure are also lost during smelting. This processing technique has another disadvantage of poor selectivity towards individual metals, meaning a series of refining process needs to be performed to obtain a pure metal. Hydrometallurgical processing fulfils this disadvantage.

1.11. Hydrometallurgical processing

The idea of hydrometallurgy is also taken from the conventional process of metal recovery from mining ores by using chemicals. The main steps involved in this method are dissolution of metals from the solid matrix into the solution and then removing the target metal from the solution in its pure form. The first step is called leaching or lixiviation, and the second step is

known as cementation/precipitation. Based on the leaching agent used, it can be classified into acid/alkaline leaching, cyanide leaching, thiosulphate leaching, and thiourea leaching [2]. The hydrometallurgical method can eliminate the problems of extensive energy usage, the release of toxic gases, and loss of metals like iron and aluminum in pyrometallurgical method [40]. However, prior to leaching, the feed must undergo size reduction to enhance leaching efficiency, consuming additional processing time and losing valuable metals [41]. Moreover, the use of toxic chemicals necessitates proper treatment of effluents before disposal to mitigate environmental risks in the downstream regions.

1.11.1. Leaching of metals into leaching solution

1.11.1.1. Acid/alkaline leaching

Inorganic acids hydrochloric acid (HCl), nitric acid (HNO₃) and sulfuric acid (H₂SO₄) are commonly used for acid leaching of metals from WPCBs. HNO₃ is found suitable for copper leaching because of its oxidizing nature, but it releases NO_x gases [42, 43]. Similarly, the use of chlorinated acids (HCl) releases harmful gases. Thus, considering the economic, environmental benefits and its established industrial application, H₂SO₄ is a suitable leaching agent for leaching metals like copper from WPCBs. However, an external oxidant (hydrogen peroxide, H₂O₂) is required with H₂SO₄ for better leaching performance [2, 44]. These inorganic acids are effective however, organic acids are more environmentally friendly [45, 46].

Alkaline leaching is another chemical leaching method popular for recovery of metals from WPCB. Jadhao et al. [47] performed alkaline leaching using NH₃-(NH₄)₂SO₄ and H₂O₂ and recovered 100% copper and nickel, followed by recovery of ~98% copper using electrowinning technique. Nan et al. [48] reported that while acid leaching projected a wider range of base metal leaching tendency, alkaline leaching demonstrated a better environment-friendly approach due to the release of toxic off-gases in acid leaching, for example while using HNO₃.

This was reported from the life cycle assessment (LCA) studies performed using OpenLCA software.

1.11.1.2. Cyanide leaching

Cyanide leaching has been traditionally used in mines for the recovery of gold and silver since 1887 [49]. It has high efficiency and the oxygen present in cyanide solution helps in selective leaching of these metals. The recovery of precious metals from WPCB can contribute to high return in a WPCB processing plant. Thus, even though cyanide leaching has been used predominantly for gold recovery from mining ores, it is viable for leaching gold and silver from WPCB. WPCBs contain a substantial amount of copper, which can result in increased consumption of cyanide during gold leaching due to the formation of copper-cyanide complexes. This effect significantly reduces the concentration of free cyanide available for gold dissolution [50]. In this regard, stage-wise leaching is performed, where copper is leached using different suitable leaching agent, followed by precious metals leaching. Cyanide leaching requires $\text{pH} \geq 10.5$, thus additional alkali will be required for obtaining the desired pH [51]. Cyanide is still used as a leaching agent for the recovery of gold because of its low cost and high efficiency, however, it is highly toxic to human health even at very low concentrations.

1.11.1.3. Halide leaching

Halide leaching of WPCB for recovery of gold from mining ores predate the use of cyanide. Gold forms both Au^+ and Au^{3+} complexes when reacted with the halides: chlorine, bromine, and iodine [52]. The efficiency of the halide leaching depends on the concentration of halides, temperature, surface area, pH, and leaching time. Among all the halides, chloride gives the highest leaching rate, but certain precautions need to be taken due to its corrosiveness. Stainless steel with rubber lining equipment should be used, and precautionary steps should be taken to capture the chlorine gas released [47]. Chlorine does not seem to be the best choice from a sustainability point of view, and so thus bromine. Iodine has, however, been demonstrated to

combine effectiveness with sustainability. Iodine is corrosive but low hazard solid at standard conditions which readily undergo sublimation [53]. High leaching efficiency (~99%) could be achieved using $I_2-H_2O_2$ by adjusting concentrations and the solid% [54].

1.11.1.4. Thiourea leaching

Thiourea ($SC(NH_2)_2$) is a sulfur-based organic ligand that forms a cationic soluble complex with noble metals. Its application in the extraction of precious metals from WPCB has attracted considerable attention due to its rapid dissolution kinetics and relatively lower environmental impact [55]. Li et al. [55] recovered 90% gold and 50% silver from mobile phone WPCB using thiourea under acidic conditions ($pH = 1$). Despite its advantages, thiourea faces several practical limitations. The reagent is chemically unstable, necessitating higher consumption, which in turn elevates the overall process cost. Moreover, the requirement for an acidic environment restricts its applicability to specific materials, while concerns regarding the potential carcinogenicity of thiourea have further constrained large-scale adoption [56]. Operational parameters, such as pH , thiourea concentration, oxidant concentration, temperature, reaction duration, and particle size, play critical roles in determining extraction efficiency. Although thiourea leaching enables rapid gold dissolution and yields environmentally benign degradation products (elemental sulfur and cyanamide), its economic and stability issues continue to hinder industrial implementation [57].

1.11.1.5. Thiosulphate leaching

Thiosulphate ($(S_2O_3)^{2-}$) is a reducing agent which is widely used in photographic industries. It is another alternative leaching agent to cyanide for the recovery of gold. It can operate under a wider range of pH values, lesser interference with other metals present in WPCB, and considered more environmentally friendly than thiourea, because of the suspected carcinogenic nature of the later [58]. However, high consumption of thiosulphate makes it uneconomical despite its environmental benefits. Ha et al. [59] reported the optimum conditions for leaching

of gold from PCBs to be 72.71 mM thiosulfate, 10.0 mM copper (II), and 0.266 M ammonia. In the presence of ammonia and copper ions, gold can be effectively solubilized into a thiosulphate medium through the formation of a gold(I) thiosulphate complex. Commonly used thiosulphates for leaching of gold or silver are ammonia thiosulphate and sodium thiosulphate. These are soluble in water. Ammonium sulfate and sodium sulfate forms ammonium ions in an alkaline medium making them unstable. So, pH of 9–10 is favorable. The temperature of 40 to 60 °C shows the better dissolution of gold and silver.

1.11.2. Recovery of metals from leachate

The solid metals present in WPCB are oxidized into its ionic form by means of the leaching agent. The ionic form of the targeted metals is reduced back to its solid phase using cementation, solvent extraction, and electrowinning techniques.

1.11.2.1. Cementation

Metals exhibiting lower reduction potential can be used to precipitate metals having higher reduction potential from the solution. Base metals like iron, zinc, and copper are used for replacing precious metals from the solution. Since the 1890s, zinc cementation has been used to recover gold from cyanide solutions commercially. The process is called the Merrill-Crowe process [60]. Similarly, cementing agents such as iron and zinc are extensively used to recover copper from the leachate solution [61]. The process is simple and easily controllable, but some of its disadvantages include formation of oxides and hydroxides on the cementing metal surface. Moreover, in acidic media, dissolution of the cementing agent occurs. Thus, a larger amount of metal powder of cementing metal is required [62]. However, the use of a large amount of metal powder may result in high impurity of the target metal, as the cementing metal will get mixed with the target metal. Furthermore, prior to cementation, the leachate should be free of any residue.

1.11.2.2. Solvent extraction

Solvent extraction or liquid-liquid extraction involves the separation of a compound or metal complex based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. Extractants like amide, amine, methyl-iso-butyl ketone are used. Park and Fray [63] recovered gold from aqua regia solutions by liquid-liquid extraction with toluene. They converted the extracted gold to nano-particles by treatment with dodecanethiol and sodium borohydride. Another example is the recovery of palladium and iridium through liquid-liquid extraction techniques, employing amines and beta-hydroxyoxime with an amine synergist for palladium, and amide-based extractants for iridium [64]. Advantages of this process are: high selectivity, mild reaction conditions, and the ability to process large quantities at a time. However, the solutions are often volatile, inflammable, toxic and not recyclable in the long term [52].

1.11.2.3. Electrowinning

It is a metal recovery process from the electrolyte containing dissolved metals by passing a current with positive redox potential. It is more efficient for metals like, gold, silver and copper but less efficient for metals like chromium and practically impossible for aluminum [65]. The electrons from the current reduces the metal ion to form a solid metal at the cathode. This method has the advantages of being environmentally friendly as it produces zero discharge. Nevertheless, it is almost not possible to obtain a selective recovery of metals from a leaching solution containing a mixture of metal ions, particularly from PCB. Thus, for achieving high selectivity electrowinning can be used at the last stage of metal recovery with other metals removed in the prior steps. However, studies have shown that, it is possible to gain selectivity by adjusting the electrochemical parameters.

This section discussed only a few technologies used in metal recovery from WPCB using hydrometallurgical processing. Various other technologies have been explored either to

improve the efficiency or make it environmentally friendly, such as, deep eutectic solvents, ionic liquids, supercritical fluid technologies, etc. [66-68].

1.11.3. Recovery of copper from WPCB using hydrometallurgy

The leaching of copper depends on various parameters such as the type and concentration of the leaching agent, time, temperature, mixing rate, and so on, including its exposure to the leaching agent [69, 70]. The solder mask present in the outer layer of WPCB hinders the penetration of the leaching agent. Thus, the powder form of WPCB is commonly used [71]. However, grinding generates dust and material loss while handling [72, 73]. The dust particles containing heavy metals, BFRs and glass fiber particles are detrimental to human health [41, 74]. In the case of larger pieces, delamination/removal of solder masks using chemicals or thermal treatment prior to leaching is required. A Few studies that employed grinding or size reduction, thermal or chemical processing as pretreatment steps are summarized in Table 1.4 [75, 76]. However, a comparative analysis of leaching efficiencies influenced by grinding and thermal pre-treatment (pyrolysis) remains unreported in the literature. Recently, Kurniawan et al. [76] reported on combined pyrolysis and leaching of copper using ammoniacal solvleaching. The study determined optimal pyrolysis and solvleaching parameters for the recovery of copper. A comparison evaluation of the copper leaching efficiency from WPCB samples in the form of cut pieces and powder, before and after pyrolysis is essential to clarify the influence of comminution and/or pyrolysis before metal extraction. Furthermore, the recovery of copper in its solid form has been overlooked in existing studies (Table 1.4). For leaching of copper, inorganic acids HCl, HNO₃ and H₂SO₄ are commonly used [42, 43]. Considering the economic and environmental concerns, H₂SO₄ is a better leaching agent for acid leaching of copper. However, an oxidant is required in addition to H₂SO₄ to obtain better leaching efficiency.

Table 1.4 Relevant literature for the recovery of metals from pretreated WPCBs using hydrometallurgy

Type	WPCB source	Feed size	Pre-treatment method in detail	Cementation	Target metal(s)	References
Thermal pretreatment	Bulk/mixed	NA	Pyrolysis at 500 °C	No	Cu	Kurniawan et al. [76]
	Mobile phone	20×15 mm ²	Microwave pyrolysis (700W)	No	Cu	Lv et al. [77]
	Mobile phone	3.1×2.4 cm ²	Microwave pyrolysis (300 W) and conventional pyrolysis at 400 °C	No	Cu, Al, Au	Huang et al. [78]
Chemical pretreatment	Mobile phone	NA	Delamination using DMA [#]	Yes	Cu, Ni, Zn, Au and Ag	Rao and Singh [79]
	Mobile phone	1×1 cm ²	Delamination using DMA	No	Cu	Rao et al. [43]
	Computer	2×2, 4×4 and 6×6 cm ²	Delamination using NaOH	No	Base and precious metals	Jadhao et al. [75]
	NA	4×4 cm ²	Delamination using NaOH	No	Base and precious metals	Jadhao and Hocheng [80]
Grinding	Mixed	<2 mm	No	No	Cu, Al, Zn,	Ishak et al. [81]
	NA	<1 mm	No	No	Cu	He et al. [72]
	Computer	250–354 µm	No	Yes	Sn and Pb	Moosakazemi et al. [82]
	Mobile phone	≤200 mesh	No	No	Cu	Hossain et al. [83]

DMA[#]: Dimethylacetamide

1.12. Bio-metallurgical processing

As the name suggests, the principle involved is the interaction of microorganisms (bacteria or fungi) with WPCB. The leaching agents required are produced by the microbes, including organic/inorganic acids, cyanide or sulfate ions. The metal ions separated out in the solution form precipitate or complexes which is then separated for direct use or further refinement [84]. The advantages of this process include small amount of wastewater discharge, and mild operating conditions. Recently, Silva et al. [85] conducted bioleaching of copper from WPCBs using the fungus *Aspergillus tubingensis* UCP 1208. In search of cleaner alternative to the existing E-waste processing methods, bio-metallurgy is gaining wide attention [86, 87]. But due to the use of microorganisms, this method has disadvantages like, microorganisms are sensitive to change in environment, requirement of a large amount of nutrients for the microbes and small particle size for higher contact area, and it takes a long time to reach a high recovery rate [46]. Efficiency of the process depends on the chemical composition of the culture media, particle size, and pH of the solution [88].

1.13. Pyrolysis

Pyrolysis is an emerging and favorable technology for the processing of WPCB. The word “pyrolysis” has been derived from the two Greek words *pyro* meaning “fire” and *lysis*, meaning “separation”. Pyrolysis is a thermochemical conversion technology which occurs in an oxygen-free environment, leading to the decomposition of organic materials into smaller chemical compounds. The volatiles present in the feedstock gets separated out in the form of hydrocarbon gas, which when passed through a condenser generates the liquid product. The non-condensable gases form the gas fraction and the non-volatile components are left inside the reactor. Thus, three different products, namely solid/char, liquid/oil and gas are produced from pyrolysis (Fig. 1.8). The yield distribution of the pyrolytic product fractions depends on the pyrolysis process parameters: temperature, heating rate, and residence time, whereas the

composition of the product fractions is dependent on the type of feedstock used. For instance, if the feed material is biomass derived, then the oil will have higher aqueous phase than the oil produced from plastic pyrolysis. Another example is that high lignin content biomass produce relatively higher amount of biochar yield [89]. In case of WPCB, brominated epoxy resin gets thermally degraded. The polymer fraction present in WPCB can be valorized to valuable oil and gas fractions, leaving behind the metal enriched char. However, it is an energy intensive process and the brominated compounds are transferred into the product fractions making them unfit for further applications due to the associated environmental risks. Hence, the distribution of bromine and its fate during pyrolysis needs to be studied.

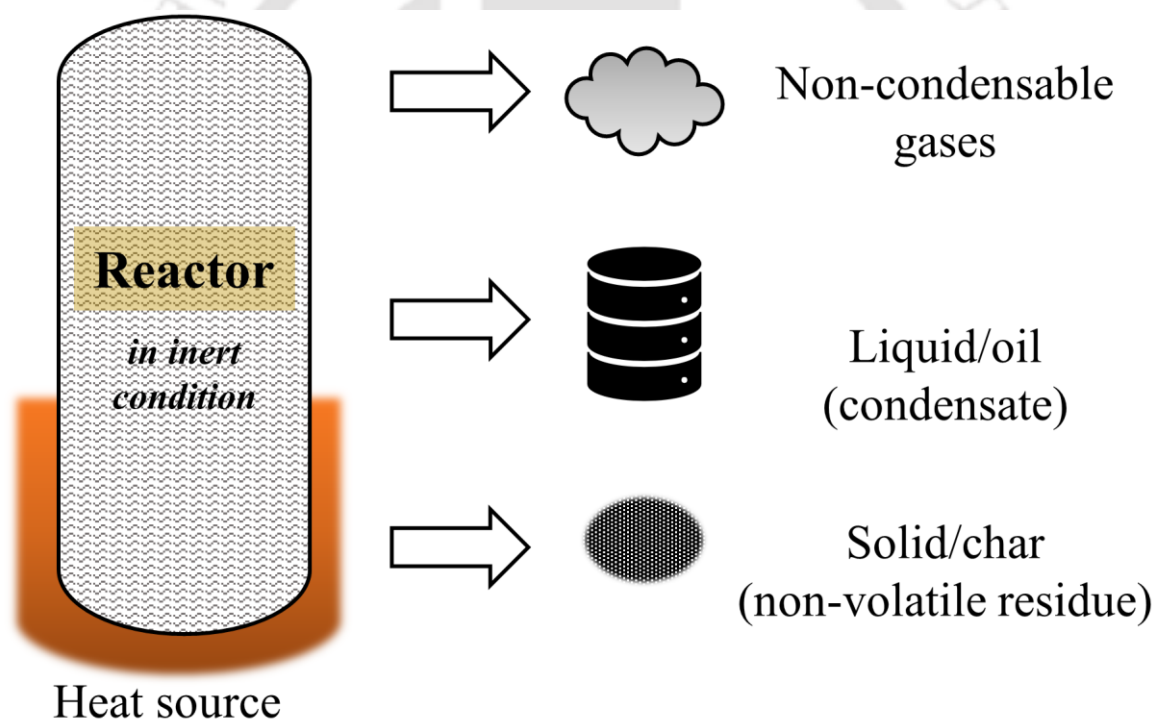


Fig. 1.8 Schematic diagram showing the pyrolysis product fractions

Pyrolysis can be classified into slow, intermediate, fast and flash based on the operating parameters (Table 1.5) [90]. The effect of the critical pyrolysis parameters temperature, heating rate and residence time has been discussed in the subsequent sections.

Table 1.5 Types of pyrolysis based on its operating condition [89, 90]

Parameters	Types of pyrolysis			
	Slow pyrolysis	Intermediate pyrolysis	Fast pyrolysis	Flash pyrolysis
Temperature	400–650 °C	400–500 °C	600–650 °C	~ 1000 °C
Heating rate	Up to 100 °C/min	1–70 °C/min	Up to 1000 °C/s	>700 °C/s
Residence time	5 to 30 min to days	2–5 min	<2 s	<0.5 s
Primary product(s)	Char	Oil and gas	Oil and gas	Oil

1.13.1. Pyrolysis temperature

Temperature plays an important role in the pyrolysis process. With the increase in pyrolysis temperature the feedstock material gets thermally degraded by breaking the bonds present in the polymers and starts to release the volatile components in the form of gas. The study conducted by Zhu et. al. [91] on WPCB pyrolysis reported an increase in oil yield from 9.58% (at 400 °C) to 10.95 and 12.24% at 500 °C and 600 °C, respectively, for the heating rate of 10 °C/min. The liquid/oil yield started reducing above 600 °C, accompanied by increased gas yield. Another study by Jadhao et al. [92] obtained the maximum weight loss for the pyrolysis of WPCB (mobile phones) within 500 °C and on increasing the hold time (at 500 °C) from 10 to 30 min, it increased from 12.4 wt% to 22.8 wt%, respectively.

1.13.2. Heating rate of pyrolysis

The heating rate of pyrolysis is another important parameter of pyrolysis process. With increase in heating rate, the decomposition curve and maximum weight loss rate shifts to higher temperature. The retention time decreases with the increase of heating rate in the condition of the same final temperature, resulting in the decomposition curves shifted to higher temperatures. Besides that, high surface temperature and lower inner temperature of the sample can delay the decomposition reaction causing lower product release.

Diaz et al. [93] compared the degradation mechanism of WPCB for slow and fast pyrolysis. It was reported that, the slow pyrolysis could be divided into three stages; stage I (220–345 °C), stage II (345–775 °C), and stage III (>600 °C). Each stage can be varied by the difference in reaction mechanism and kinetic parameters. In the stages, I and II, 98% of the organics were reported to be released, which was evidenced by the kinetic studies. It was also reported that, the degradation speed of stage I is 7.5 times faster than stage II. The fast pyrolysis at a temperature above 600 °C produced high value syngas with a lower amount of H₂O (g) and high amount of CH₄ and H₂. Moreover, in the case of fast pyrolysis, the variety of compounds

in the product stream increased. Similarly, Cao et al. [94] compared slow (10 °C/min) and fast (600 °C/min) heating rates of WPCB pyrolysis. The study revealed that the composition of pyrolytic product fractions is dependent on the pyrolysis heating rate. At fast heating speed, the chemical bonds in WPCBs were almost simultaneously cracked because of the high energy supply. Therefore, the BRFs were broken down into HBr, Br₂ and bromophenol. Moreover, the fast heating speed may increase the yield of pyrolysis gas because of the facilitating the formation of small molecular such as phenol, CH₄, and C₂H₄. The low heating speed produced some long-chain alkanes, polycyclic aromatic hydrocarbons and polybrominated compounds [95].

1.13.3. Residence time

Residence time or hold time signifies the amount of time the polymers are present in the reactor system [96]. Prolonged residence time allows the formation of oil and gas fractions. However, longer residence time leads to the occurrence of secondary cracking reaction of the vapors, thereby producing unwanted compounds leading to unfavorable product yields. Thus, determination of optimum residence time is essential. Several studies across various feedstock materials have reported the influence of residence time on the pyrolytic product fractions [97, 98]. Zhu et al. [99] reported that pyrolysis of WPCB at high temperature and longer residence time promotes the formation of alkenes and aromatics.

1.13.4. Thermal degradation kinetics of WPCB

Prior to designing a pyrolysis process, it is essential to understand the thermal degradation kinetics of the feedstock material, particularly for a complex sample like WPCB. Thermogravimetric analysis (TGA) is an analytical technique to determine the thermal degradation behavior of a material using minimal sample quantities, thereby minimizing heat and mass transfer limitations and approximating ideal pyrolysis conditions [100]. Thermal degradation kinetic analysis derived from TGA data provides a reliable means to determine the

kinetic triplets: activation energy (E), reaction model $\{f(\alpha)\}$, and pre-exponential factor (A). In addition to establishing reliable kinetic parameters, understanding the influence of material composition is crucial for the pyrolysis of WPCBs. These boards comprise a heterogeneous mix of metals, organic polymers, inorganic fillers (glass fibers), and hazardous substances (BFRs and heavy metals). Consequently, WPCB valorization employs diverse technologies tailored to specific recovery targets, such as metals or organics. Moreover, effective management of toxic constituents remains dominant to mitigate environmental risks associated with the recycling techniques. Thus, prior to designing a pyrolysis process, comprehensive evaluation of WPCB thermal degradation characteristics, along with the impacts of embedded metals and the toxic chemicals such as BFRs on kinetic parameters is essential. This will give an idea on the influence of these materials on the thermal degradation mechanism of WPCB and lead us to develop a viable route for valorization of WPCBs.

Liu et al. [101] performed a kinetic study on the influence of copper on the thermal degradation of epoxy-based printed circuit boards using the Ozawa–Flynn–Wall (OFW) model. The copper altered the degradation stages, increased the reaction rate and decreased the activation energy. The thermogravimetric-fourier transform infrared spectroscopy (TG-FTIR) analysis augmented that copper also reduced the carbonyl and brominated compounds to some extent. Gao et al. [102] reported that the coexisting copper had reduced the activation energy from 175 to 164 kJ/mol using Šesták–Berggren model and the organic bromides (bromophenols) were converted to inorganic bromides (Br_2 and HBr). The random nucleation and random growth reaction pathways were changed to the phase boundary reaction, diffusion reaction, and nucleation reaction pathway. Furthermore, Lie et al. [103] showed the effect of in-situ metals in FR4-PCB using Kissinger–Akahira–Sunose (KAS) and thermodynamic properties. The in-situ metals reduced the degradation temperature by 15 K. Moreover, the presence of metals accelerated the production of lighter hydrocarbons and aromatics.

Previous studies have primarily focused on the activation energy to examine the impact of metals on the pyrolysis of WPCB applying kinetics; however, the essence of the kinetic triplets for a complete understanding of the process and verification of the kinetic parameters has not been considered (Table 1.6).

Most importantly, the effect of the presence of BFR during the thermal degradation kinetics of WPCB has not been reported. BFRs are directly related to the thermal degradation process as they are supposed to delay the degradation process and hence, it is important to check the kinetic parameters. The current literature available is mainly focused on the technologies involved in the reduction of the release of brominated compounds during the pyrolysis process.

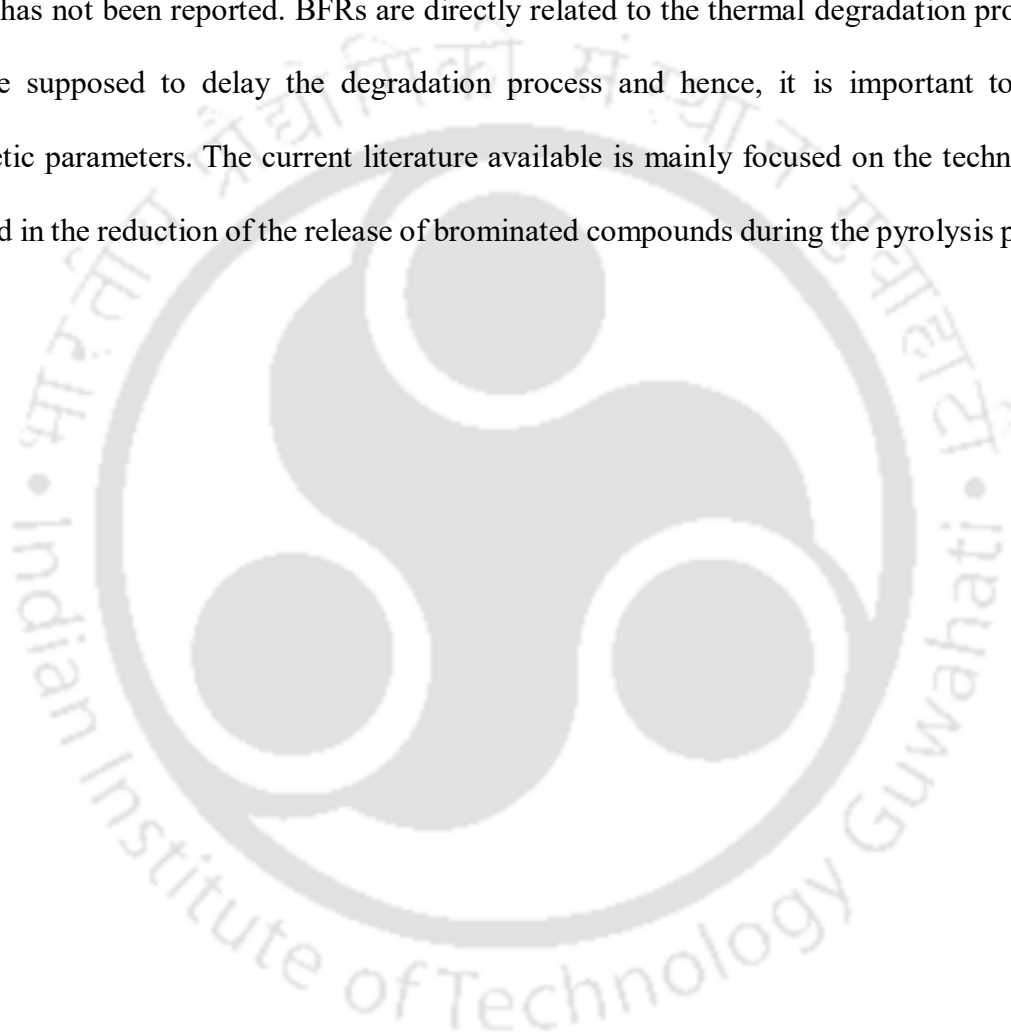


Table 1.6 Kinetic parameters for thermal degradation of waste printed circuit board

Material information	Method	Activation Energy, E_a (kJ/mol)	Pre-exponential Factor, A (1/s)	Kinetic Model, $f(\alpha)$	References
PCB (motherboard), metals removed	Vyazovkin	158.90	-	-	Krishna et al. [104]
PCB with some Cu, size <0.5 mm	OFW KAS Tang	215.00 247.80 216.90	-	Mampel (P3) and A2	Wu et al. [105]
PCB with metals	DAEM [#] and Vyazovkin	188.40	$(\alpha = 0.1-0.7)$ $9.0 \times 10^7 - 4.3 \times 10^{12}$	-	Krishna et al. [106]
PCB with metals	KAS	128.28–329.70	$(\alpha = 0.05-0.7)$ $4.3 \times 10^9 - 2.8 \times 10^{28}$ $(\alpha = 0.10-0.70)$	-	Liu et al. [103]
PCB with Cu	Differential	164.45, average ($\alpha = 0.2 - 0.8$)	$\ln A = 16.61945$, average	Šesták-Berggren model	Gao et al. [102]

[#]DAEM: Distributed activation energy model

1.13.5. Optimization of lab-scale WPCB pyrolysis parameters

Pyrolysis has been considered as the most acceptable form of WPCB recycling process as, it converts the organic fraction into valuable oil and gas fractions, which are mostly discarded after the recovery of higher market value components, the metals. WPCB material composition contains majority of inorganic fraction (~70%) resulting into minimal oil yield. Thus, it is essential to determine the optimum parameters that could produce maximum oil yield. The product distribution in a pyrolysis process depends on the independent parameters temperature, heating rate, and hold time. However, previous studies did not employ advanced statistical tools such as response surface methodology (RSM) for systematic optimization. RSM is a trusted tool for identifying the significant and optimum parameters of a system. A limited number of RSM studies on different aspects of thermal degradation behavior of circuit board have been reported in the literature for example, Jayapradha et al. [107] studied liquefaction of WPCB, Liu et al. [108] reported vacuum pyrolysis of integrated circuits, which is an electronic component in a WPCB. In a recent publication Kurniawan et al. [109] reported RSM studies on WPCB pyrolysis considering maximization of 'weight loss' as the objective function and focused on the solid characterization. These studies primarily focused on broader degradation characteristics rather than optimizing pyrolysis parameters to maximize oil yield and minimize char yield.

1.14. Reduction of brominated compounds

Pyrolysis has emerged as a promising and sustainable technology for material recovery from WPCBs. A major challenge in WPCB pyrolysis is the formation of brominated compounds in the volatile (oil and gas) phase due to the BFRs, primarily present in the epoxy resin. Moreover, the presence of organo-brominated compounds in the oil makes it unsuitable for the application. Understanding the distribution of bromine during the pyrolysis is crucial as it enables optimization of experimental conditions to obtain the desired product. Brominated compounds

in the gas phase can be removed by passing the gas through an alkaline solution before release into the environment or use in downstream applications [110]. Zhu et al. [91] used 0.5 mol/L NaOH solution to absorb the brominated gases produced during the WPCB pyrolysis. However, the removal of brominated compounds from the oil fraction remains challenging. The reduction of bromine content in the oil phase can be performed using two routes. Bromine content reduction in the feed material (before pyrolysis) or deviation of bromine (during pyrolysis) into other phases by use of additives/catalyst.

Pre-treatment methods employing extraction such as Soxhlet, microwave-assisted, ultrasound-assisted extraction, solvothermal and supercritical fluid have been studied to reduce bromine content in E-waste components. These studies were primarily focused on the components other than WPCB (such as E-waste plastics), which do not contain a metal fraction [111-114]. The extraction efficiency of bromine also varies depending on its material composition. Moreover, these studies did not encounter the effect of the extraction process (quantitative and qualitative) on the pyrolysis product fractions. Hence, the effect of pre-treatment step on the product characteristics needs to be studied. Among these extraction processes, Soxhlet extraction provides an exhaustive extraction efficiency at lower cost.

Another strategy to control the bromine content in the volatile phase is the inclusion of additives (such as metal oxides, catalysts, or co-pyrolysis) during pyrolysis without requiring any pre-treatment steps [115-119]. Pyo et al. [120] demonstrated that zeolite-based catalysts can effectively capture bromine species during pyrolysis, thereby limiting their transfer into the volatile fractions. Similarly, Zhang et al. [121] reported enhanced bromine fixation efficiencies using basic additives such as NaOH, K_2CO_3 , and Na_2CO_3 . Despite their effectiveness, the use of external additives or catalysts can increase overall process costs and complexity. To avoid this additional cost factor, the ability of embedded metals in WPCB to reduce the bromine content in the volatile phase needs to be studied. The effect of the embedded

metals in WPCB on kinetic and thermal degradation parameters has been reported [100]. However, to the best of our knowledge, a comprehensive investigation into the effects of these metals on the distribution and characteristics of pyrolysis products (char, oil and gas) has not yet been established. Co-pyrolysis studies with biomass and plastic have also been reported to regulate the product characteristics in favorable conditions. Shen et al. [122] studied the co-pyrolysis of the nonmetallic fraction of WPCB (pre-treated with acid) with rice-husk and NaOH loading for bromine fixation in char and the application of the produced syngas was discussed. Kinetic studies on co-pyrolysis of WPCB with plastic and biomass materials such as *Sargassum wightii* (microalgae), cotton stalk, rice husk and tea seed shell have been reported [123-126].

1.15. Simulation of a WPCB recycling plant and techno-economic assessment

Lab-scale studies provide an idea about the quantitative and qualitative aspects of the recovered products. However, before setting up a process plant at an industrial scale, it is essential to perform the scale-up studies and techno-economic assessment of the plant [127]. In case of WPCB recycling process, a plant containing a combination of size reduction, pyrolysis and metal extraction has the potential to recover both the organic and inorganic materials, thereby reducing the loss of materials. Such complex process plants can be simulated using Aspen Plus® software for determining the mass and energy balance and then, an optimum flowsheet can be developed. Moreover, Aspen Plus® has an in-built economic analyzer, which can be used to perform the techno-economic assessment of the plant. Recently, Debnath et al. [128] performed the Aspen Plus® simulation of WPCB pyrolysis process, followed by techno-economic analysis, however, did not consider the comminution and the metal extraction process. To the best of our knowledge, a combined simulation and techno-economic analysis of pyrolysis and hydrometallurgical methods has never been reported [129, 130]. The economic evaluation parameters: net present value (NPV), internal rate of return (IRR), profitability

index (PI), and payback period (PBP) are used to evaluate the performance of a plant. Discounted cash flow (DCF) analysis provides a detailed investigation of the cash flow occurring annually throughout the plant's life time. In case of WPCB pyrolysis, the selling price of oil is uncertain because of its unestablished market, thus determining its minimum selling price (MSP) is a suitable option, rather than assuming price of other type of oil.

1.16. Research gap

Based on the literature review performed on the resource recovery processes from WPCB, the following research gaps have been identified.

1. The previous kinetic studies on WPCB have mainly focused on the determination of activation energy, but not the kinetic triplets and reconstruction. Additionally, the effect of the presence of metals and reduced bromine content in WPCB on the kinetic triplets has not been studied.
2. The optimization of WPCB pyrolysis parameters using RSM for the objective function, minimization of char and maximization of oil yield has not been studied.
3. A study of reduced bromine content in pyrolytic oil via two routes, (a) bromine reduction in the feed before pyrolysis, and (b) the presence of embedded metals, has not been discussed.
4. Comparison of copper leaching efficiency from WPCB for the effect of (a) grinding and (b) pyrolysis of cut pieces has not been discussed. Most of the studies focus on optimizing the operating parameters to obtain the maximum leaching efficiency. Moreover, very few studies have reported the precipitation of copper from leachate.
5. Simulation of a plant containing combined comminution, pyrolysis, and metal extraction using Aspen Plus[®] and its techno-economic assessment has not been reported.

1.17. Research objectives

Based on the research gaps, the following objectives were framed:

1. Kinetic study for the thermal degradation of waste printed circuit board using isoconversional methods and the effect of metals and reduction of bromine content on the kinetic parameters
2. Optimization of pyrolysis parameters to achieve minimum char and maximum oil yield using response surface methodology
3. Study for the reduction of bromine content in pyrolytic oil
4. Recovery of copper from waste printed circuit boards using acid leaching and cementation
5. Simulation of a material recovery plant from WPCB using Aspen Plus[®] and techno-economic assessment of the plant

The key challenges faced during the recycling of E-waste is its complex mixture of materials. Hence, development of a systematic approach for the recovery of materials from the E-waste is essential.

1.18. Thesis outline

Considering the research gap and formulated research objectives, the thesis has been divided into eight chapters.

Chapter 1: This chapter outlines the overview of E-waste, highlighting the global and Indian scenarios. Environmental impacts caused by the unprofessional handling of E-waste and recycling methods are discussed. Relevant literature related to the objectives is discussed in detail.

Chapter 2: This chapter includes a complete description of the materials and chemicals used, experimental setup, operating conditions of the experiments, and details on characterization techniques used for the feed materials and the product fractions.

Chapter 3: This chapter includes the kinetic parameter determination using isococonversional methods, reconstruction, and the effect of WPCB composition (presence of metals and bromine) on kinetic triplets.

Chapter 4: The optimization of lab-scale pyrolysis parameters using response surface methodology and the identification of the most significant parameter has been discussed. Further, qualitative analysis of the pyrolytic products produced at increasing temperature were performed using analytical techniques.

Chapter 5: This chapter presents a study on the reduction of bromine content in oil by means of Soxhlet extraction of feed material and the action of embedded metals during pyrolysis.

Chapter 6: This chapter compares the leaching efficiencies of copper from WPCB for different sizes and their pyrolyzed versions. The cementation of copper after acid leaching has been presented.

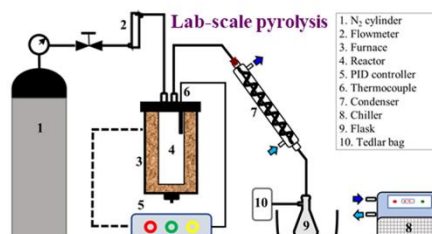
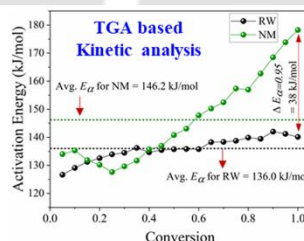
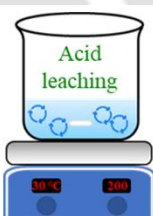
Chapter 7: This chapter contains a simulation of a plant containing comminution, pyrolysis and metal extraction sections using Aspen Plus® software. The techno-economic assessment of the plant has been discussed.

Chapter 8: This chapter presents the combined summary and conclusion of the thesis work, and suggestions for future work are also presented.

Chapter 2

Materials and methodology

- Feedstock preparation
- Characterization techniques
- Analytical instruments
- Kinetic analysis
- Lab-scale pyrolysis
- Response surface methodology
- Aspen Plus® simulation



Aspen Plus® simulation & Techno-economic assessment

Material composition

Proximate analysis

TGA

CHNSO

FTIR

ICP-MS

XRF

NMR

GC

GC-MS

Bomb calorimetry

Ion chromatography

2. Materials and methodology

This chapter includes a comprehensive discussion on the feedstock material, experimental procedures and characterization techniques. The samples acquired, its preparation techniques, and its nomenclature has been introduced in this chapter. The lab-scale experiments performed to fulfil the research gaps introduced in Chapter 1 has been described, such as the operating conditions of the pyrolysis experiments, about the reactor set-up, the acid leaching and the Soxhlet extraction set-up, etc. The theories associated with the determination of kinetic triplets (activation energy, reaction model, and pre-exponential factor), and the methodology associated with the kinetic triplet determination and validation of the calculated parameters has been discussed in detail. This chapter provides a complete explanation of the analytical instruments used for the determination of the composition of the prepared samples, effect of various pre-treatment methods on these samples, and characteristics of the product fractions obtained. This thesis also includes simulation studies and techno-economic assessment, hence all the relevant assumptions and concepts associated with them will be discussed.

Overall this chapter contains the theories associated with proposed objectives in Chapter 1, and Chapter 2 is connected to all the future chapters. Thus, this chapter plays an important role in developing a foundation for the thesis.

2.1. Feedstock preparation

Waste printed circuit boards (WPCBs) from computer systems (commonly referred to as motherboards) were collected from a local vendor and the Indian Institute of Technology Guwahati campus. Approximately 50 motherboards from various manufacturers, including Asus, Dell, HP, and Acer, were procured. These boards contained mounted electronic components (ECs) such as resistors, capacitors, cooling fans, memory slots, CPU sockets, USB ports, and ISA slots. These ECs were mechanically removed to obtain bare/depopulated WPCBs. The boards were then cut into fragments of approximately $1 \times 1 \text{ cm}^2$ using an angle grinder (PMAG4-670B, Polymak, India) and an aviation snip (Stanley, India). The fragmented pieces were thoroughly washed with deionized (DI) water and subsequently dried in a hot air oven at 102°C for 12 h (Reico, India). These cleaned and dried WPCB fragments were denoted as “RW-cut” (meaning raw WPCB cut) and will be used as such in the subsequent chapters. A portion of the RW-cut was further subjected to size reduction using a heavy-duty mixer grinder (Imperium Ventures, India) and sieved using 150 British standard sieves (BSS). The obtained WPCB samples in the powder form ($<100 \text{ }\mu\text{m}$) were named as “RW”. These samples (RW-cut and RW) were subsequently characterized to determine the material composition and used for experimental purposes in its original form as well after modification(s), whenever required.

2.2. Chemical reagents used

All chemical reagents used, including hydrochloric acid (HCl, 35%), nitric acid (HNO_3 , 69%), hydrofluoric acid (HF, 48%), sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), acetone, toluene, dichloromethane, and 2-propanol, were of reagent grade and that used for chromatography purposes were of chromatography grade. These chemicals were used procured from Merck Chemicals and used as received without any alterations.

2.3. Characterization techniques for the feedstock and product fractions

2.3.1. Composition of polymer, metals and ceramic fraction in WPCB

Waste printed circuit boards primarily consist of three major components: polymer, metal, and ceramic fractions. The weight percentage (wt%) of each component was determined using a mass loss approach. Initially, weighed samples were subjected to thermal treatment (ignition) at 600 °C for 2 h in a crucible with open lid inside a muffle furnace (Reico, India). The mass loss observed in this process was attributed to the polymeric content (Eq. 2.1). The residual inorganic material was then acid leached using a freshly prepared acid mixture of hydrochloric acid (HCl, 35%) and nitric acid (HNO₃, 69%) in the ratio 3:1 (v/v), with solid to liquid (S/L) ratio of 1:10 (g/mL). After 4 h of leaching time, the leachate was diluted with DI water, and the residue was washed and filtered out using a vacuum filtration unit (Borosil, India) and the oven-dried residue was weighed. The mass loss observed during the acid leaching was allocated to the metal content (Eq. 2.2) and the remaining mass, white fibrous in appearance, was attributed to the ceramic fraction (glass fibers), determined using Eq. 2.3.

$$\text{Polymer (wt\%)} = \frac{X - Y}{X} \times 100\% \quad (2.1)$$

$$\text{Metal (wt\%)} = \frac{Y - Z}{X} \times 100\% \quad (2.2)$$

$$\text{Ceramic (wt\%)} = 100 - (\text{Polymer} + \text{Metal}) \quad (2.3)$$

where X , Y and Z are the weights (g) of WPCB sample, WPCB sample after ignition, and WPCB sample after ignition and acid leaching, respectively.

2.3.2. Proximate and CHNSO analyses

The proximate analysis determines the moisture (MC), volatile matter (VM), ash (AC), and fixed carbon (FC) content present in the sample. It is an important analysis to get an idea on

the fuel property of the sample. The weighted sample WPCB samples were kept in a hot air oven (Reico, India) at 102 °C for 12 h to calculate the moisture content. Using a muffle furnace (Reico, India) and the ASTM D-5142 technique, the analysis was performed [131]. The composition of the elements C, H, N and S were obtained from the CHNSO analysis (Vario MACRO Cube, Elementar, Germany). In this case, since powder sample is required, the oven-dried RW sample was used for the analysis. The oxygen content was calculated using Eq. 2.4.

$$\text{Oxygen content (wt\%)} = 100 - (\text{C} + \text{H} + \text{N} + \text{S} + \text{Ash}) \quad (2.4)$$

2.3.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was employed to identify the functional groups present in the samples by analyzing their interaction with infrared radiation. This non-destructive analytical technique offers rapid results and is well-suited for compositional analysis. FTIR measurements were carried out using a Spectrum Two spectrometer (PerkinElmer, United States) in transmittance mode over a wavenumber range of 4000–450 cm⁻¹ to characterize the samples. This analysis was performed on the feedstock (<100 µm), oil and the char fractions obtained under varying pyrolysis conditions. This facilitated the identification of polymer types in the WPCB and enabled monitoring of structural changes in the polymeric fraction during the thermal degradation.

2.3.4. Thermal degradation study

Thermogravimetric-derivative thermogravimetric (TG-DTG) analyses are the base for kinetic study and pyrolysis experiments. The thermal degradation characteristics of the WPCB samples were studied using NETZSCH, TG 209 F1 Libra, Germany, in the temperature range of 30 to 1000 °C. A sample weighing 7–8 mg was used in an inert atmosphere created by purging N₂ gas (99.999 % purity) as purge (40 mL/min) and protective gases (20 mL/min). The non-isothermal temperature programs with heating rates of 5, 10, 20 and 50 °C/min were

employed for the experiments. The heating profiles and the degradation range obtained were used to perform the kinetic study (section 2.4) and lab-scale pyrolysis experiments (section 2.5).

The degradation profile has three parameters: onset temperature (T_{onset}), meaning the beginning of the thermal degradation, maximum degradation temperature (T_{max}) which tells the temperature at which the degradation rate is the fastest and the offset temperature (T_{offset}) which gives the temperature value at which the thermal degradation ends. These parameters were determined by using the tangent method in the plot of normalized mass loss (%) versus temperature ($^{\circ}\text{C}$).

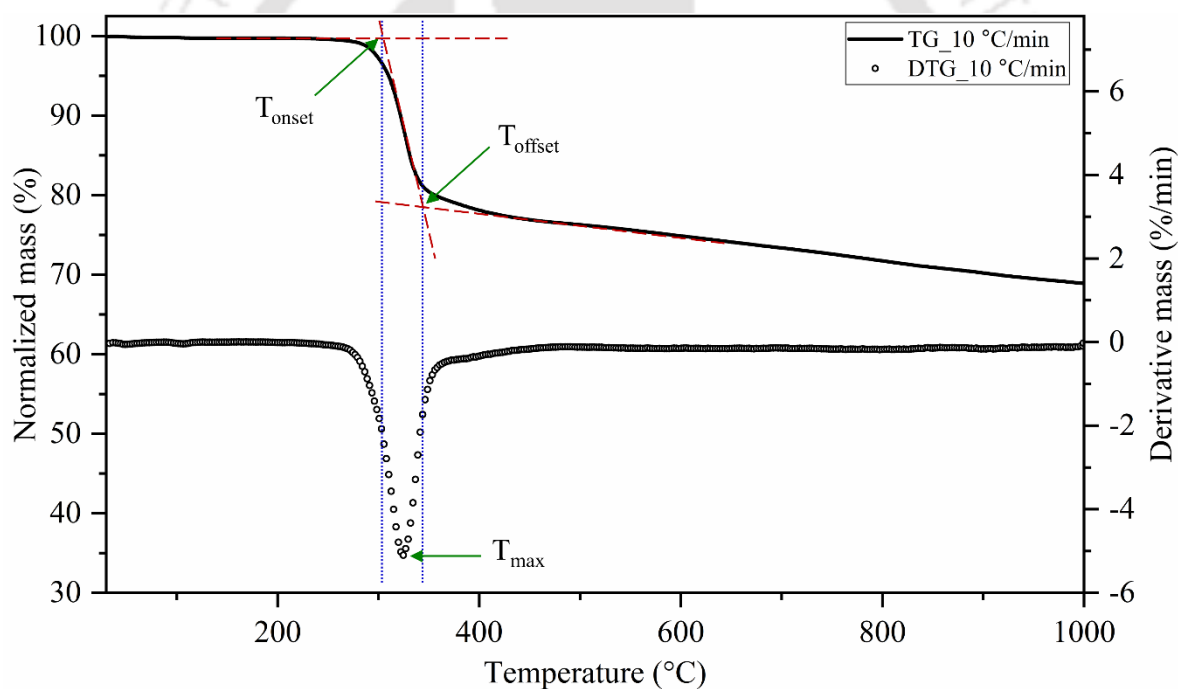


Fig. 2.1 Determination of T_{onset} , T_{max} and T_{offset} temperatures in a TG-DTG profile of WPCB

2.3.5. Inductively coupled plasma mass spectrometry analysis

Inductively coupled plasma mass spectrometry (ICP-MS) was employed for determination of metal concentration due to its exceptional sensitivity, precision, and ability to detect elements at trace-level. The technique utilizes an argon plasma to atomize and ionize the sample,

followed by mass spectrometric detection of the resulting ions. Solid samples, including the feedstock and char samples, were subjected to microwave-assisted acid digestion using an acid mixture of 10 mL containing HNO₃, HCl, HF and H₂O₂ in Teflon-lined closed vessels (ETHOS EASY, Advanced Microwave Digestion System, MILESTONE, Italy). The digestion was carried out at 230 °C for 1.5 h [132]. Metal concentrations were quantified using an ICP-MS instrument (7850 ICP-MS, Agilent Technologies, United States), calibrated with a standard solution containing 24 analytes from Agilent. A linear calibration curve with a correlation coefficient (R^2) greater than 0.99 was established prior to sample analysis to ensure quantification accuracy. Then the metal concentrations were reported in wt% (Eq. 2.5).

$$\text{Metal concentration (wt\%)} = \frac{C_{\text{ICP}} \times \text{DF} \times V_{\text{final}}}{W_{\text{sample}}} \times 100 \quad 2.5$$

where, C_{ICP} = concentration of analyte in final solution obtained from ICP-MS (mg/L), DF = dilution factor, V_{final} = total volume of the final solution in which the sample is dissolved (L), and W_{sample} = mass of the original sample digested (g)

The ICP-MS instrument was also used to evaluate copper and zinc concentrations in the liquid solutions obtained from leachate and the solution after cementation processing.

2.3.6. X-ray fluorescence spectroscopy analysis

X-ray Fluorescence (XRF) spectroscopy was utilized to determine the composition of the inorganic elements such as Si, Al, Ca, etc., including Bromine present in RW and its counterparts after modification(s). The analysis was conducted using a Zetium DY 2942 XRF spectrometer (Malvern PANalytical, United Kingdom), which enables non-destructive elemental analysis across a broad range of elements (Na to U). For sample preparation, 1 g of powder sample was homogenized with boric acid using a mortar and pestle, and the mixture was then compressed into pellets. In XRF analysis, high-energy X-rays excite the sample

atoms, causing the ejection of inner-shell electrons. The subsequent electronic transitions from higher to lower energy levels result in the emission of characteristic X-ray fluorescence, which serves as a unique elemental fingerprint. The emitted spectra allow for qualitative, semi-quantitative, and quantitative determination of major, minor, and trace elements present in the sample. This analysis facilitated the indication of BFRs, as indicated by bromine content, and other inorganic elements, with all elemental concentrations expressed in normalized form to represent their relative abundance within the sample.

2.3.7. Oxygen bomb-Ion chromatography

The absolute concentration (wt%) of bromine was measured using the combination of a bomb calorimeter (Toshniwal Technologies Pvt. Ltd, India) and an ion chromatography using EPA-5050 method. This method provides accurate halide (including bromine) concentration present in solid as well as liquid samples. To perform the analysis, weighted samples were combusted inside a high-pressure bomb containing 10 mL of 0.1 M NaOH solution to trap the brominated compounds in it. This solution was then analyzed using a 236 Ion chromatograph (792 Basic IC, Switzerland) equipped with a METROSEP A Supp 5- 237 250/4.0 separation column (4×100 mm²) to determine the bromide concentrations. The concentration (µg/g) of bromine (C_{Br}) was calculated using Eq. 2.6.

$$C_{Br} = \frac{C_{com} \times V_{com} \times DF}{W_o} \quad (2.6)$$

where, C_{Br} = concentration of bromine in the sample (µg/g), C_{com} = concentration of bromine in the combustate (µg/mL), V_{com} = total volume of combustate (mL), DF = dilution factor and W_o = weight of sample combustate (g).

2.3.8. Simulated distillation analysis

Simulated distillation (SimDist) analysis was conducted on the pyrolytic oil samples obtained at varying operating conditions of WPCB pyrolysis process, which were diluted in chromatography-grade dichloromethane (DCM) in 1:30 (v/v) ratio and syringe filtered (0.45 μm) before the analysis. The carbon number distribution of the oil samples was determined using gas chromatography (GC) (Trace 1110, Thermo Fisher Scientific, USA), equipped with a TR-SD capillary column (10 m $\times$ 0.53 mm $\times$ 2.65 μm). The injector and detector temperatures were maintained at 280 $^{\circ}\text{C}$ and 340 $^{\circ}\text{C}$, respectively. The oven temperature program included an initial hold at 40 $^{\circ}\text{C}$ for 2 min, followed by a ramp of 10 $^{\circ}\text{C}/\text{min}$ to 310 $^{\circ}\text{C}$, with a final hold for 10 min at 310 $^{\circ}\text{C}$. A hydrocarbon standard mixture (C_7 to C_{40} alkanes standard, Sigma Aldrich) containing hydrocarbons from C_7 to C_{40} (each at equal weight percentage) was used for calibration and classification of the pyrolytic oil components into light ($\text{C}_7\text{--C}_{11}$), middle ($\text{C}_{12}\text{--C}_{20}$), and heavy carbon fractions (C_{20+}).

2.3.9. Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GC-MS) analysis was employed to determine the chemical composition of the pyrolytic oil fractions using a TRACE 1600 gas chromatograph coupled with an ISQ 7610 single quadrupole mass spectrometer (Thermo Fisher Scientific, USA). In addition to identifying hydrocarbon compounds, the analysis also focused on detecting brominated species present in the oil samples obtained from pyrolysis of WPCB at varying conditions. Prior to analysis, the oil samples were diluted in chromatography-grade DCM in the ratio 1:30 (v/v) and filtered through a 0.45 μm syringe filter. The injector and detector temperatures were maintained at 260 $^{\circ}\text{C}$. The heating program inside oven began with a 1 min hold at 60 $^{\circ}\text{C}$, followed by a ramp to 150 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, and then to 280 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$. The separation was performed using a TR-5 MS capillary column. Compound

identification was carried out by comparing the acquired mass spectra with entries in the National Institute of Standards and Technology (NIST) spectral library.

2.3.10. Nuclear magnetic resonance spectroscopy

Proton nuclear magnetic resonance (^1H NMR) spectroscopy was performed on the pyrolytic oil samples using an AVANCE III HD 600 MHz spectrometer (Bruker, USA), with a total of 16 scans. Prior to analysis, the oil samples were diluted in deuterated chloroform (CDCl_3) at a sample-to-solvent ratio of 1:20 (v/v). The resulting spectra were processed and analyzed using ACD/NMR software. This technique enabled the identification of the hydrogen bonding contexts, providing insight into the molecular structure of the compounds present in the oil.

2.3.11. Calorific value using bomb calorimeter

Bomb calorimeter (Toshniwal Technologies Pvt. Ltd., India) was used to determine the calorific value of the feedstock (WPCB), and its pyrolytic product fractions char and oil. 1 g of the sample was combusted in a bomb under high pressure (30 bar) O_2 environment to ensure complete combustion. This analysis estimates the energy released by the sample when burnt under ideal conditions. Comparing the calorific values of the feedstock and the pyrolytic product fractions will provide insight on how much the energy the products hold in comparison to the feedstock.

2.3.12. Gas chromatography

The composition of the non-condensable gas fractions (vol%) obtained from pyrolysis of WPCB samples was analyzed using a gas chromatography (GC) system (Trace 1110, Thermo Fisher Scientific, United States) equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). Permanent gases such as H_2 , CH_4 , CO , and CO_2 were quantified using the TCD and a Carboxen 60/80 packed column fitted inside the GC oven. Light hydrocarbon gases ($\text{C}_2\text{-C}_5$) were detected using the FID with a TG-Bond Alumina

capillary column. The TCD analysis was performed under isothermal conditions, with the oven maintained at 180 °C, whereas the injector at 150 °C, and the detector at 200 °C. For FID analysis, a ramped temperature method was employed: an initial hold at 60 °C for 2 min, ramped to 80 °C at 10 °C/min with a hold of 5 min, followed by a further ramp to 150 °C at 10 °C/min. Gas composition was determined using certified gas standards obtained from Centurion Scientific Pvt. Ltd., and concentrations were calculated based on linear calibration curves.

2.3.13. Field emission scanning electron microscope

The Field emission scanning electron microscope (FESEM) (Zeiss, Sigma 300, Germany) was used to obtain magnified images (top-view and side-view) of the RW-cut samples and its pyrolyzed forms (char), which were pyrolyzed at different conditions. The samples were first oven dried at 102 °C overnight to remove the moisture content and then carefully placed in a sample stub using carbon tape. The samples were gold coated for improving conductivity and image quality. This analysis served to verify the removal of the polymeric fraction in the RW-cut samples after its pyrolysis and to examine the morphological characteristics of the glass fibers after pyrolysis.

2.3.14. Energy dispersive X-ray spectroscopy

Energy dispersive X-ray (EDX) spectroscopy (Sigma) analysis was performed to study the composition of samples at different locations using point, area and mapping analyses. This was primarily used to investigate the side view of the RW-cut samples before and after pyrolysis to investigate the delamination of the layers in substrate of the WPCB samples. This analysis was also used to assess the precipitate obtained after leaching and cementation process. The detailed information on the methodology of the leaching and cementation process is given in section 2.8. The samples were first dried in hot air oven at 102 °C overnight before the analysis. Then

a tiny amount of the dried samples was transferred into a sample stub covered with carbon tape. For better image quality and improve conductivity, the samples were gold coated.

2.4. Kinetic study of WPCB samples

The thermogravimetric data for RW at the heating rates of 5, 10, 20 and 50 °C/min were used to determine the kinetic parameters activation energy (E), reaction model $f(\alpha)$, and pre-exponential factor (A). The parameters were determined as per the International Confederation for Thermal Analysis and Calorimetry (ICTAC) guidelines published by Vyazovkin et al. [133] provided a thorough guiding principle and recommendations to calculate the thermal degradation kinetic parameters of solid state materials.

The organic decomposition range was demarcated from the DTG curve (Fig. 2.1) and the conversion extent (α) was determined using the mathematical expression (Eq. 2.7).

$$\text{Extent of conversion } (\alpha) = \frac{m_o - m_t}{m_o - m_f} \quad (2.7)$$

where m_o , m_t , and m_f are the initial mass, mass at time t , and final mass of the sample.

The rate of a single-step reaction is given by,

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2.8)$$

where, α is the extent of conversion, t is time, T is the temperature, E is the activation energy, $f(\alpha)$ is the reaction model and A is the pre-exponential factor.

2.4.1. Isoconversional methods for determination of activation energy

The isoconversional methods determine the activation energy without making any model-specific assumptions beforehand because of which it is also known as the model-free approach. This method is based on the idea that the rate of reaction at a constant amount of conversion

depends solely on temperature, irrespective of heating rate magnitude. Generally, a change in activation energy with conversion can be associated with the change in reaction mechanism, called the E_a dependency [133]. Thermal degradation of WPCB is a complex phenomenon owing to its heterogeneous composition. Thus, to determine the thermal degradation kinetics of WPCB samples, a model-free approach was considered. The computational methods of the isoconversional method can be categorized into differential and integral.

The most commonly used differential isoconversional method is the Friedman method, which can be expressed as Eq. 2.9, where the subscript i denotes the temperature program.

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_a}{RT_{\alpha,i}} \quad (2.9)$$

For linear non-isothermal conditions, i.e., for a single heating rate, Eq. 2.9 can be expressed as:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_\alpha] - \frac{E_a}{RT_{\alpha,i}} \quad (2.10)$$

The term $g(\alpha)$ defines the integral form of the reaction model and is given by,

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (2.11)$$

Any temperature program is applicable to Eq. 2.11. For linear non-isothermal conditions, the above equation can be transformed to:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (2.12)$$

Eq. 2.12 has no analytical solution; hence a number of approximate solutions were provided.

Many of these approximations give rise to the following linear equations of the general form:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{B'}}\right) = \text{const} - C' \left(\frac{E_\alpha}{RT_\alpha}\right) \quad (2.13)$$

Various approximations lead to the following equations. Doyle's approximation leads to the values of $B' = 0$ and $C' = 1.052$. Putting the values, the above Eq. 2.13 becomes,

$$\ln(\beta_i) = \text{const} - 1.052 \left(\frac{E_\alpha}{RT_\alpha}\right) \quad (2.14)$$

This equation is also known as Ozawa, and/or Flynn and Wall, or OFW equation.

The more precise estimates of Murray and White, which result in $B' = 2$ and $C' = 1$, give birth to the well-known Kissinger-Akahira-Sunose (KAS) equation,

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Const} - \left(\frac{E_\alpha}{RT_\alpha}\right) \quad (2.15)$$

A somewhat more accurate value can be obtained by the approximation provided by Starink, which gave the values of $B' = 1.92$ and $C' = 1.0008$. Thus, the equation can be modified to,

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{const} - 1.0008 \left(\frac{E_\alpha}{RT_\alpha}\right) \quad (2.16)$$

The apparent activation energies for linear non-isothermal temperature programs using various isoconversional methods were obtained from the slope of the plots.

2.4.2. Reaction model

The isoconversional methods determine the kinetic parameters using the model-free approach. The determination of the reaction model $\{f(\alpha)\}$ predicts the thermal degradation reaction mechanism. The Criado master plot was used for the identification of the reaction model. The master plot $\{z(\alpha)/z(0.5)\}$ versus α consists of a set of theoretical models (Table A. 3), which

can be compared with the experimental results by using the expression Eq. 2.17. The notations have similar meaning as described previously.

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} = \left(\frac{T_\alpha}{T_{0.5}} \right)^2 \frac{(d\alpha/dt)_\alpha}{(d\alpha/dt)_{0.5}} \quad (2.17)$$

The similarity index among the experimental and the theoretical models was obtained by calculating the sum of the residual square (RSS) value. The lowest RSS value obtained between the experimental curve and the set of theoretical models available was chosen as the best fit and hence, considered for further calculations.



Table 2.1 List of the solid-state kinetic models used for the determination of reaction mechanism using Criado master plot [133]

Reaction model	Code	$f(\alpha)$	$g(\alpha)$
Power law	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law	P2/3	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
One-dimensional diffusion	D1	$1/2\alpha^{-1}$	α^2
Mampel (first order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
Avrami-Erofeev	A4	$4(1-\alpha)\{-\ln(1-\alpha)\}^{3/4}$	$\{-\ln(1-\alpha)\}^{1/4}$
Avrami-Erofeev	A3	$3(1-\alpha)\{-\ln(1-\alpha)\}^{2/3}$	$\{-\ln(1-\alpha)\}^{1/3}$
Avrami-Erofeev	A2	$2(1-\alpha)\{-\ln(1-\alpha)\}^{1/2}$	$\{-\ln(1-\alpha)\}^{1/2}$
Three-dimensional diffusion	D3	$3/2(1-\alpha)^{2/3}\{1-(1-\alpha)^{1/3}\}^{-1}$	$\{1-(1-\alpha)^{1/3}\}^2$
Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Two-dimensional diffusion	D2	$\{-\ln(1-\alpha)\}^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Ginstling-Brounshtein	D4	$3/2\{(1-\alpha)^{-1/3}-1\}^{-1}$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
Second Order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third Order	F3	$(1-\alpha)^3$	$\{(1-\alpha)^{-1}-1\}/2$

2.4.3. Pre-exponential factor

The pre-exponential factor (A) conveys information about the frequency of collisions between the reactant molecules in a reaction. For a given system, the activation energy and the pre-exponential factor obey a logarithmic relation. This is known as the compensation effect and can be expressed as Eq. 2.18. When there is a change in the model, there appears to be a

compensatory effect. This effect was monitored using the constable plots, and the pre-exponential factor was determined. Taking logarithm and rearranging the rate gives,

$$\ln[Af(\alpha)]_a = \frac{E_a}{RT_a} + \ln\left[\left(\frac{d\alpha}{dt}\right)_a\right] \quad (2.18)$$

The generalized form of the above expression can be written as,

$$b = \ln[Af(\alpha)]_a - aE_a \quad (2.19)$$

where, $a = 1/RT_a$ and $b = \ln(d\alpha/dt)$

The intercept of the plot of 'b' versus 'a' may be used to calculate the kinetic parameter pre-exponential factor. Finally, the pre-exponential factor was determined by substituting $f(\alpha)$ obtained from the Criado master plot in the intercept.

2.4.4. Reconstruction of conversion profile

The conversion profiles were reconstructed to confirm the calculated kinetic parameters. The reconstruction was done by solving the differential equation Eq. 2.20 using an ODE45 solver in MATLAB (version R2021a). The conversion (α) was considered the dependent variable, and temperature (T) the independent variable. Each sample's T_{onset} and T_{offset} values were taken as the initial and final points.

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{a,i}\right] = \ln[A.f(\alpha)] - \left(\frac{E_a}{R.T_{a,i}}\right) \quad (2.20)$$

Regression analysis was further used to determine which isoconversional approach have the best fit. The obtained activation energy from the best match isoconversional method was reported and used for further calculations.

2.5. Lab-scale pyrolysis experiments

The lab-scale pyrolysis experiments were performed in a fixed bed tubular reactor of 1 L capacity using semi-batch mode. The experimental setup consisted of an electric furnace mounted on a Proportional-Integral-Derivative (PID) controller system to regulate the temperature program. A condensation system to supply chilled water into the condenser (spiral-type) was used to produce the oil fraction (Fig. 2.2). Feedstock amount of 30 g was fed into the reactor for each run and the reactor was sealed properly. The outlet was subsequently connected to a condenser, followed by a flask placed in an ice bath to collect the oil. A water circulating chiller (Reico, India) set at 8 °C was used to supply the cooling medium into the condenser. The N₂ gas (99.95% purity) was purged at the rate of 150 mL/min inside the reactor system for at least 15 min before the heating program was commenced. The heating program was set as per the requirement using the PID controller. On heating the feedstock inside the reactor at the desired temperature program, the polymer fraction in the feedstock gets thermally degraded and then the volatile phase was condensed in the condenser and collected in the flask. The non-condensable gases were collected in Tedlar[®] gas sampling bags for subsequent compositional analysis using GC at pre-decided pyrolytic operating conditions. After the reactor was cooled to ambient temperature, the residual char was recovered and weighed to determine its yield. Then, the reactor outlet, condenser line and the flask were washed thoroughly using low a boiling-point solvent, DCM. The DCM was removed using reduced-pressure distillation rotary evaporator (R300, Buchi, Switzerland). The remaining brown colored fraction was labeled for the oil yield. The yield of the product fractions: char and oil were calculated using Eqs. (2.21 and 2.22).

$$\text{Response 1: Char yield (wt\%)} = \frac{\text{Weight of char fraction}}{\text{Weight of feed taken}} \times 100\% \quad (2.21)$$

$$\text{Response 2: Oil yield (wt\%)} = \frac{\text{Weight of oil fraction}}{\text{Weight of feed taken}} \times 100\% \quad (2.22)$$

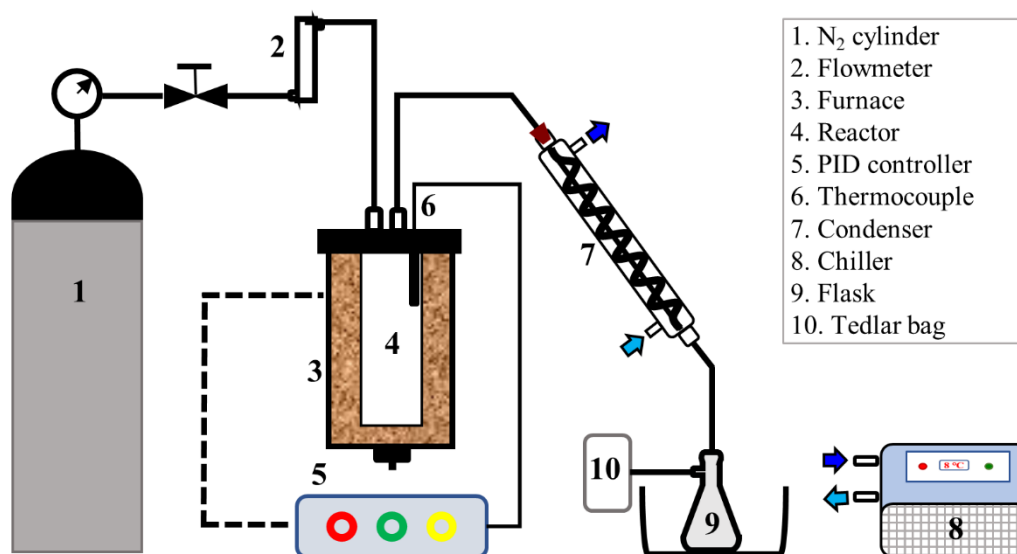


Fig. 2.2 Schematic diagram of the lab-scale pyrolysis experimental set-up

2.6. Response surface methodology study

Response surface methodology (RSM) is a trusted tool for identifying the significant and optimum parameters of a system. RSM study was used to optimize the pyrolysis process parameters to obtain the desired responses. Pyrolysis is a thermochemical conversion process in an inert environment; hence, its key parameters include the temperature program supplied to the feedstock. The heating program varies the products' properties quantitatively as well as qualitatively. Hence, to determine the significant parameter(s) in the WPCB pyrolysis process, as well as to optimize the operating conditions to obtain the targeted product fraction, RSM study was performed. Consequently, temperature (coded as A), heating rate (coded as B), and hold time (coded as C) were considered as the independent factors (Table 2.1) to acquire the quantitative information on the yield distribution of the products. The responses include the char and oil yields (in wt%). Other parameters, such as the feed amount (30 g), N₂ flow rate (150 mL/min), and chiller temperature (8 °C), were kept constant. The factors were input into the face-centered ($\alpha = 1$) central composite design (CCD) using the Design Expert Software (v.13). A total of 20 randomized runs were established consisting of six central and axial points

each and eight factorial points. The lab-scale pyrolysis experiments were performed according to the methodology described in the section 2.5.

Table 2.2 The range of independent factors chosen for the design of experiment

Parameters	Levels	
	Lower bound	Upper bound
Temperature (A), °C	300	600
Heating rate (B), °C/min	5	30
Hold time (C), min	60	180

The responses obtained experimentally were analyzed using ANOVA, and the best-fit model was selected. The optimization study was performed to achieve the objective function of ‘maximum oil yield’ and ‘minimum char yield’. The factors were selected to be ‘in range’. The dependency of the parameters on the responses was analyzed and the significant parameter(s) was/were determined. The responses at the optimized parameters suggested by the model were further validated by performing experiments at the optimized conditions.

2.7. Soxhlet extraction for reduction of bromine content

The WPCB contains BFR which gets transferred into the pyrolytic product fractions, making them unsuitable for use because of environmental concerns. Hence, it is important to keep a track of the fate of bromine during the pyrolysis process and reduce its content in the desired product fraction. One of the ways is to reduce the bromine content in the feedstock (WPCB) itself. Soxhlet extraction provides an exhaustive extraction efficiency at lower cost, hence, it was chosen as a pre-treatment method for reducing bromine in the pyrolytic product fractions before pyrolysis. The Soxhlet extraction was performed for 24 h using various organic solvents; toluene, dichloromethane, acetone, and 2-propanol, to reduce BFR content in the WPCB

sample before pyrolysis. For each gram of the WPCB sample, 10 mL of solvent was used for the extraction at the temperature adjusted for different solvents depending on their boiling point. The Soxhlet extracted samples were dried in a hot air oven at 70 °C for overnight and used for characterization and experimental purposes.

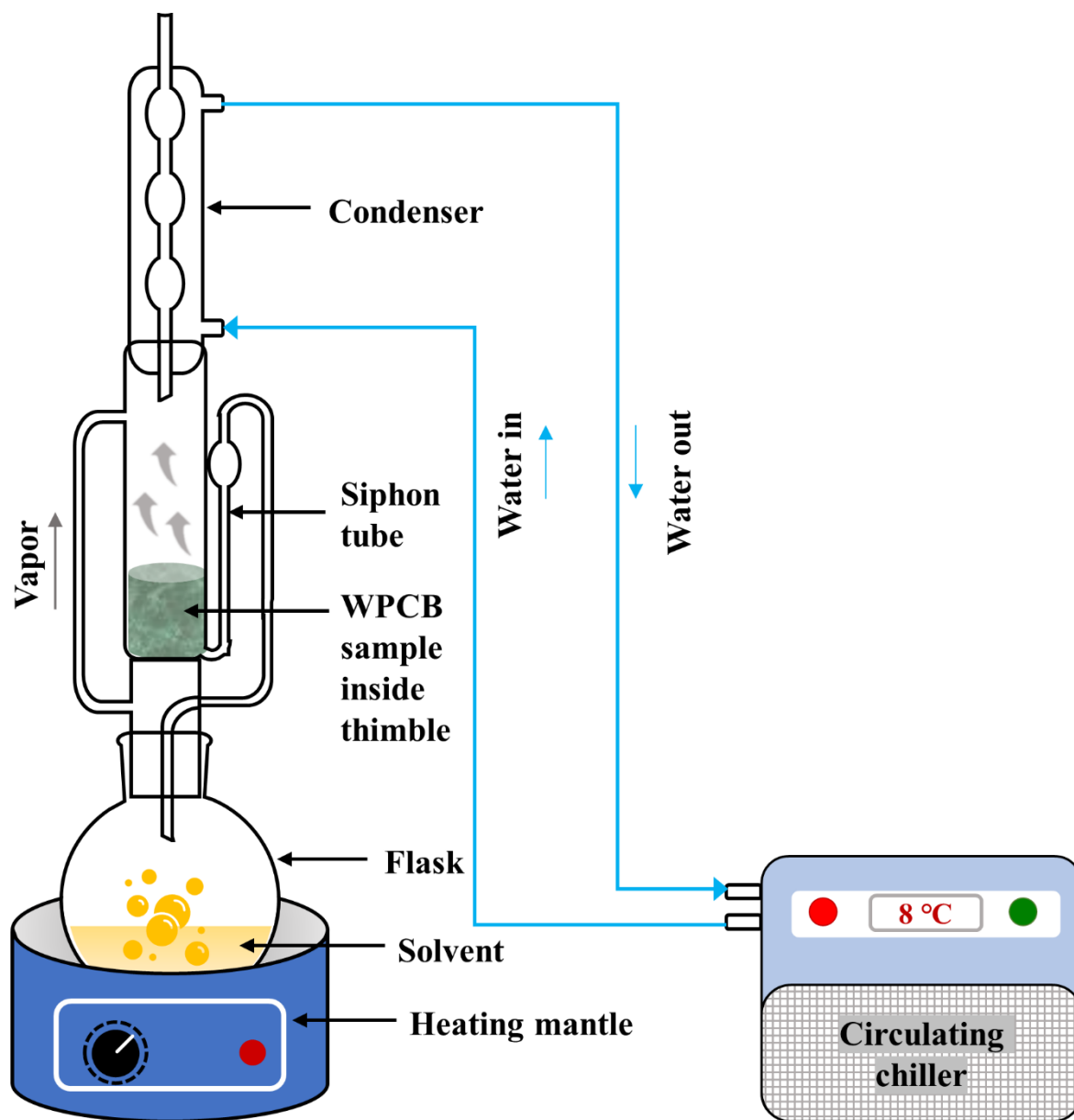


Fig. 2.3 Schematic diagram for the experimental setup of Soxhlet extraction of WPCB samples using various organic solvents

2.8. Extraction of copper

Copper is one the most abundantly available metals in WPCB, and it contributes the highest amount of wealth of all the metals present in E-waste (Table 1.3). The extraction efficiency of copper was examined using acid leaching (H_2SO_4 and H_2O_2). This study investigated the copper leaching efficiency for a variety of WPCB materials, RW-cut and RW, and their pyrolyzed fractions RW-cut-char and RW-char, respectively. The leaching experiments were performed in a glass beaker (Borosil, India) at a constant mixing rate of 200 RPM and at ambient conditions. H_2SO_4 (1 M, 2 M, 3 M and 4 M) and H_2O_2 (5% and 10%) concentrations were varied. The leachate obtained was used to determine the leaching efficiency of copper using ICP-MS instrument. Then, the leachate obtained was further subjected to precipitation reaction using Zn powder to obtain copper in solid form. The purity of the Cu precipitate was examined using EDX analysis (section 2.3.14) and that of the remaining solution using ICP-MS instrument to examine the reduction of Cu^{2+} to its metallic form Cu.

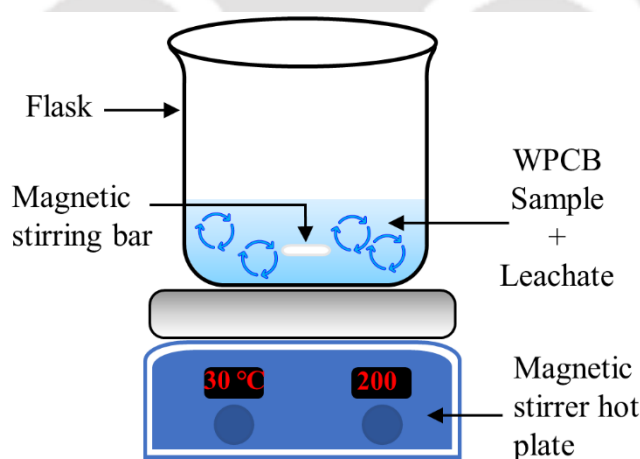


Fig. 2.4 Schematic diagram for the experimental setup of acid leaching of WPCB samples

2.9. Simulation using Aspen Plus®

The pyrolysis of WPCB and recovery of materials using combined effort of pyrolysis and hydrometallurgical approach was simulated using Aspen Plus® v14 software (AspenTech, USA), licensed by the Indian Institute of Technology Guwahati. The process flowsheet and

nomenclature of the reactors and the streams are given in Fig. 2.3. Simulating the pyrolysis of WPCB using Aspen Plus[®] software enables accurate mass and energy balance calculations for the process. The software offers comprehensive thermodynamic and thermophysical property database, which are essential for performing simulations of complex systems such as WPCB pyrolysis that involve heterogeneous mixture of materials.

The simulation involves completion of two sections: Properties and Simulation. In the **Properties section**, the name and type of components used in the simulation were defined (Table A. 5). Different types of components can be used in Aspen Plus[®] such as conventional, non-conventional, solid, etc. WPCB is not present in the Aspen Plus[®] database as a conventional compound, hence it is to be treated as unconventional and need to be described according to its proximate and CHNSO analyses data. Similarly, the CHAR fraction was also defined as the unconventional component. HCOALGEN and DGOALIGT were used to define the enthalpy and density parameters of the unconventional components. The OIL was defined based on its compositional analysis (GC-MS) and availability of those compounds in the Aspen Plus[®] database. Hence, the composition may not exactly replicate the actual oil [134]. The base method chosen was Peng-Robinson-Mathias (PR-BM) [135].

In the **Simulation environment**, the flowsheet was designed using reactor/process blocks that are available and connected them using streams. The stream class was set to MCINCPSD as it includes mixed, solid, non-conventional and particle size distribution. Three different sections were included in the flowsheet: (i) Comminution, (ii) Pyrolysis, and (iii) Metal extraction. The comminution section includes size reduction operations of the feed material consisting of the blocks, CRUSHER and SCREEN. The crusher unit was used to crush the WPCBs from 10 cm to small pieces and passed through a SCREEN with 1 cm size opening [136, 137]. The prepared feed in the desired size was then sent to the pyrolysis section. The RYIELD reactor was used

to convert the unconventional component (WPCB) into conventional components using the block CALCULATOR, which runs using FORTRAN code (Appendix C. 1).

The pyrolysis or thermal degradation of the WPCB was carried out using the RGIBBS reactor at 500 °C in the presence of N₂ gas. The RGIBBS reactor works by minimizing the Gibbs free energy, hence it gives the maximum possible conversion [130]. The outlet from the RGIBBS was then sent to the SSPLIT block, which separates the solid and the gas phases. The solid phase contained the glass fibers and the metallic fraction, whereas the gas phase contained the volatile fraction. The gas fraction was sent to a COOLER for its condensation. The condensate (oil) and the non-condensable gases were then separated using a FLASH separator. The char obtained contains valuable inorganic fractions (metals and glass fibers). In a WPCB, the metallic fraction is the costliest component, and the glass fibers contribute the highest wt% (~40%) as compared to the polymer and metallic fraction. Hence, recovery of these materials was also simulated. The pyrolysis process delaminates the copper sheets and the glass fibers, making it very easy to separate manually, but it is impractical and time-consuming for large-scale production. Moreover, carbon deposition also occurs on the surface of the copper films. Kurniawan et al. [76] reported that the metal sheets were stuck to the glass fibers because of the melting of the materials. The copper and glass fibers were separated by means of acid leaching so that the copper can be leached out into the leaching solution and the glass fibers will remain as the residue. This SOLID stream was sent to the metal extraction section to leach out copper using H₂SO₄ and H₂O₂, and then precipitated using zinc powder. The hydrometallurgical approach, one of the low-cost technologies with high selectivity, has been considered for metal recovery [138]. A few modifications were made for the simulation of copper extraction from char. Since copper could not be incorporated in the char fraction, it was used as a separate stream along with the leaching solution (H₂SO₄ + H₂O + H₂O₂) into the CSTR-1 (RSTOIC block). Hence, a splitter (FSPLIT) was used to remove a mass fraction

equivalent to the copper wt% from the SOLID stream, and the remaining mass was designated as CHAR. The copper concentration was taken as 9 wt% (45 kg) (ICP-MS analysis). The LEACHSOL ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{H}_2\text{O}_2$), CHAR, and CU streams were mixed using MIX-1 and then sent to the CSTR-1 reactor for the reaction (Eq. 2.23) to occur [139]. The conversion of the RStoic reactor was taken as 96% with respect to copper. The amount (weight or volume) of LEACHSOL depends on the pulp density. The pulp density of 1 g/L considered in the experiments was very low. Tran et al. [140]. reported that the lower pulp densities increase the consumption of reagents and water and necessitate larger reactors, which further challenge the environmental benefits and scalability of the process. Hence, a pulp density of 700 g/L was selected, and the concentration (1 M H_2SO_4 and 10 vol% H_2O_2) was taken from the experimental results. At this density, approximately 93% of H_2SO_4 was consumed; increasing the pulp density to 750 g/L resulted in over 99% acid consumption. To prevent complete acid depletion and optimize leaching efficiency, a slightly lower pulp density of 700 g/L was fixed, thereby ensuring sufficient reagent availability throughout the process. The residue containing the non-metallic fraction, glass fibers (GF), was then separated out from the leachate using a separator (SEP-1). The leachate containing the CuSO_4 solution was further sent to CSTR-2 and allowed to react with zinc powder to obtain the copper precipitate (CU-PPT) (Eq. 2.24). The detailed mass balance of the sections: comminution, pyrolysis, and metal extraction are provided in (Fig. 7.2 (a), 7.2 (b) and A. 4). The simulation was then run and checked for error. The error-free simulation was sent to the inbuilt economic analyzer in Aspen Plus[®], and then techno-economic assessment of the process flowsheet developed was performed.



2.10. Techno-economic assessment

The techno-economic assessment (TEA) for the material recovery from WPCB was estimated using a combination of Aspen Plus Economic Analyzer (APEA) and Microsoft Excel. The material recovery process containing comminution, pyrolysis, and metal extraction was simulated (section 2.9) for an imaginary plant located in India with a feed capacity of 500 kg/h and a lifetime of 20 years. The capacity has been chosen based on the amount of WPCB generated per year in one of the most populated cities, Delhi. Details of the plant has been provided in Table 7.1. Considering that 9.5% of total E-waste generated in India is from Delhi and 5% of the E-waste is contributed by WPCB, the capacity of the plant was chosen [141]. For detailed calculation, please refer to the Appendix C .2. Aspen Plus® maps and sizes the equipment based on the mass balance, which is an essential component for performing the techno-economic assessment of a plant [142].

2.10.1. Capital and operating expenses

The main components of an economic assessment are the capital expenditure (CAPEX) and the operational expenditure (OPEX). The CAPEX includes the costs of land and equipment, whereas the OPEX includes all the costs related to the plant operation to generate product, including maintenance costs. The OPEX component can be further classified into fixed and variable operating costs. The detailed list of parameters associated with the CAPEX and OPEX has been elaborated in Table 7.2 [142]. An additional investment called the working capital (WC) is needed over the fixed capital until the income is earned to start a plant. It includes the cost of startup, raw materials, and intermediates in the process, finished product inventories. The total investment needed for a project is the sum of the fixed and working capital. The cost of equipment used was taken from the Aspen Plus® database (year 2022) [143, 144]. These prices were updated for the year 2024 using the cost index CEPCI (Chemical Engineering Plant Cost Index®) published by the Chemical Engineering magazine (Eq. 2.25).

$$\text{Cost}_{2024} = \text{Cost}_{\text{ref}} \left(\frac{\text{CEPCI}_{2024}}{\text{CEPCI}_{\text{ref}}} \right) \quad (2.25)$$

where, Cost_{2024} and Cost_{ref} are the costs in the year 2024 and reference year (2022), respectively. CEPCI for 2022 and 2024 were 816 and 800, respectively. The high CEPCI value for 2022 was primarily driven by increased inflation and supply chain challenges during the recovery period following the pandemic [145].

The total equipment cost was estimated by considering the installation, piping, instrumentation, etc., by considering a factor of 4. To run the equipment, utilities are required. Cooling water and electricity were considered utilities. The electricity (energy) consumed by the equipment was obtained from Aspen Plus[®], which was used to calculate the cost associated with the electricity usage. The number of labors (N_L) required to run the plant was calculated by using Eq. 2.26 [146].

$$N_L = (31.7P^2 + 0.23N + 6.29)^{0.5} \quad (2.26)$$

where, N represents the number of non-particulate processing steps (mixing, heating, cooling, and compression) and P represents solid handling steps (including dissolved solids). Using this equation, the total no. of labors obtained was 18. The labor cost was considered as per the recent current minimum wage rate published by the Government of National Capital Territory of Delhi w.e.f. 1 April 2025 and estimated for 8000 working h per year [147]. The supervision charge was also estimated from the labor cost (Table 2.3).

Table 2.3 CAPEX and OPEX components used for the economic assessment of the proposed plant

CAPEX components		OPEX components	
Purchased equipment (1)	100% of EPC [#]	Supervision (1)	25% of labor cost
Total cost (2)	4×Purchased equipment	Direct overhead (2)	50% of (labor + supervision)
Direct cost, DC (3)	(3) = (1) + (2)	General overhead (3)	50% of (labor + supervision + direct overhead)
Indirect cost, IDC (4)	(4) = 21.9% of DC	Insurance and tax (4)	1% of FCI
Fixed capital investment, FCI (5)	(5) = (3) + (4)	Maintenance labor and materials (5)	5% of FCI
Land cost	2% of FCI	Additional expenses (marketing, logistics, operating services, etc.) (6)	1% of FCI
Working capital, WC (6)	15% of FCI	Laboratory cost (7)	1% of labor cost
Startup cost, SUC (7)	5% of FCI	Financing working capital (8)	0.1% of WC
CAPEX	FCI + WC + SUC	Fixed operating cost, FOC (9)	(9) = (1) + (2) + ... + (8)
		Cooling water (10)	nil
		Electricity (11)	kWh × \$/kWh
		Total cost of raw material	0 + 20% of DC

[#]EPC = Equipment purchase cost

The feedstock is a waste material; hence, no cost was considered, whereas transportation charges of 20% of the direct fixed cost were included in bringing the material from the collection center to the plant [136, 143]. The cost of water to be used as a utility was considered nil, considering the water was from a nearby river, and the cost of electricity was calculated based on the consumption and the rate provided for the industrial electricity tariff in India [148]. The price of chemicals was considered for bulk purchase from the Indiamart website [149-151]. The organic material in the WPCB was converted into oil and gas fractions, while the char consists of metals (copper) and glass fibers. The oil was considered to be sold without further treatment, and gas for energy generation, while copper recovered in metallic form was sold as pure metal. The remaining residue, glass fibers, was assumed to be sold as an additive for construction purposes. The selling price for the recovered copper and that of chopped glass fibers (grade: recycled) were considered as 8.16 \$/kg and 0.64 \$/kg, respectively, based on the grade and the price listed in the commercial market [152-154]. Since the price of pyrolytic oil is not fixed yet in the commercial market, its minimum selling price (MSP) was determined. Thus, the economic assessment was performed by considering copper and glass fibers as the products.

2.10.2. Discounted cash flow analysis

The economic assessment for the WPCB pyrolysis process has been carried out by performing discounted cash flow (DCF) analysis (Table 2.4). The cash flow analysis gives detailed information on the economic performance of the plant throughout its lifetime. However, it is essential to consider the time value of money; hence, discounted parameters were calculated. A tax rate of 15% on the sales, discount rate (r) of 10% and salvage value of 20% were considered for the calculation of cumulative discounted cash flow [155, 156].

Table 2.4 Discounted cash flow analysis calculation

Sales (\$/year)	Total price of the products sold in a year
Revenue (\$/year)	Sales – Operating cost
Depreciation (straight line)	$\frac{\text{Capital cost} - \text{Salvage value}}{\text{Plant life}}$
Earning before tax (\$/year)	Revenue – Depreciation cost
Tax (\$/year)	Tax rate $\times$ earning before tax
Earning after tax (\$/year)	Earning before tax – tax
Annual net income (\$/year)	Earnings after tax – operating cost
Discounted cash flow (\$/year)	Discount factor $\times$ Annual net income
Cumulative discounted cash flow (\$/year)	$\sum_{i=1}^n \frac{\text{Net cash flow}}{(1+r)^i}$, r is the discount rate, and n is the no. of year

2.10.3. Economic evaluation of the plant and Minimum selling price of oil

From the DCF analysis, the economic parameters net present value (NPV), internal rate of return (IRR), profitability index (PI), and discounted payback period (PBP) were calculated. The NPV is the summation of the present values of the future cash flows for the plant life (Eq. 2.27). The value of NPV should be greater than or equal to zero for the plant to be profitable. The present value (PV) is the amount of future cash flow that has been discounted to obtain its value in the present time. The relation between future value (FV) and PV for a particular year t is given by Eq. 2.27.

$$\text{NPV} = -\text{CAPEX} + \sum_0^{20} \text{net PV} \quad (2.27)$$

$$PV = \frac{FV}{(1+r)^t} \quad (2.28)$$

The future cash flows and the NPV depend on the assumed discount rate. Hence, IRR was determined. It is the discount rate that would produce $NPV = 0$ [157]. It was determined using iteration in Microsoft Excel. Profitability index is another economic evaluation parameter that tells for every \$ spent, how much is achieved in return. It is the ratio of total cash inflow to total cash outflow. Another important parameter is the discounted PBP. It is the number of years that would take to recover all the money invested in the project. The pyrolytic oil from WPCB has no organized market yet; hence, the sales generated were not considered, rather MSP was calculated. The MSP is the selling price of the product for which the NPV is equal to zero.

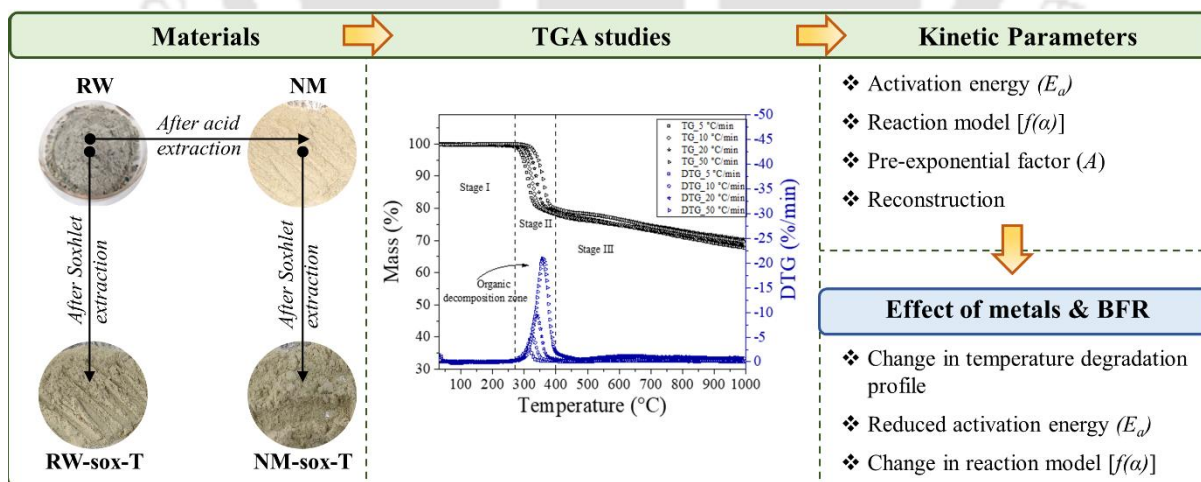
2.11. Summary

This chapter presented a comprehensive description of the methodologies adopted to achieve the research objectives outlined in Chapter 1. It incorporated the procedures for material collection, material and product characterization, and the associated analytical techniques. Furthermore, the chapter discussed the theoretical foundations of kinetic analysis, experimental studies at the laboratory scale, process simulation using Aspen Plus®, and the techno-economic assessment. Overall, this chapter established the methodological framework and background necessary for the subsequent chapters. The chapter provided a base for the remaining chapters.

Chapter 3

Effect of metals and brominated flame retardants on thermal degradation kinetics of WPCB

- Brominated flame retardants
- Isoconversional principle
- Kinetic triplets
- Reconstruction
- Waste printed circuit board



Publication: B. Boro and P. Tiwari, "Effect of metals and brominated flame retardants on thermal degradation kinetics of waste printed circuit board", *Thermochimica Acta*, 736, 179747, 2024.

3. Thermal degradation kinetics of WPCB

This chapter includes the determination of thermal degradation kinetic triplets (activation energy (E), reaction model ($f(\alpha)$) and pre-exponential factor (A)) for WPCB pyrolysis and study the effect of metals and brominated flame retardants (BFRs) on the kinetic triplets. Thus, four samples were prepared, namely (a) RW (raw WPCB), (b) NM (non-metallic WPCB), (c) RW-sox-T (bromine reduced from RW using Soxhlet extraction) and (d) NM-sox-T (bromine reduced from NM using Soxhlet extraction). The activation energy parameters were calculated using the isoconversional methods, Friedman, Ozawa-Flynn-Wall (OFW), Kissinger–Akahira–Sunose (KAS), and Starink, and validated using reconstruction of conversion profiles. The reaction model ($f(\alpha)$) was determined using Criado master plots and the pre-exponential factor using the concept of compensation effect. The parameters obtained in this study can be used in designing applications and developing an energy-efficient pyrolysis process. The understanding of the effect of the presence of metals and BFR during pyrolysis provides a pathway to design a process flowsheet to recover materials from WPCB using pyrolysis and metal extraction using hydrometallurgy.

3.1. Elemental analysis of the WPCB samples prepared using X-ray fluorescence spectroscopy

The thermal degradation kinetic triplets (activation energy, reaction model and pre-exponential factor), and the effect of the presence of metals and reduced bromine concentration in these parameters were analyzed using four different WPCB samples: (a) RW, (b) NM, (c) RW-sox-T and (d) NM-sox-T. The NM sample is the residue obtained after acid leaching of the RW sample for 4 h at a 200 RPM mixing rate, using freshly prepared HCl and HNO₃ in a 3:1 (v/v) ratio. The RW-sox-T and NM-sox-T are Soxhlet-extracted samples of RW and NM, respectively, using toluene as the solvent [158]. Acid leaching was performed to remove the metals from RW, and the Soxhlet extraction was performed to reduce the bromine content in the RW and NM samples. The elemental compositions of the samples were determined using X-ray fluorescence (XRF) to evaluate the acid leaching and Soxhlet extraction processes (Table 3.1). XRF is used to determine the major as well as the trace elemental compositions of a material in a non-destructive manner. The untreated WPCB (RW) sample was found to be rich in Si, Al, and Ca due to the presence of ceramic materials originating from glass fibers in the substrate part of the WPCB. The concentrations of Cu and Sn were relatively high, as compared to the heavy metal Pb, and precious metals such as Au, Ag, and Pt were below the detection limit (BDL). The bromine concentration of 8.47% falls within the expected range. The elemental composition of the RW was compared with those of the NM, RW-sox-T, and NM-sox-T to determine the impact of acid leaching and Soxhlet extraction using toluene (Table 3.1). Metals such as Cr, Ni, Cu, Sn, and Pb were removed entirely from the samples NM and NM-sox-T; thus, the metal extraction process was highly efficient. However, Soxhlet extraction using toluene showed a reduction in bromine content, but it could not be entirely removed.

3.2. Thermal degradation behavior of the WPCB samples

TG-DTG analysis was performed for all four samples: RW, NM, RW-sox-T, and NM-sox-T, at four heating rates (5, 10, 20 and 50 °C/min) under a nitrogen environment. The onset temperature (T_{onset}), offset temperature (T_{offset}), and maximum degradation temperature (T_{max}) values were calculated using the tangent method (Fig. 2.1), and reported in Table 3.2. With the increase in heating rate, a similar trend was observed, where the T_{max} increased to higher temperatures (Fig. 3.1) for all the samples. This trend can be attributed to the heat transmission retardancy at faster heating rates, which causes the thermal degradation process to take longer to complete. Additionally, it was observed that, for the same heating rate, the T_{max} for NM was higher compared to RW, whereas the T_{max} for NM-sox-T was found at a lower temperature.

A similar trend was also observed by Evangelopoulos et al. [158] where the degradation of brominated plastic was reduced by 25 °C on the reduction of BFR content in the sample. The thermal degradation profiles for all the samples depicted a similar pattern, consisting of three stages, with the maximum degradation observed at stage II. This stage represents the degradation of the organic material, epoxy resin, present in the WPCB.

On comparing RW for T_{onset} , no significant temperature reduction was observed for NM. However, a reduction was observed for the samples treated with toluene irrespective of the presence or absence of metals. Nonetheless, more temperature reduction was observed for the NM-sox-T as compared to the RW-sox-T. The individual impact of BFR on T_{onset} was established from the T_{onset} values for NM and NM-sox-T to eliminate the effect of metals. The T_{onset} was reduced to 259.2 °C (NM-sox-T) from 273.7 °C (NM) at 5 °C/min. It can be related to the BFRs, which are supposed to delay the thermal degradation processes. Hence, it can be concluded that the BFR has an impact on the value of T_{onset} .

In the case of T_{offset} , the behavior was different. When comparing the T_{offset} values of RW with those of NM, RW-sox-T, and NM-sox-T samples, it was observed that T_{offset} had shifted to a higher temperature. A significant increase in temperature of up to 37 °C at a heating rate of 50 °C/min was observed for NM, whereas a minor increase was observed for RW-sox-T and NM-sox-T. Hence, the presence of the combined metallic fraction and BFR has narrowed the thermal degradation temperature window ($T_{\text{offset}} - T_{\text{onset}}$) for WPCB. The difference between the T_{offset} and T_{onset} for RW, RW-sox-T, NM and NM-sox-T was 68.0, 75.4, 99.0 and 102.0 °C for at 5 °C/min (Fig. 3.2). It is to be noted that the T_{onset} , T_{offset} and T_{max} values might vary depending on the method of analysis chosen. For example, in this work, the parameters were determined using the tangent technique (ASTM E2550-21). However, the variation trend with the material (RW, NM, RW-sox-T, or NM-sox-T) will remain the same.

Table 3.1 Elemental composition of RW, NM, RW-sox-T and NM-sox-T using XRF

Elements	Elemental composition (wt%)			
	RW	NM	RW-sox-T	NM-sox-T
Si	43.78	49.03	45.71	44.95
Al	10.71	11.22	11.4	10.44
Fe	2.17	0.57	2.16	0.78
Mg	1.15	0.54	1.04	0.49
Ca	20.98	22.36	20.98	21.14
Na	0.36	0.36	0.39	0.36
K	0.16	0.15	0.15	0.14
Ti	0.67	0.64	0.63	0.56
S	1.42	0.82	1.13	0.56
Cr	0.44	BDL	0.45	BDL
Ni	0.29	BDL	0.27	BDL
Cu	4.45	BDL	3.32	BDL
Br	8.47	8.48	7.90	5.11
Sr	0.18	0.19	0.18	0.16
Sn	2.72	BDL	2.27	BDL
Ba	1.50	1.19	1.27	1.19
Pb	0.13	BDL	BDL	BDL
F	BDL	0.42	0.35	0.38
Cl	BDL	3.80	0.10	13.86

*BDL = below detection limit

Table 3.2 The values of onset, offset, and maximum degradation temperatures for RW, NM, RW-sox-T and NM-sox-T at heating rates of 5, 10, 20, and 50 °C/min

Heating rate, β (°C/min)	Onset temperature (T_{onset} , °C)				Offset temperature (T_{offset} , °C)				Maximum degradation temperature (T_{max} , °C)			
	RW	RW-sox-T	NM	NM-sox-T	RW	RW-sox-T	NM	NM-sox-T	RW	RW-sox-T	NM	NM-sox-T
5	273.0	272.9	273.7	259.2	341.3	348.3	375.4	358.2	314.9	313.8	325.0	304.6
10	288.0	283.1	289.5	272.0	359.0	363.5	376.7	367.2	323.6	326.7	339.7	315.3
20	304.1	298.5	302.7	296.1	371.9	379.9	402.2	380.9	339.8	341.5	348.0	332.5
50	321.1	320.0	319.3	309.0	393.1	401.5	430.2	401.9	358.1	358.4	370.0	355.2

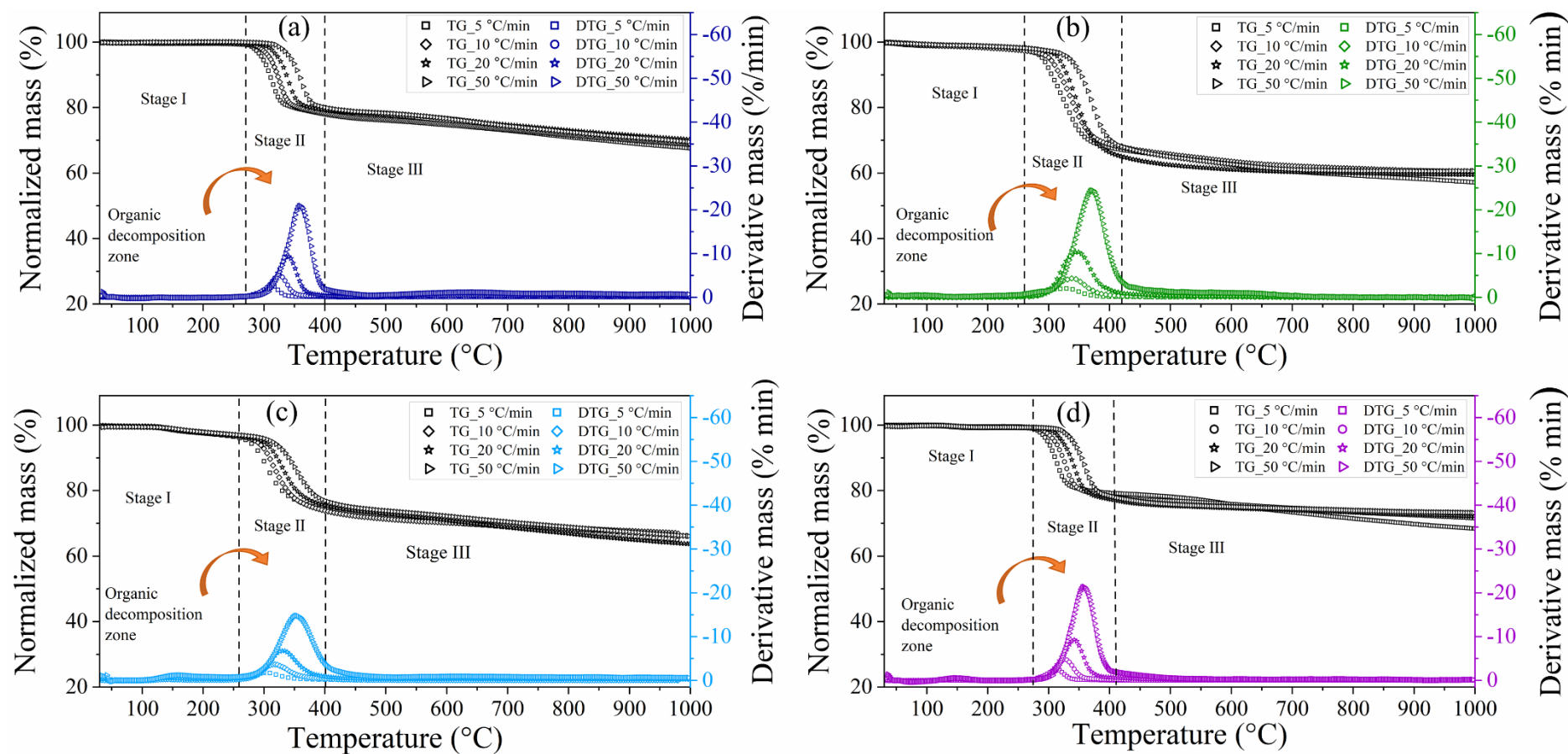


Fig. 3.1 TG-DTG plot for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T from 30 to 1000 °C at heating rates of 5, 10, 20, and 50 °C/min

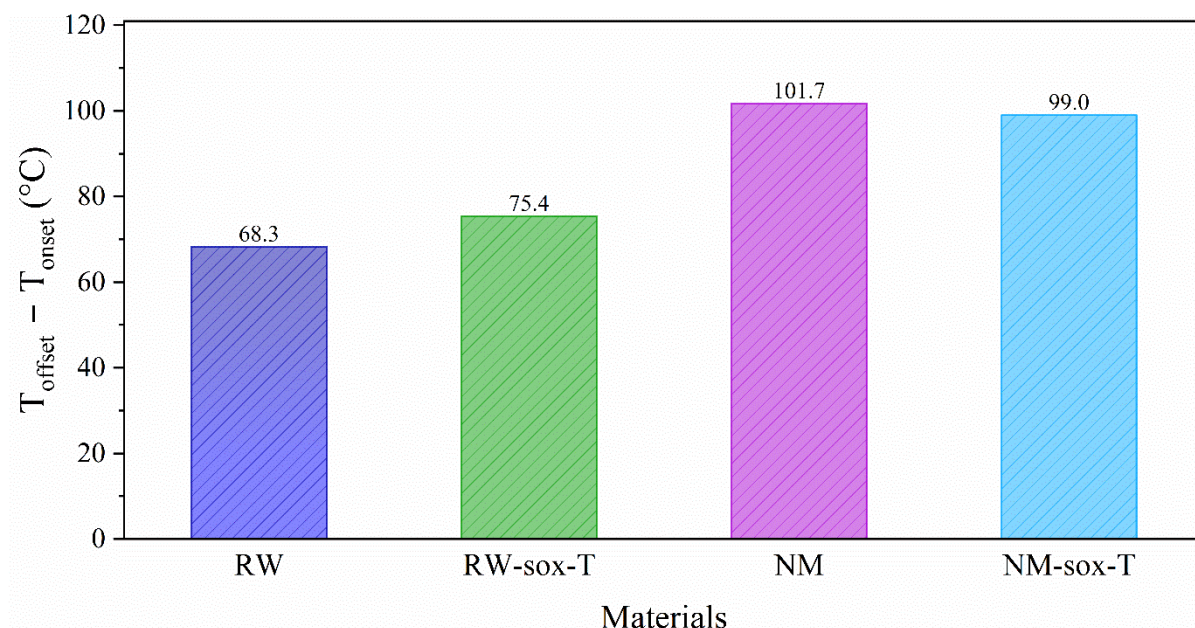


Fig. 3.2 Temperature degradation window ($T_{\text{onset}} - T_{\text{offset}}$) for RW, RW-sox-T, NM and NM-sox-T at 5°C/min

3.3. Kinetic parameter determination

3.3.1. Activation energy

The apparent activation energy (E_{α}) values for the RW, NM, RW-sox-T, and NM-sox-T were determined by four isoconversional methods of Friedman, OFW, KAS, and Starink (Table 3.3) and plotted against conversion (α) (Fig. 3.3). The activation energy distribution obtained for OFW, KAS, and Starink showed a similar trend; however, the Friedman method showed a noisy pattern. This is because numerical differentiation was performed on integral (TGA) data, resulting in noisy reaction rate data. The apparent activation energies ranged from 121.6–178.3 kJ/mol, 137.6–152.6 kJ/mol, 126.2–141.6 kJ/mol and 126.6–142.0 kJ/mol for RW determined using Friedman, OFW, KAS and Starink, respectively. The average values of all the samples for each isoconversional method are listed in Table 3.3. Liu et al. [103] found activation energies in the range of 128.28–144.40 kJ/mol for $\alpha = 0.05$ –0.65 and 329.70 kJ/mol for $\alpha = 0.70$ using KAS.

In the current study, the activation energy distribution with conversion remained relatively constant for RW; however, it showed fluctuation in the case of the NM, R-sox-T and NM-sox-T (Fig. 3.3). This was also reflected in the Criado master plot, which showed a change in reaction mechanism $\{f(\alpha)\}$. Thus, the material composition must have caused the change in activation energy trend and hence, the reaction mechanism $\{f(\alpha)\}$. To get a clear picture of the effect of metals and BFR, the activation energy distribution for (a) acid treated and (b) toluene treated samples was plotted (Fig. 3.4). It can be seen that the average activation energy increased after acid leaching, from 136.0 kJ/mol (RW) to 146.2 kJ/mol (NM). A minor decrease in average activation energy on the BFR removal was also observed from 146.2 to 142.8 kJ/mol for NM and NM-sox-T, respectively. Thus, the presence of metals has a greater influence on reducing the activation energy than the decrease in BFR content.

A maximum difference of 38 kJ/mol in the apparent activation energy value at $\alpha = 0.95$ was observed (Fig. 3.4). Therefore, performing pyrolysis without removing the metals present in WPCB is advantageous, as it leads to reduced energy consumption. The decrease in activation energy in the presence of metals clearly demonstrates the catalytic effect of the in-situ metals in WPCB, consistent with the findings of Gao et al. [102]. Previous studies have proved the ability of metals like Cu and Fe to interfere with the pyrolysis process and form metallic bromides. Liu et al. [103] reported the release of similar species of compounds in the presence and absence of embedded metals; however, the concentration were different.

Table 3.3 Plots for determination of activation energy using isoconversional methods

Isoconversional methods	Types	Expressions	Plots
Friedman	Differential	$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln\left(\beta \frac{d\alpha}{dT}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}}$	$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] \text{ vs } \frac{1}{T_{\alpha,i}}$
FWO	Integral	$\ln(\beta_i) = \text{Const} - 1.052 \left(\frac{E_\alpha}{RT_\alpha}\right)$	$\ln(\beta_i) \text{ vs } \frac{1}{T_{\alpha,i}}$
KAS	Integral	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{Const} - \frac{E_\alpha}{RT_\alpha}$	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) \text{ vs } \frac{1}{T_{\alpha,i}}$
Starink	Integral	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.008 \left(\frac{E_\alpha}{RT_\alpha}\right)$	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) \text{ vs } \frac{1}{T_{\alpha,i}}$

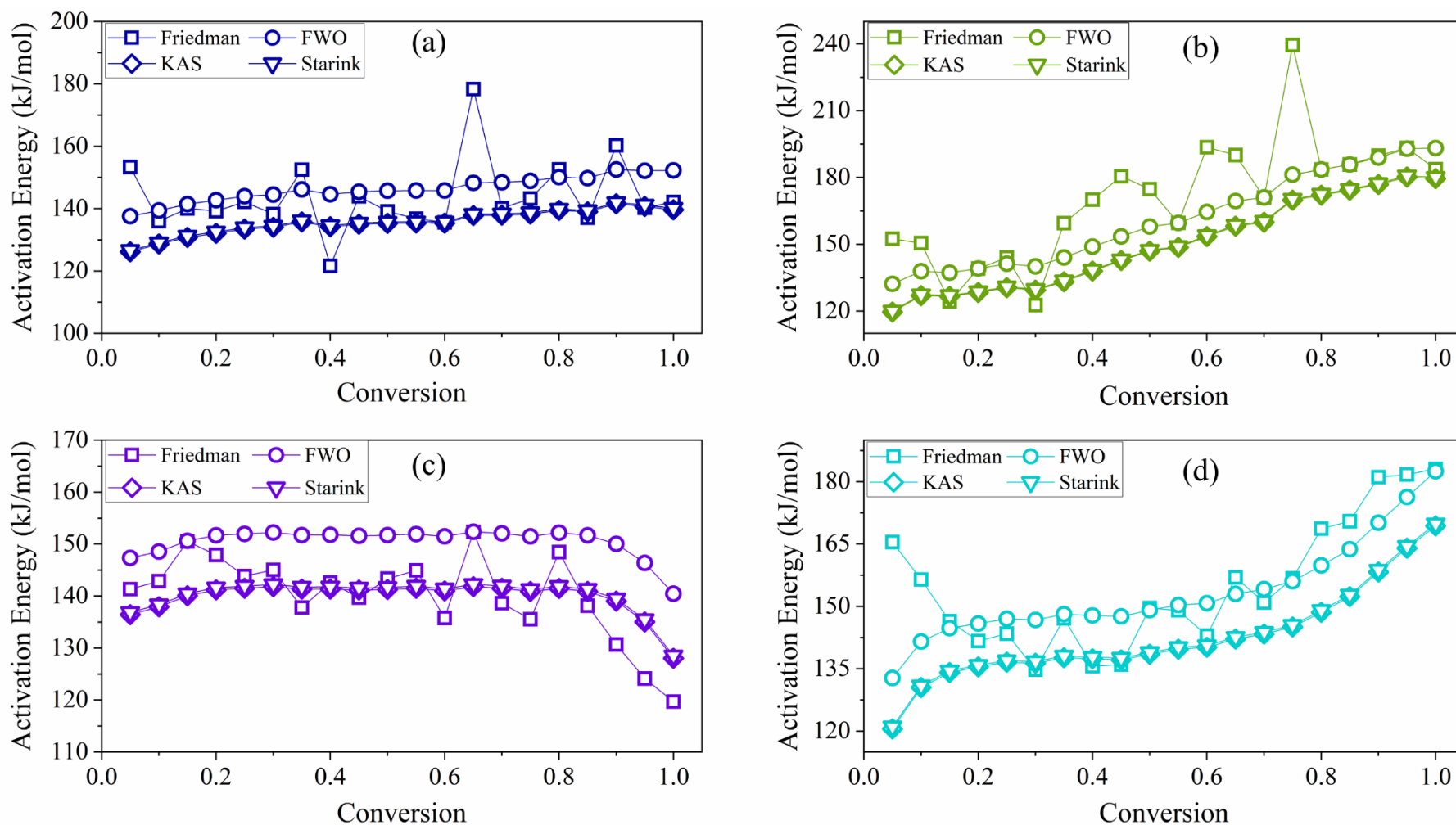


Fig. 3.3 Activation energy distribution with conversion determined by isoconversional methods of Friedman, OFW, KAS and Starink for the materials (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T

Table 3.4 Average activation energies of the RW, NM, RW-sox-T, and NM-sox-T samples determined using isoconversional methods of Friedman, OFW, KAS, and Starink

Materials	Average activation energy (kJ/mol)			
	Friedman	OFW	KAS	Starink
RW	143.7	146.3	135.5	136.0
NM	159.6	157.2	145.8	146.2
RW-sox-T	145.6	152.9	142.0	142.4
NM-sox-T	154.9	153.4	142.4	142.8

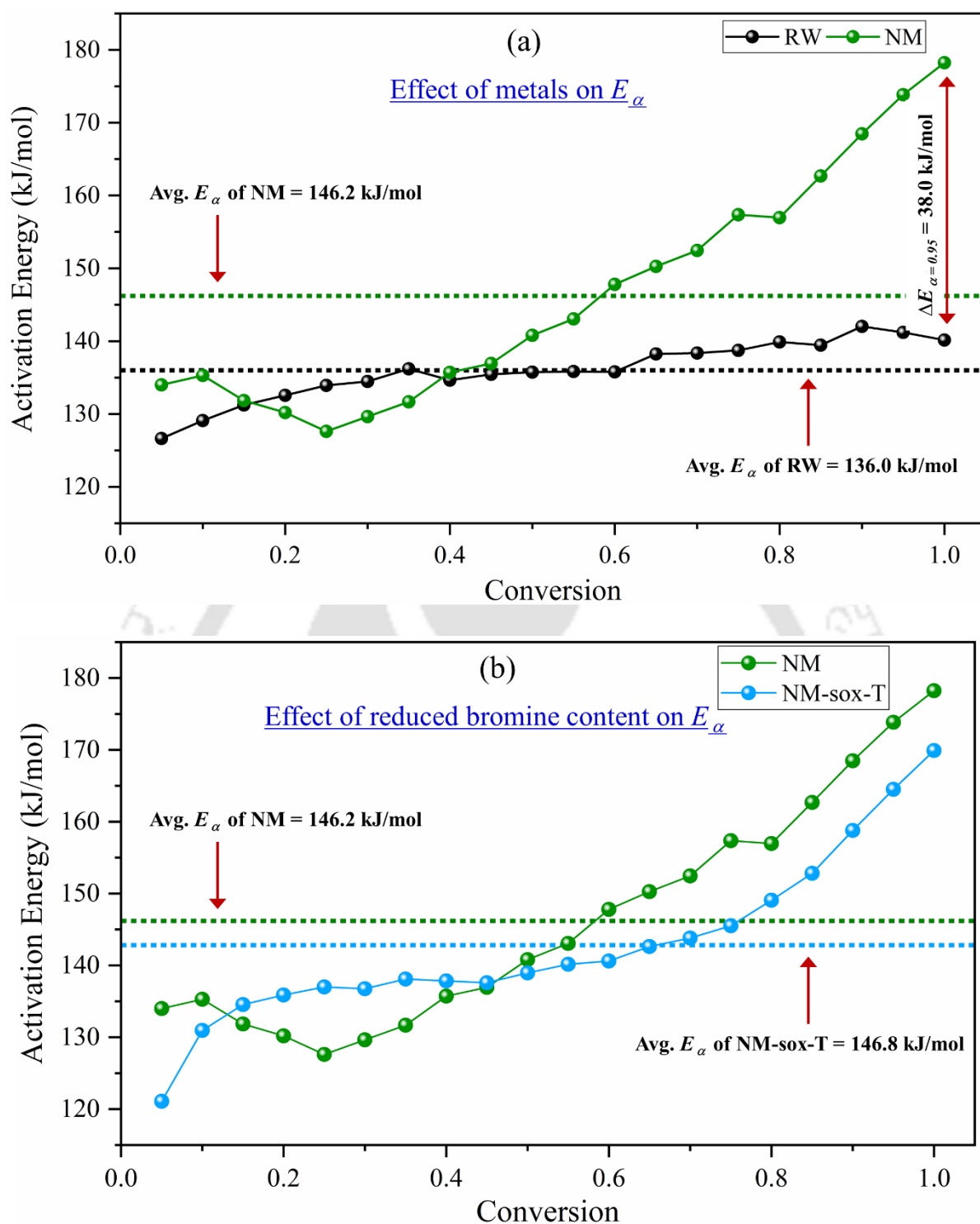


Fig. 3.4 Variation of activation energy with conversion ($\alpha = 0.05$ to 1.00) determined using the Starink method for the effect of (a) metals (RW versus NM) and (b) reduced bromine content (NM versus NM-sox-T)

3.3.2. Reaction model and Pre-exponential factor

Activation energy values were determined using multiple differential and integral model-free isoconversional methods, followed by identification of the reaction model $\{f(\alpha)\}$ via Criado-master plot (Fig. 3.5) [159]. The sum of residual squares (RSS) values was used to establish the reaction mechanism. The locus for the plot of $z(\alpha)/z(0.5)$ versus α for RW closely followed the Avrami-Erofeev (A2, A3, and A4) and Mampel (first order, F1) models. This was supported by the low values of RSS obtained for all the heating rates. The least RSS value of 0.019 was obtained for 5 °C/min. Wu et al. [105] determined the reaction mechanism using a master plot and found that the mechanism followed the Mampel power model (P3) and Avrami Erofeev (A2) model. For the NM sample, the change in the reaction model was observed in the master plot, which also complemented the activation energy variation with conversion (Fig. 3.3). At lower conversion ($\alpha = 0$ to 0.5), the thermal degradation process followed the Second order (F2) model, whereas at higher conversion levels ($\alpha = 0.55$ to 0.95), the Avrami-Erofeev (A2, A3, and A4) and Mampel (first order, F1) models were followed. The RW-sox-T showed a similar reaction mechanism as RW throughout the thermal degradation process ($\alpha = 0.05$ to 0.95), however, the NM-sox-T followed the F2 model closely from $\alpha = 0.05$ to 0.95. The similarity observed in the reaction mechanism at lower conversion between RW and RW-sox-T, and between NM and NM-sox-T, followed a pattern consistent with the apparent activation energy distribution. Since more than one reaction model exhibited a comparable RSS value, the final model selection was based on the Constable plot.

The pre-exponential factor (A), was determined using the concept of compensation effect, expressed in the form of Eq. 2.18. The pre-exponential factor obtained using the compensation effect involves the use of the reaction model, $f(\alpha)$, from the Criado Master plot. If the determined reaction model is the accurate one, then the plot of the logarithm of the pre-exponential factor versus activation energy should generate a straight line [160]. These are

known as the constable plots. In the previous section, the RSS values obtained for the F1, A2, A3, and A4 models coincided in the case of RW. Hence, to determine the correct reaction model, R^2 values of the Constable plots were obtained for the models F1, A2, A3, and A4; and compared (Fig. 3.6). The F1 model showed the highest value of $R^2 = 0.96$ for RW. Hence, it was concluded that the thermal degradation of the RW follows the mechanism as per the F1 model. F1 is an exceptional/special case of Avrami-Erooveef, where $n = 1$ [161]. According to the F1 model, the rate is directly proportional to the concentration of the reactant. Similarly, for NM ($\alpha = 0.55$ to 0.95) and RW-sox-T ($\alpha = 0.05$ to 0.95), the highest R^2 values of 0.99 and 0.76 , respectively, were obtained for F1. The lower value of $R^2 = 0.76$ for RW-sox-T could be attributed to the slight deviation of the reaction mechanism from F1 at higher conversion (Fig. 3.6). However, as compared to other standard reaction mechanisms under consideration (Table 2.1), F1 showed the best fit. Considering the best fit reaction mechanisms, the pre-exponential factor values were obtained. The range of pre-exponential factor for RW, NM, RW-sox-T, and NM-sox-T obtained were, 6.5×10^8 – 2.03×10^{10} , 6.5×10^8 – 1.36×10^9 , 1.12×10^{10} – 3.67×10^{10} and 1.17×10^8 – 1.52×10^{13} 1/s, respectively.

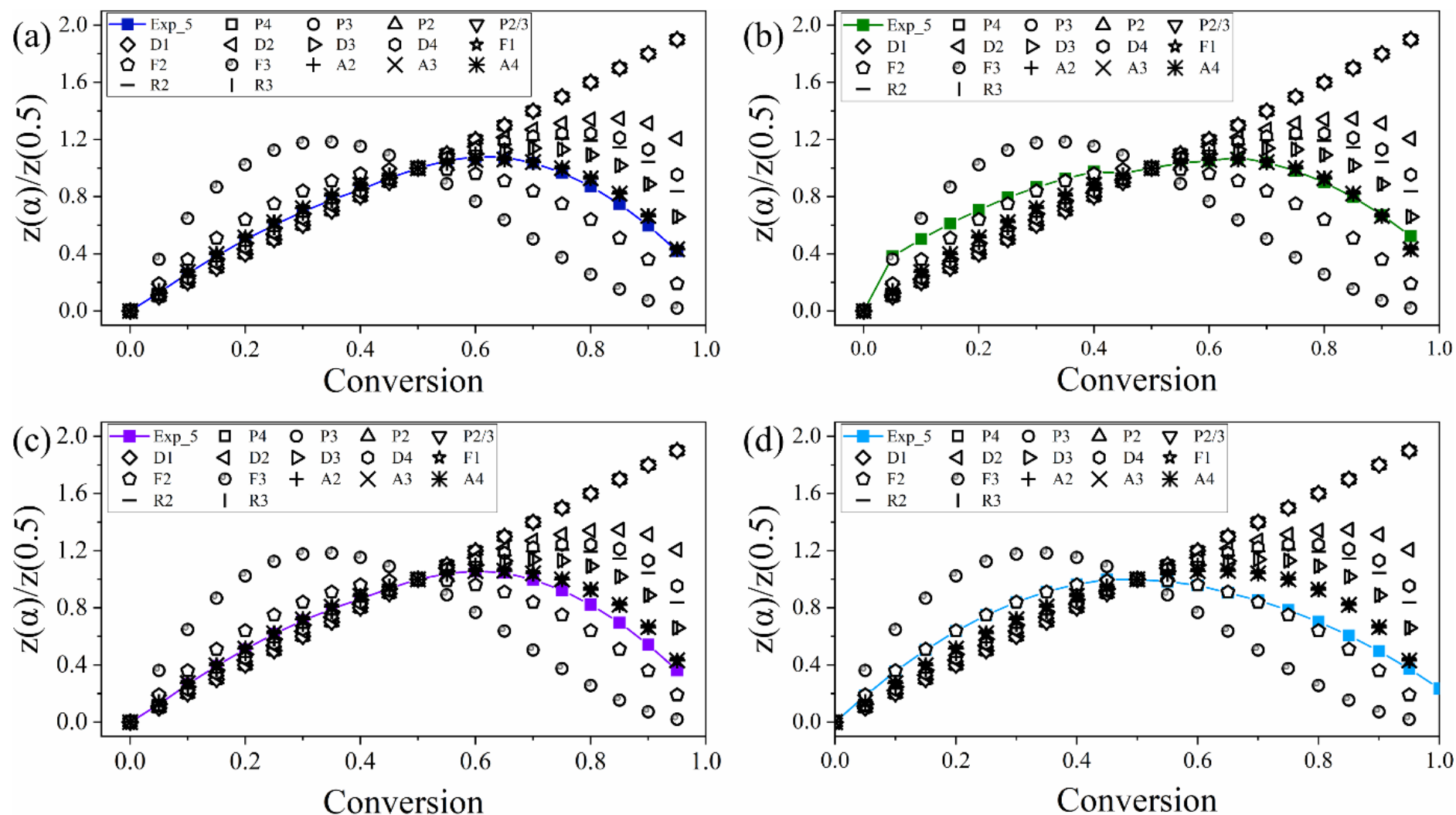


Fig. 3.5 Criado master plot at 5 °C/min for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T

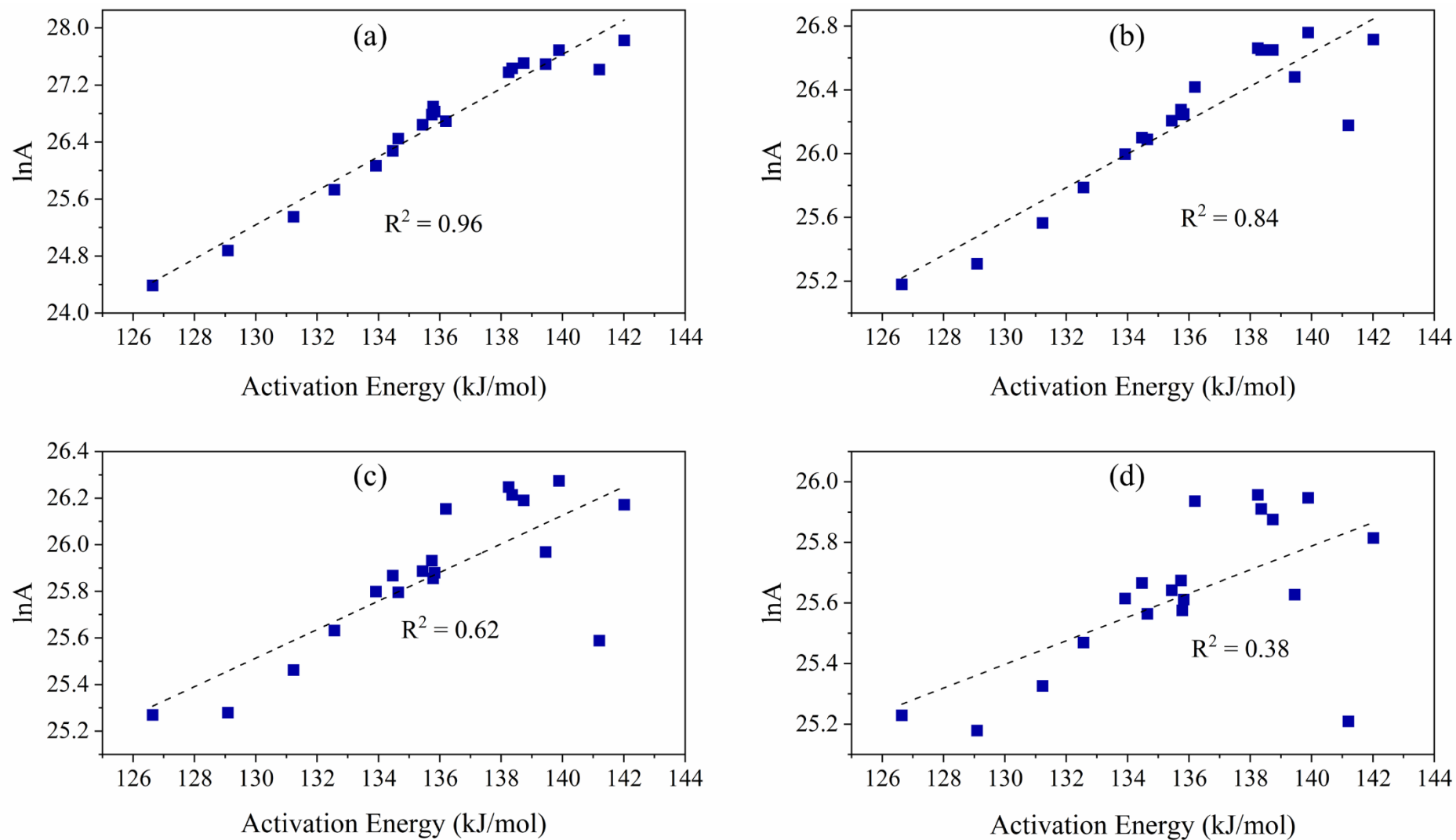


Fig. 3.6 Constable plots for RW determined using Starink method and (a) F1, (b) A2, (c) A3, (d) A4 reaction models

3.3.3. Reconstruction of conversion profiles

The purpose of the reconstruction of the conversion profile is to determine the best-fit isoconversional method. The experimental and simulated conversion profiles for the heating rates of 5, 10, 20 and 50 °C/min were compared for each sample (Fig. 3.7). To determine the best-fit method, the average R^2 value for the heating rates considered was calculated for each sample [161]. Average R^2 values of 0.9946, 0.995, 0.9822, and 0.9950 for the RW, NM, RW-sox-T, and NM-sox-T samples, respectively, were established. Fig. 3.8 shows that a high R^2 value was obtained for all samples using the Starink method. This is acceptable because the approximation considered ($B = 1.92$ and $C = 1.0008$) in the Starink method is more accurate compared to other integral isoconversional methods, which is also mentioned in the ICTAC guidelines of 2011 [133, 160]. Thus, activation energy values obtained using the Starink method were registered and considered for the calculations. Hence, the kinetic triplets (E_a , $f(\alpha)$, and A) were carefully determined, analyzed, and validated. The final values obtained after validation in the current work and the similar studies previously conducted are listed in Table 3.4 and Table 3.5, respectively.

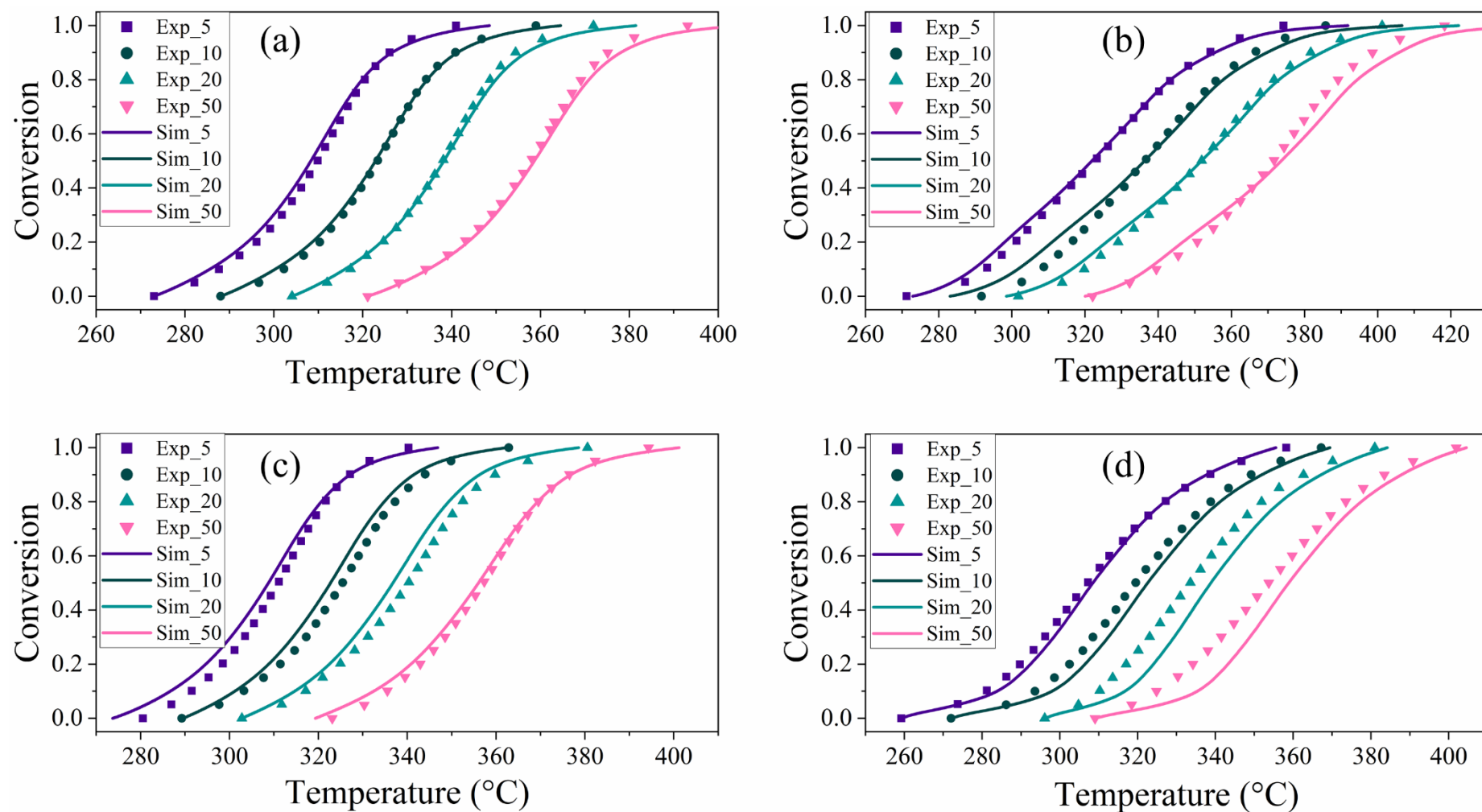


Fig. 3.7 Experimental and simulated conversion profiles for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T for heating rates of 5, 10, 20, and 50 °C/min

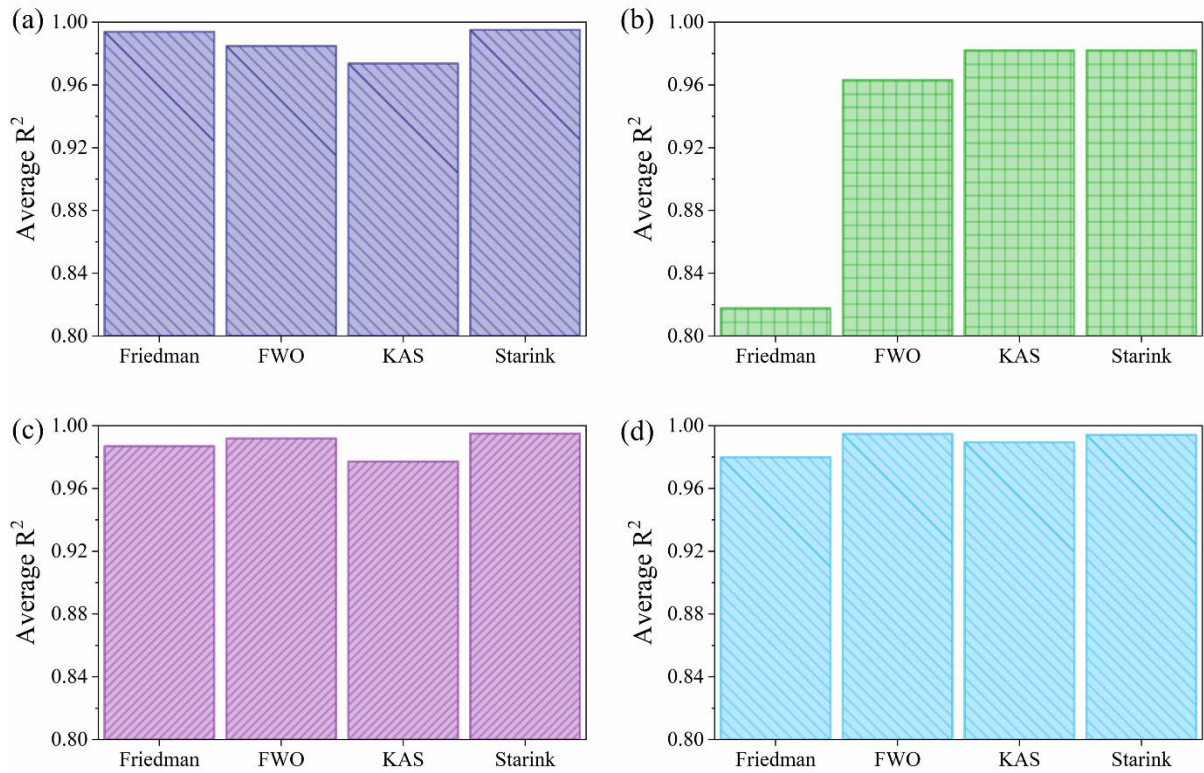


Fig. 3.8 Average R^2 values obtained for the isoconversional methods Friedman, OFW, KAS, and Starink for (a) RW, (b) NM, (c) RW-sox-T, and (d) NM-sox-T

Table 3.5 Kinetic triplets for the materials RW, NM, RW-sox-T, and NM-sox-T (using Starink)

Materials	Average activation energy (kJ/mol)	Model	Average pre-exponential factor (1/s)
RW	136.0	F1 ($\alpha = 0.05 - 0.95$)	8.5×10^9
NM	146.2	F1 ($\alpha = 0.05 - 0.50$), F2 ($\alpha = 0.55 - 0.95$)	1.31×10^{11}
RW-sox-T	142.4	F1 ($\alpha = 0.05 - 0.95$)	2.7×10^9
NM-sox-T	142.8	F2 ($\alpha = 0.05 - 0.95$)	9.83×10^{11}

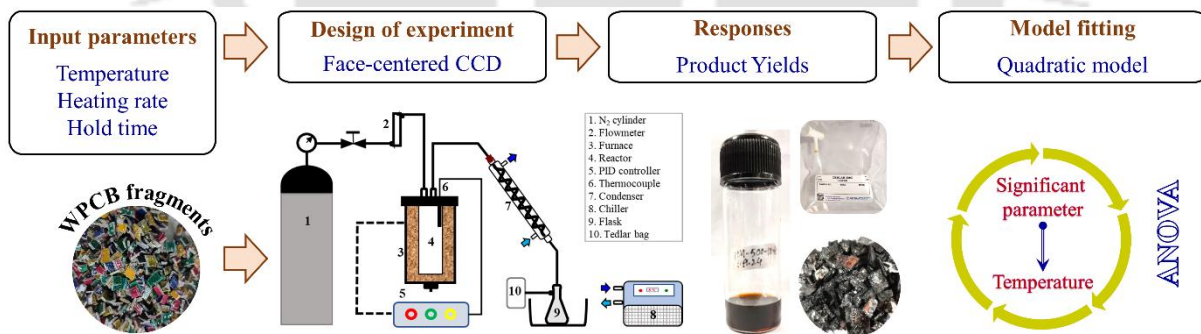
3.4. Summary

This chapter demonstrated the thermal degradation characteristics and kinetic parameters of WPCB samples (RW, NM, RW-sox-T, and NM-sox-T) in the presence and absence of metals and reduced bromine concentrations. The TG-DTG data obtained at increasing heating rates of 5, 10, 20 and 50 °C/min were used to analyze both the thermal degradation characteristics and determination of the kinetic parameters. The TG-DTG data revealed that all the samples underwent three degradation stages, with maximum degradation observed at stage II, whereas the degradation window varied with the change in sample composition. The reduction of bromine content shifted the T_{onset} to a lower value and the presence of metals reduced the T_{offset} value. The kinetic triplets were calculated from TGA data and using the reconstruction of conversion profiles, Starink was found to be the best-fit isoconversional model. The best fit kinetic data were compared for the prepared four WPCB samples. The RW (untreated WPCB) showed reduced activation energy compared to the acid-treated NM sample. The reaction model determined using the Criado master plot showed that the RW and RW-sox-T followed the same F1 model, whereas the NM-sox-T followed the F2 model, and NM followed F1 ($\alpha = 0.05$ to 0.5) and F2 ($\alpha = 0.55$ to 0.95) models. Thus, from this study, it can be concluded that the pyrolysis of WPCB should be conducted with pre-treatment for the removal/reduction of BFR and without the removal of metals. As it was observed, the presence of BFR has no beneficial impact on the thermal degradation process; therefore, its removal prior to pyrolysis is recommended to prevent contamination of the pyrolysis products with BFR traces. The presence of metals significantly reduced the energy required for WPCB degradation, thereby lowering the energy demand of the process. In addition, pyrolysis will produce metal-enriched solid residue, facilitating the recovery of metals, which represent the most valuable fraction of WPCB. The lab-scale optimization of the lab-scale pyrolysis conditions and product characterization has been presented in Chapter 4.

Chapter 4

Optimization of lab-scale pyrolysis of WPCB using RSM

- Waste printed circuit board
- Pyrolysis
- Central composite design
- Response surface methodology
- Temperature
- Resource recovery



Publication: B. Boro and P. Tiwari, "Pyrolysis of waste printed circuit board fragments: Response surface methodology optimization and effect of temperature on product characteristics", *Energy*, 319, 134892, 2025.

4. Optimization of lab-scale pyrolysis of WPCB using RSM

The direct pyrolysis of waste printed circuit board (WPCB) produces metal-enriched char, while its polymer fraction converts to valuable gas and oil fractions. However, the large inorganic fraction and low polymer fraction lead to the production of less oil yield. This chapter is focused on optimizing the pyrolysis parameters (temperature, heating rate, and hold time) towards the objective functions maximum oil and minimum solid (char) yields using response surface methodology (RSM). The purpose of the objective functions of RSM is to completely remove the organic material from the feedstock, and convert most of it to oil fraction, while producing metal-enriched char. The RSM study was employed using a face-centered central composite design (CCD) in Design Expert software (v13). The responses (oil and char yields) were analyzed using the analysis of variance (ANOVA), to identify the most significant parameter, and determine the best-fit model. The 'temperature' was found to be the most significant parameter. Hence, further pyrolysis experiments were conducted for the optimized heating rate and hold time and varying the temperatures of 300, 500 and 600 °C. The obtained products at these pyrolysis experimental conditions were subjected to detailed characterization to observe the effect of temperature qualitatively. The oil samples were characterized to determine their composition, compound type (aromatic or aliphatic), and other physical characteristics such as calorific value, density, and viscosity. The char fraction was characterized for the effect varying pyrolysis temperature by comparing with the feedstock. The gas fractions were also characterized using gas chromatography to determine their compositions. This study provides a comprehensive approach, integrating both quantitative and qualitative analyses, to optimize WPCB pyrolysis for enhanced resource recovery.

4.1. Physical and chemical properties of raw WPCB sample

The raw WPCB sample was subjected to characterization using analytical techniques before performing pyrolysis to understand its physical and chemical properties. The detailed methodology has been provided in Chapter 2, while the results and discussion have been presented in this chapter.

4.1.1. Material composition, proximate, and CHNSO analyses

The feed material (RW-cut) was examined for its composition and thermal degradation behavior. The mean values of triplicate runs were reported for the material composition, proximate and CHNSO analyses in Table 4.1. The RW-cut sample's material composition (wt%) includes approximately 30% polymer, 30% metals and 40% ceramic materials [162]. Xiu et al. [163] reported a similar material composition of WPCB with 30.8% organic materials and 40.1% glass fibers for the cut pieces of depopulated WPCB. The proximate analysis showed minor moisture content (0.48%), which is an advantage over other organic materials, such as biomass [164, 165]. The volatile matter (VM) content of 28% indicated the presence of a polymer fraction, which is in line with the literature [115]. The ash (AC) content of approximately 70% can be accounted for the metals and glass fibers, which again is in agreement with the reported wt% of metals (40%) and ceramics (30%) by Chen et al. [166]. The CHNSO analysis showed that the H/C molar ratio is slightly higher than 1. The low sulfur content in the WPCB sample is an advantage over the conventional feedstock for energy generation. The fixed (FC) content was calculated by difference, and it is also in agreement with literature [166].

Table 4.1 Material composition, proximate and CHNSO analysis of the feed material

Material composition (wt. % $\pm$ S.D.)		Proximate analysis (wt. % $\pm$ S.D.)		CHNSO analysis (wt. % $\pm$ S.D.)	
Organic	29.67 $\pm$ 1.31	Moisture	0.48 $\pm$ 0.38	C	17.44 $\pm$ 0.12
Metal	30.18 $\pm$ 0.44	VM	27.73 $\pm$ 0.96	H	1.50 $\pm$ 0.02
Ceramic	40.14 $\pm$ 0.80	AC	70.51 $\pm$ 0.36	N	0.47 $\pm$ 0.01
		FC	1.28 $\pm$ 0.82	S	0.90 $\pm$ 0.58
				O*	9.18 $\pm$ 0.71
				H/C (molar)	1.03

*Calculated at mean value. S.D. = standard deviation

4.1.2. Functional group determination of solid samples: feedstock and char

Fourier transform infrared (FTIR) spectroscopy analysis depicted the functional groups present in the WPCB samples. The spectra obtained was further compared with the char fractions obtained post pyrolysis at different temperatures. The major type of functional group present in the WPCB sample was of phenolic -OH and benzene ring. The detailed discussion on the functional groups have been provided in section 4.3.3.

4.1.3. Metal concentration of WPCB feedstock

The WPCB consists of a wide range of metals. To know the metals' concentration present in WPCB sample, the inductively coupled mass spectroscopy (ICP-MS) analysis was performed for the RW-cut ($\sim 1 \times 1 \text{ cm}^2$) and RW ($< 100 \text{ }\mu\text{m}$) samples. Average values for duplicate runs are listed in Table 4.2. The variation of metal concentration in the samples RW-cut and RW depicts the heterogeneity in distribution of metals over the surface of a WPCB. In the RW-cut sample, compared to other elements, the analyte Cu showed a higher value of $89459.68 \text{ }\mu\text{g/g}$ ($\sim 8.94 \text{ wt\%}$), which falls within the 5–26 wt% of Cu in WPCB as reviewed by Zhu et al. [26]. Cu is used as the connection lining among the electronic components (ECs) in WPCB [162]. The heavy metals Cd, Pb, and Bi were not present. Pb is primarily used in the solder parts in the circuit boards [26]. Nevertheless, since the solder part has not been considered in the sampling of RW-cut, the result is expected. In the powdered sample, a variety of metals were detected, including bromine depicting the heterogeneous metal distribution throughout the WPCB.

Table 4.2 ICP-MS analysis for metal concentration in the WPCB cut pieces (RW-cut) and powdered (RW) samples

Analytes	Metal concentration in raw WPCB ($\mu\text{g/g}$)	
	RW-cut	RW
Li	BDL*	BDL
Be	BDL	BDL
B	BDL	368.43
Na	913.09	1257.62
Mg	3.76	643.94
Al	3150.35	1546.24
K	BDL	BDL
Ca	1095.97	1214.14
Cr	BDL	33.25
Mn	BDL	38.01
Fe	BDL	1198.08
Co	BDL	BDL
Ni	BDL	95.52
Cu	89459.68	42717.41
Zn	BDL	234.4
Ga	BDL	BDL
Se	BDL	BDL
Sr	43.62	123.24
Cd	BDL	BDL
Te	BDL	BDL
Ba	BDL	BDL
Tl	BDL	BDL
Pb	BDL	157.1
Bi	BDL	BDL

*BDL = below detection limit

4.1.4. Thermal degradation study of WPCB feedstock

The thermal degradation characteristic of RW-cut in the N₂ environment was investigated using a thermogravimetric-derivative thermogravimetric (TG-DTG) study (Fig. 4.1). The initial degradation temperature (T_{onset}) of 250 °C for the heating rate of 5 °C/min was obtained. The T_{onset} was noted at the spot where the locus of mass loss started to drop from the baseline. The maximum peak (T_{max}) observed at 296 °C reported the maximum mass loss rate and the end of degradation temperature (T_{offset}) was observed at 440 °C. The degradation profile demonstrated three stages of degradation where stage II can be stated for the organic matter decomposition, with approximately 27% mass loss [91]. This is the most significant part where the epoxy resin (organic part) gets converted into volatiles such as aromatics, phenols and even lighter compounds such as methane and hydrogen [94]. Stage III showed minor mass loss, which could be accounted for char formation [15, 103, 167, 168]. Stage I showed no significant mass loss, which again justifies the minor moisture content in WPCB (Table 4.1).

The TG-DTG study provided an idea of the pyrolysis behavior of RW-cut. Thus, pyrolysis experiments were designed based on this analysis and the design of experiment (DoE) was obtained to perform the optimization of parameters. The details of the range of parameters has been provided in section 2.6 of Chapter 2.

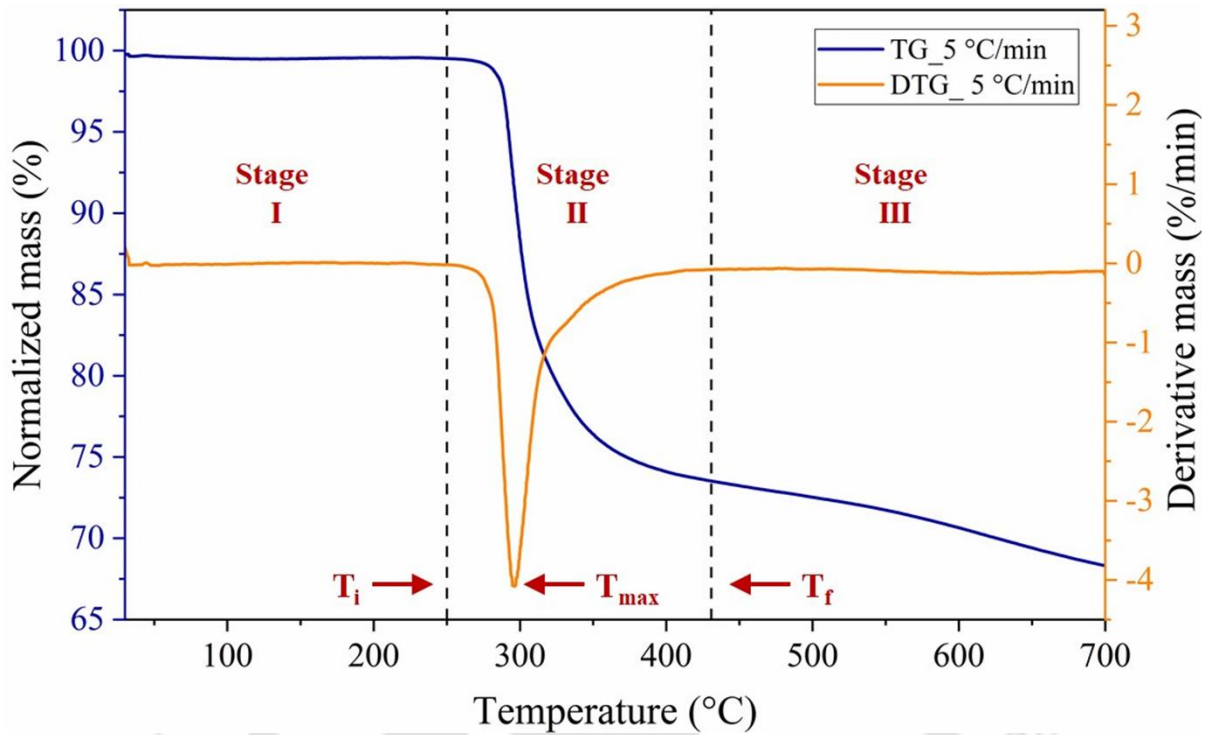


Fig. 4.1 TG-DTG curve for WPCB cut piece (RW-cut) at 5 °C/min from 30 to 700 °C to determine the thermal degradation stages

4.2. Design of experiment, ANOVA and RSM optimization

A set of 20 lab-scale pyrolysis experiments were performed according to the DoE formulated, by varying the independent parameters/factors (temperature (A), heating rate (B) and hold time (C)). The detailed information on the experimental set-up and DoE can be found in sections 2.5 and 2.6. The responses (oil and char yields) obtained were analyzed to determine the best-fit model. Based on the criteria of p-value, lack-of-fit, and the values of adjusted, and predicted R^2 (Table 4.3 and Table 4.4), quadratic model was selected. The coded equations for the quadratic model are represented by Eqs. 4.1 and 4.2 for the oil and char yields (wt%), respectively.

$$\begin{aligned} \text{Oil yield (wt\%)} = & 6.68 + 0.78A + 0.22B + 0.42C + 0.22AB + 0.24AC + 0.13BC \\ & - 0.54A^2 - 0.11B^2 - 1.19C^2 \end{aligned} \quad (4.1)$$

$$\text{Char yield (wt\%)} = 77.35 - 3.61A - 0.17B - 0.62C - 0.49AB - 0.46AC + 0.12BC + 1.23A^2 + 0.03B^2 + 0.28C^2 \quad (4.2)$$

Table 4.3 ANOVA table for the selection of a model for oil yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	22.85	9	2.54	40.8	<0.0001	significant
A	6.15	1	6.15	98.78	<0.0001	
B	0.48	1	0.48	7.71	0.02	
C	1.74	1	1.74	27.95	0.0004	
AB	0.39	1	0.39	6.29	0.03	
AC	0.45	1	0.45	7.18	0.02	
BC	0.13	1	0.13	2.05	0.18	
A ²	0.81	1	0.81	12.95	0.0049	
B ²	0.03	1	0.03	0.5	0.50	
C ²	3.87	1	3.87	62.2	<0.0001	
Residual	0.62	10	0.06			
Lack of Fit	0.42	5	0.08	2.03	0.2278	not significant
Pure Error	0.20	5	0.04			
Cor Total	23.47	19				
R ²						0.9735

Table 4.4 ANOVA table for the selection of a model for char yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	148.19	9	16.47	26.88	<0.0001	significant
A	130.03	1	130.03	212.26	<0.0001	
B	0.28	1	0.28	0.45	0.52	
C	3.91	1	3.91	6.38	0.03	
AB	1.89	1	1.89	3.09	0.11	
AC	1.68	1	1.68	2.75	0.13	
BC	0.12	1	0.12	0.192	0.67	
A ²	4.17	1	4.17	6.8	0.03	
B ²	0.0026	1	0.0026	0.0043	0.95	
C ²	0.21	1	0.21	0.34	0.57	
Residual	6.13	10	0.61			
Lack of Fit	4.12	5	0.82	2.05	0.22	not significant
Pure Error	2.01	5	0.40			
Cor Total	154.31	19				

The three independent parameters showed varying significance. Temperature proved to be the highest significant parameter with a p-value <0.0001, followed by hold time (p-value = 0.0004) and heating rate (p-value = 0.0196) for the response: oil yield. The findings are in agreement with the RSM study conducted by Muhammed et al. [169], Baruah et al. [170], and Baruah and Tiwari [171] that heating rate is a less significant parameter.

The responses obtained from experiments (actual) were tabulated (Table 4.5) against the predicted values obtained from the best-fit model for their respective runs (Fig. 4.2). The

influence of independent parameters A, B, and C on the char and oil yields are shown in Fig. 4.3 in the form of 3D surface plots. The oil yield indicated an increasing trend with the increase in temperature, which further reduced at higher temperatures (600 °C). The gas yield showed a constant increase with the increase in temperature (Fig. A. 1). Thus, thermal cracking might have occurred at higher temperatures, which led to the increase in the gas yield, and it also complements the reduction of oil yield at higher temperatures [172]. The char yield continuously reduced with the increase in temperature. The heating rate had a minimal impact on all the responses. It may be noted that even though the heating rate did not show a significant effect, it is an important parameter in pyrolysis. The effect will depend on the chosen range; a higher range might show an impact on the pyrolysis product yield distribution. The third factor, 'hold time,' showed a significant effect on the oil yield. An increasing trend of the oil yield with the increase in hold time was observed, followed by a decreasing trend at longer hold time. This was accompanied by an increasing trend of gas yield at longer hold time.

The criteria for RSM optimization were 'maximization of oil yield' and 'minimization of char yield.' The optimized conditions obtained were approximately 500 °C, 30 °C/min and a hold time of 156 min. The responses obtained for the optimized condition were 75.70% char and 7% oil yields. The solution was validated by performing experiments at the optimized conditions, which produced $76.39 \pm 1.53\%$ char and $6.93 \pm 0.45\%$ oil yields. Further pyrolysis experiments were performed at the optimized conditions of heating rate and hold time, but the temperature was varied to check the effect of the most significant parameter on the product characteristics. Thus, the char, oil and gas samples obtained at 300 °C (lower bound), 500 °C (optimized), and 600 °C (upper bound) were collected and subjected to qualitative analysis using various analytical instruments.

Table 4.5 Experimental runs based on the DoE formulated for the WPCB pyrolysis and the responses (char and oil yields) obtained

Run no.	Experimental conditions			Char yield (wt%)		Oil yield (wt%)	
	A (°C)	B (°C/min)	C (min)	Actual	Predicted	Actual	Predicted
1	450	17.5	120	77.35	77.36	6.79	6.68
2	450	17.5	180	77.10	77.00	5.85	5.91
3	600	17.5	120	76.26	74.98	6.51	6.92
4	600	5.0	180	74.24	74.73	5.82	5.71
5	450	17.5	120	76.26	77.35	6.51	6.68
6	450	17.5	120	77.10	77.35	6.72	6.68
7	450	17.5	120	77.89	77.35	7.00	6.68
8	300	30.0	180	83.10	82.77	4.26	4.36
9	600	5.0	60	76.76	77.14	4.83	4.66
10	300	30.0	60	83.30	82.86	3.71	3.75
11	450	17.5	120	77.08	77.35	6.55	6.68
12	450	30.0	120	76.86	77.22	6.80	6.79
13	450	5.0	120	78.13	77.55	6.08	6.35
14	450	17.5	120	78.00	77.35	6.96	6.68
15	300	5.0	60	82.55	82.46	4.01	4.02
16	600	30.0	60	75.33	75.60	5.36	5.29
17	450	17.5	60	78.38	78.25	4.87	5.07
18	300	17.5	120	81.13	82.19	5.50	5.35
19	300	5.0	180	82.10	81.89	4.11	4.12
20	600	30.0	180	73.53	73.67	6.91	6.85

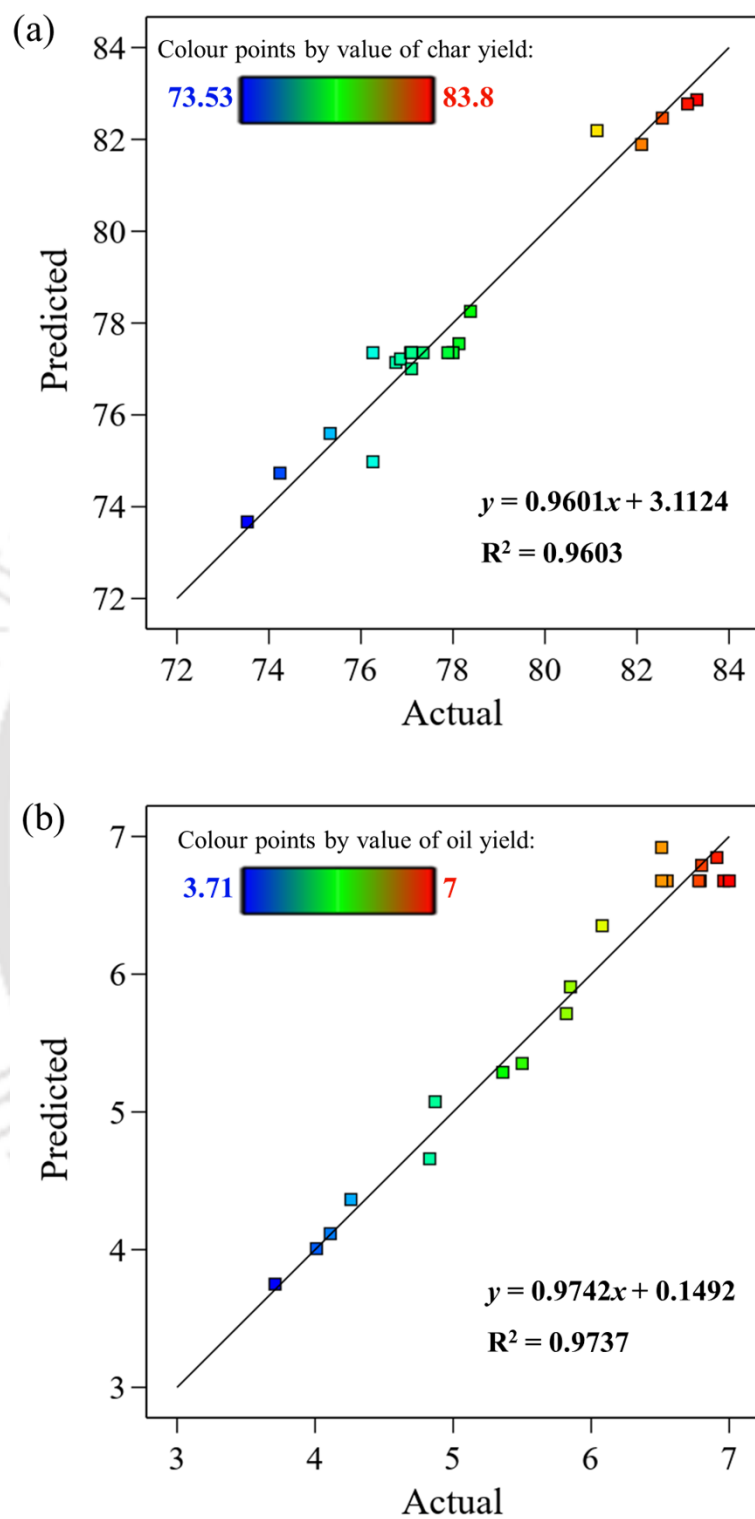


Fig. 4.2 Actual versus predicted plots for product yields obtained for the (a) char, (b) oil yields

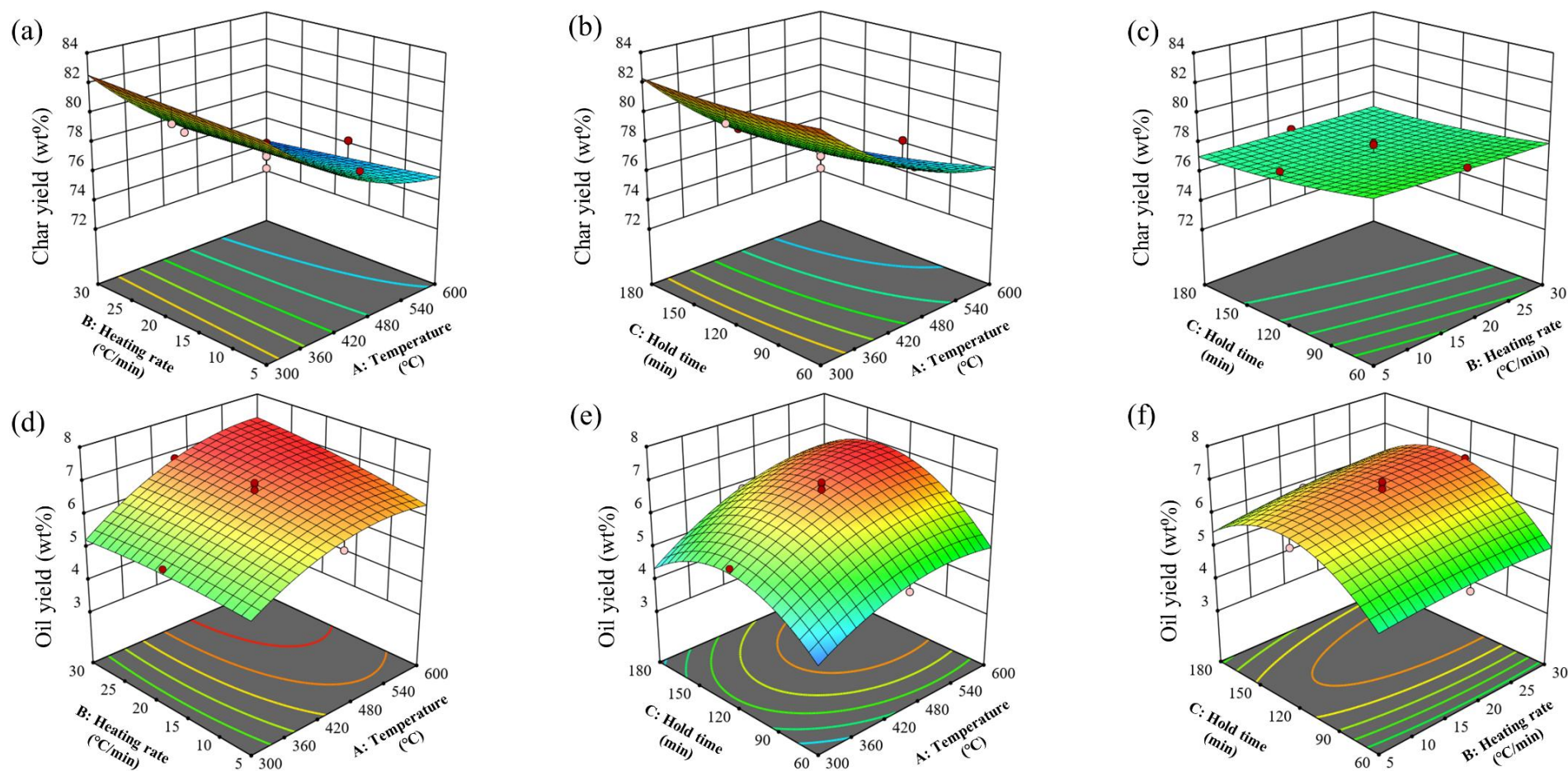


Fig. 4.3 3D Response surface plots for the WPCB pyrolysis char yield (wt%) with varying (a) A and B, (b) A and C, and (c) B and C, and oil yield (wt%) with varying (d) A and B, (e) B and C and (f) B and C

4.3. Characterization of pyrolytic products obtained at different temperatures

The qualitative analysis of the product fractions obtained at the pyrolysis temperatures of 300, 500 and 600 °C was performed using various analytical techniques, as discussed below.

4.3.1. Oil characterization

4.3.1.1. FTIR analysis

This analysis confirmed the presence of the -OH group from phenol, represented by the broad peak at 3670–3134 cm^{-1} . The peaks at 2960 and 2868 cm^{-1} gave a hint for the presence of alkane and alkene groups, respectively [173]. The stretching vibrations of C=C from the benzene ring observed at the wavenumber of 1596, 1470 and 1361 cm^{-1} clearly indicated the presence of aromatic compounds [174]. In addition, the presence of in-plane bending vibration of the benzene ring was identified from the peaks at 1224 and 1069 cm^{-1} . Similarly, the out-of-plane bending vibrations of the benzene ring were recognized from the 814, 745 and 687 cm^{-1} peaks. The peak at 506 cm^{-1} showed the presence of C-Br stretch [121]. The analysis indicated the existence of primarily aromatic compounds and also brominated compounds (Fig. 4.4). The compiled FTIR spectra for the oil fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C showed similar functional groups. Thus, GC-MS and NMR (^1H and ^{13}C) studies were also performed for the improvised compositional analysis.

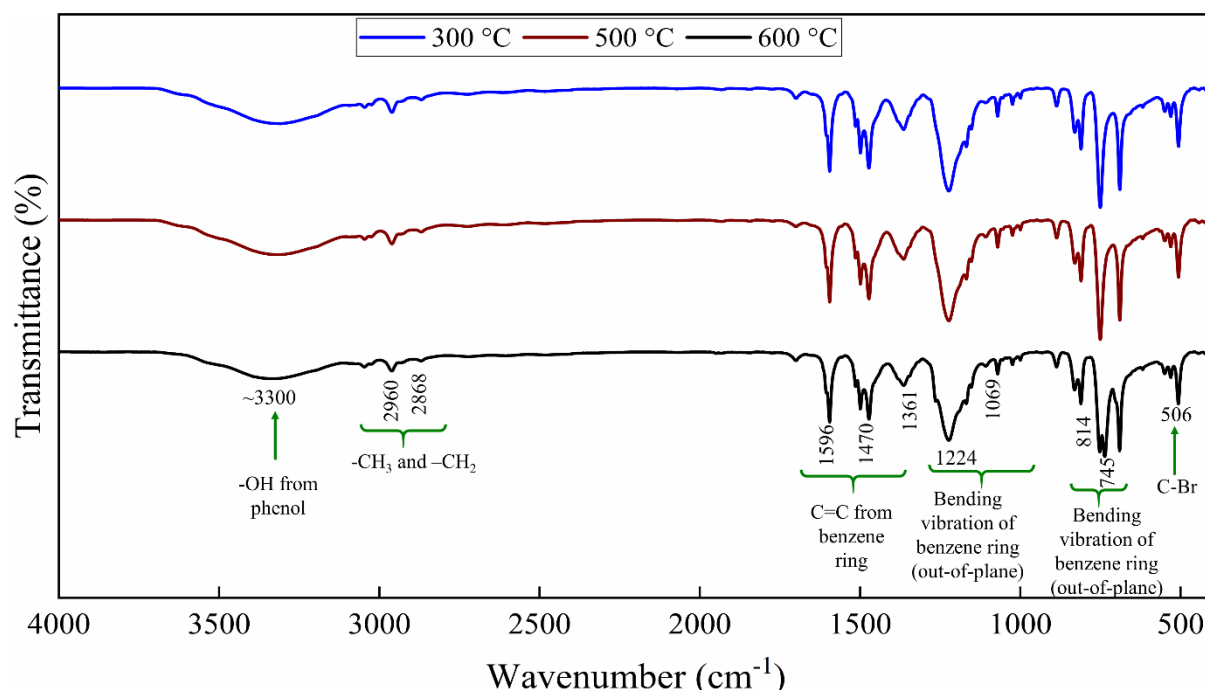


Fig. 4.4 FTIR analysis for the liquid fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C to determine the type of functional groups

4.3.1.2. GC-MS analysis

The compounds detected in the GC-MS analysis include a majority of phenol (59%) and phenol derivatives (30%), along with other aromatics (0.9%), furan derivatives (0.07%) and brominated compounds (0.2%) [168]. The detailed compound list is given in Appendix A (Table A. 2). Sun et al. [175] reported over 70% phenol compounds, whereas Zhu et al. [91] reported 33.96 to 37.16 GC-MS area% for phenol compounds depending on pyrolysis temperature. Gao et al. [167] showed various possible pathways for the degradation of WPCB during pyrolysis and concluded that all the pathways led to the formation of phenolic compounds; hence, higher phenol content was anticipated in the pyrolytic oil fraction. Zhu et al. [26] pointed out that the presence of halogenated compounds reduces the heating value of the oil fraction. Hence, pre-treatment or post-treatment of the pyrolytic oil fraction is essential for removing the brominated compounds, which has been discussed in Chapter 5.

4.3.1.3. ^1H NMR and ^{13}C NMR analysis

The examination of the spectra obtained for the oil samples was performed by the use of ACD-NMR software (free version) to identify the structural components using ^1H and ^{13}C NMR, as shown in Fig. 4.5 (a) and (b), respectively [176]. The proton and carbon assignments are indicated in Tables 4.6 and 4.7, respectively. For ^1H NMR, the aromatic content reduced from 57% at 300 °C to 52% at 600 °C. This was also supported by the ^{13}C NMR analysis, where the aromatic content was reduced from 93% to 77% at similar pyrolysis temperatures. Chiang and Lin [177] observed that the aromatic constituent was the major species for WPCB pyrolysis at <300 °C, which later decreased at higher pyrolysis temperatures. However, the olefin compounds increased with the increase in pyrolysis temperatures. In ^{13}C NMR, the overall alkyl group showed an increasing trend with the increase in pyrolysis temperature.

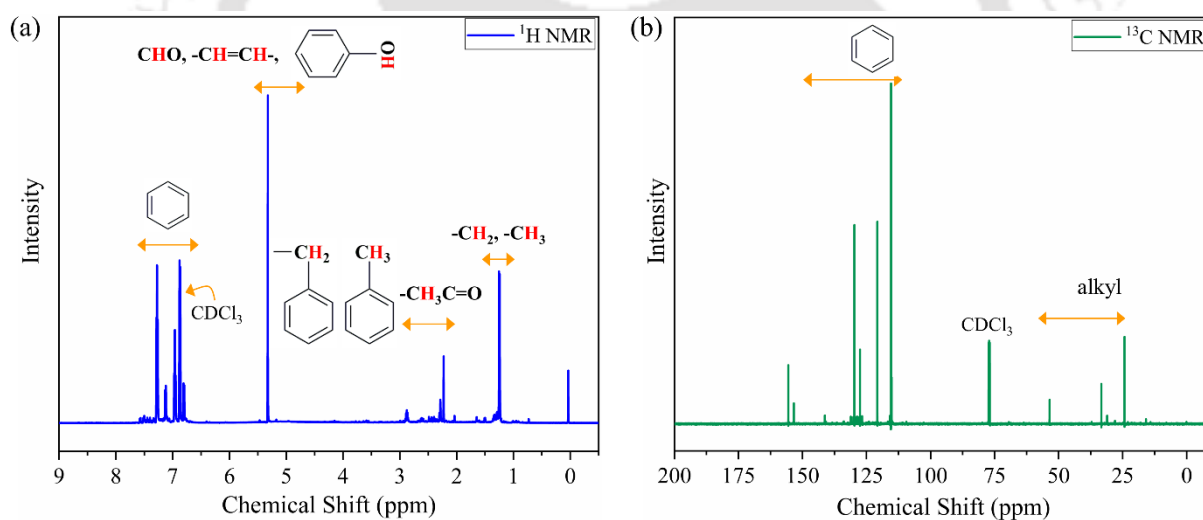


Fig. 4.5 (a) ^1H NMR and (b) ^{13}C NMR spectra for the oil fraction obtained at pyrolysis temperature 600 °C

Table 4.6 ^1H NMR chemical shift integral regions and area% for the oil fractions obtained at pyrolysis temperatures 300, 500 and 600 °C

Chemical shift (ppm)	Proton assignments	Peak area (%) for pyrolytic oil obtained at temperatures		
		300 °C	500 °C	600 °C
8.0–6.8	Aromatic ring	56.89	55.87	51.59
6.4–4.2	CHO, *ArOH, HC=C- (nonconjugated)	14.64	14.85	20.17
3.0–2.2	CH ₃ C=O, CH ₃ -Ar*, -CH ₂ -Ar*	10.49	11.01	11.63
1.6–0.0	-CH ₃ , -CH ₂	18.00	18.27	16.61

*Ar = aromatic ring

Table 4.7 ^{13}C NMR chemical shift integral regions and area% for the oil fractions obtained at pyrolysis temperatures 300, 500 and 600 °C

Chemical shift (ppm)	Carbon assignments	Peak area (%) for pyrolytic oil obtained at temperatures		
		300 °C	500 °C	600 °C
0–28	short aliphatic	1.73	13.86	11.69
28–55	long and branched aliphatic	4.54	7.12	11.08
95–165	Aromatics	93.74	79.03	77.23

4.3.1.4. ICP-MS analysis

The ICP-MS analysis of the oil fraction (a potential fuel source) was carried out to assess the presence of metal compounds if any [178]. Pulles et al. [179] studied the emission of heavy metals from petrol and diesel in Europe and found that the range of metal emission is within the ppb ($\mu\text{g}/\text{kg}$) range. The presence of heavy metals might cause serious environmental issues during oil spills or leaching of these metals from storage tanks while storing, from dumping sites of used oil, etc. Thus, it is essential to determine the metal concentration in oil. The ICP-MS analysis of the oil fractions showed minor concentrations of metals (Table 4.8). Lin and Chiang [180] conducted a similar analysis and reported low heavy metal concentrations with total elements ranging from 0.17 to 0.2 mg/g-PCB. According to Zhu et al. [99] metal volatilization occurs during WPCB pyrolysis due to the reaction of metals with HBr forming metal bromides such as CuBr. In the current study, the total concentration of metals ranged from 145 to 280 $\mu\text{g}/\text{kg}$ of the oil fraction for different pyrolysis temperatures. Trace amounts of metals in the oil fraction indicated that most metals remained in the char [105]. Yuan et al. [178] conducted an environmental risk assessment for the presence of heavy metals in bio-oil produced from pyrolysis/liquefaction of sewage sludge. A similar analysis can be performed for the oil fraction obtained from pyrolysis of WPCB for better understanding.

Table 4.8 Metal concentration in oil fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C using ICP-MS analysis

Analytes	Concentration (µg/kg-oil fraction) of metals present in pyrolytic oil produced at temperatures		
	300 °C	500 °C	600 °C
Li	BDL*	BDL	BDL
Be	BDL	BDL	BDL
B	BDL	BDL	BDL
Na	1.5	BDL	BDL
Mg	4.4	7.3	3.5
Al	5.3	9.1	7.9
K	0.4	BDL	BDL
Ca	27.1	78.4	25.3
Cr	1.5	2.9	3.1
Mn	BDL	0.3	0.1
Fe	21	16.6	17.9
Co	BDL	0.1	BDL
Ni	0.2	0.1	0.1
Cu	2.7	2.6	4.3
Zn	73.6	155.9	87.1
Ga	BDL	BDL	BDL
Se	0.1	0.2	0.1
Sr	0.7	1.5	0.6
Cd	BDL	BDL	BDL
Te	0.2	0.2	0.1
Ba	BDL	BDL	BDL
Tl	BDL	BDL	BDL
Pb	6.4	5.2	6.3
Bi	BDL	BDL	BDL

*BDL = below detection limit

4.3.1.5. Physical properties of the oil fraction

The calorific value of the oil fraction obtained using a bomb calorimeter reduced from 35 MJ/kg at 300 °C to 31 MJ/kg at 600 °C. This can be associated with reduced aromatic content at higher pyrolysis temperatures, as obtained in NMR analyses (^1H and ^{13}C). Jadhao et al. [92] reported a calorific value of 34 MJ/kg for the oil fraction obtained from pyrolysis (temperature = 500 °C, heating rate = 10 °C/min, hold time = 30 min) of mobile phone WPCB. The viscosities measured at ambient conditions were found to increase from 0.053 at 300 °C to a constant value of 11 cP at 500 and 600 °C (Table 4.9). The density of the oil fractions (at 23 °C) increased from 1.07 g/cm³ to 1.13 g/cm³ at pyrolysis temperatures of 300 and 600 °C, respectively.

Table 4.9 Calorific value, viscosity and density of the oil fraction obtained at pyrolysis temperatures of 300, 500 and 600 °C

Pyrolysis temperature (°C)	Calorific value (MJ/kg)	Viscosity (cP)	Density (g/cm ³)
300	35.33	5	1.07
500	33.97	11	1.07
600	30.81	11	1.13

4.3.2. Gas characterization

The gas fractions obtained at increasing pyrolysis temperature were subjected to compositional analysis using gas chromatography (GC) containing the flame ionization (FID) and thermal conductivity detectors (TCD). Gases H₂ and CH₄ showed an increasing trend with pyrolysis temperature (Fig. 4.6). Initially, a minor H₂ (0.08%) was produced at 300 °C, which could be because of the commencement of the condensation and dehydrogenation reactions [91]. The formation of CH₄ could be caused by the combination of methyl groups present in WPCB and

the H_2 generated. At higher temperatures, the concentrations of both hydrogen and methane increased in the gas phase. This may be due to the secondary reaction (the cracking of hydrocarbons) at elevated temperatures, which also results in a higher gas yield [181]. This shows the occurrence of dehydrogenation and methanation reactions at higher pyrolysis temperatures. The release of CO and CO_2 could be due to the thermal degradation of the epoxy group [182]. The production of high calorific value gases (H_2 and CH_4) showed that the gas fraction has the potential to be used for energy generation required in the pyrolysis process itself. Hence, making it a process that sustains its own energy needs. Furthermore, the lower concentration of global warming gases CO and CO_2 indicates an environment-friendly process. The analysis using FID showed the presence of hydrocarbon gases ($C_2 - C_5$). These were found to be present in less than 1%, except for n-butane (Fig. 4.7).

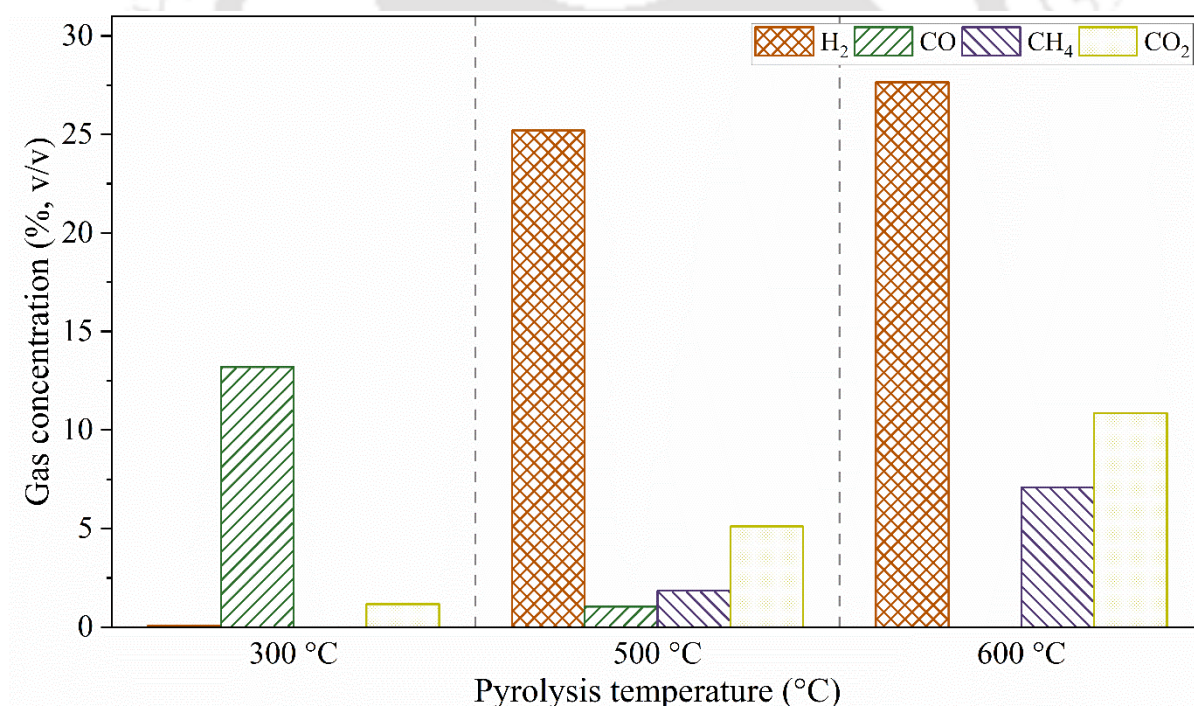


Fig. 4.6 Gas composition analysis at pyrolytic temperature 300, 500 and 600 °C using GC-TCD

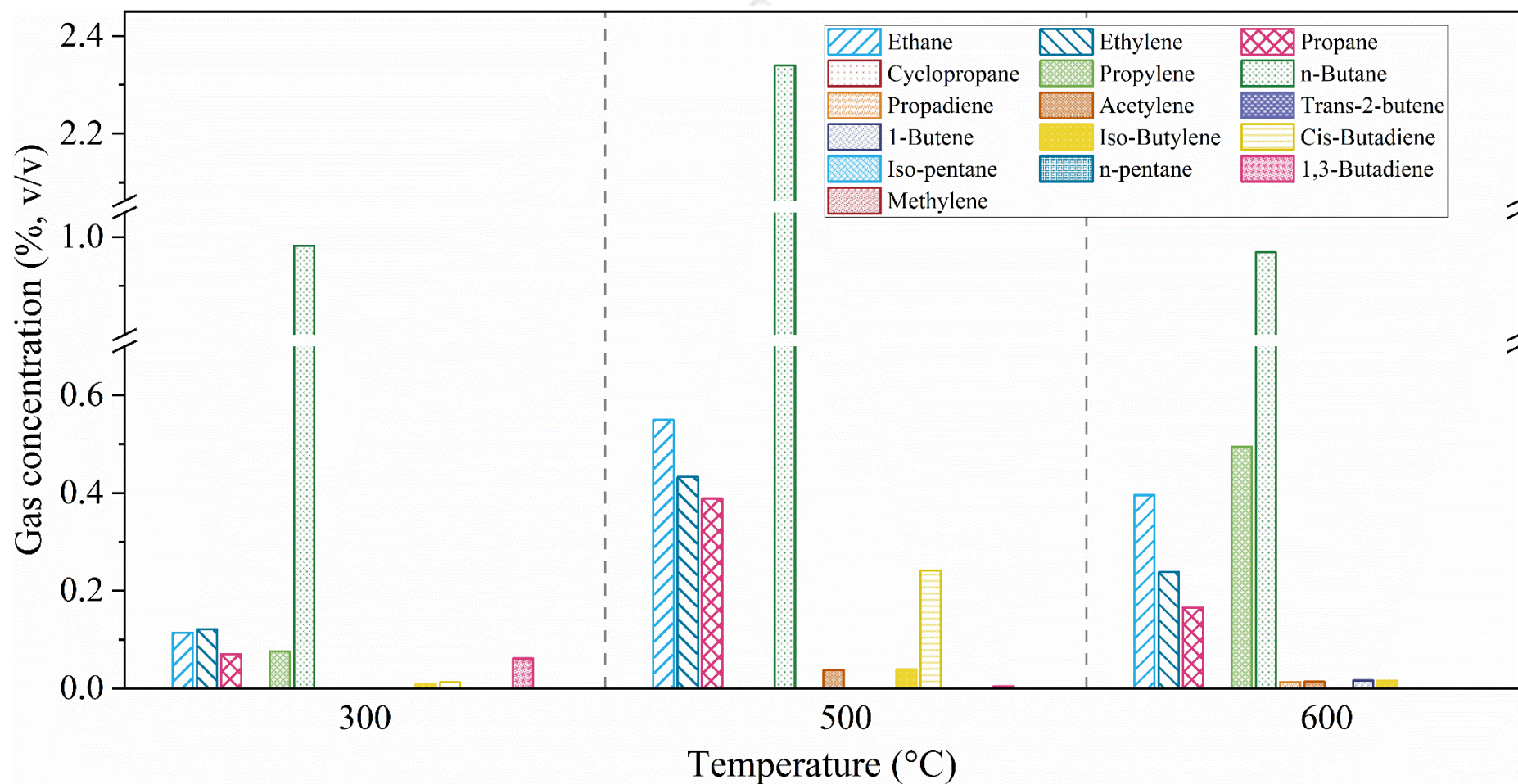


Fig. 4.7 Gas composition analysis at pyrolytic temperatures 300, 500 and 600 °C using GC-FID

4.3.3. Char characterization

The compositional and morphological changes caused due to the increasing pyrolysis temperature (300, 500 and 600 °C) was presented by the CHNS, FESEM and FTIR analyses. At 300 °C, the C and H composition reduced to 11.73 and 0.97 wt%, respectively. This accounts for 5.7 (for C) and 0.53 (for H) wt% reduction as compared to the raw WPCB (Table 4.10). The maximum weight loss of C and H was observed when the pyrolysis temperature increased from 300 to 500 °C. However, for an increase of 100 °C (500 to 600 °C), a minor weight loss (wt%) of 0.57 for C and 0.07 for H was observed. Hence, it is evident that the thermal degradation is severe up to 500 °C and minor after that. Thus, pyrolysis can be performed to a maximum of 500 °C from the energy conservation perspective [92].

The FESEM image (top-view) of the raw WPCB was compared with the char fractions obtained at pyrolysis temperatures of 300, 500 and 600 °C (Fig. 4.8 (a) to (d)). The images clearly depicted the gradual removal of organic material from the WPCB cut pieces with the increase in temperature, leaving behind the glass fibers. The glass fibers retained their rod-like structure, allowing them to be reused in a variety of applications such as construction or making composites, provided the required tensile strength is maintained [45, 183]. Chen et al. [166] also found that the glass fibers retained its structure but shortened in length after pyrolysis of WPCB granules. Fig. 4.8 (b) shows that clean glass fibers were not obtained at 300 °C. This is because of the incomplete removal of organic material, which was confirmed by the elemental analysis as showing 11.7% C and 0.97% H.

The FTIR analysis of the char samples at similar pyrolysis temperatures to the CHNS analysis also supports the removal of the organic functional groups when compared to the raw WPCB (RW). The FTIR spectra indicated the presence of characteristic peaks of C-H stretching at 2961 and 2870 cm^{-1} , respectively [15]. The 1735 cm^{-1} peak can be assigned to the C=O. The

peaks at 1500 cm^{-1} represent the C=C stretch from the aromatic ring of the epoxy resin, which is mostly used for the fabrication of the WPCB substrate. The 1177 cm^{-1} peak is assigned to the Si-O-Si or Si-C [166]. The peaks at 564 and 463 cm^{-1} can be assigned to the aromatic C-Br and C-Br, respectively [115]. These functional groups were observed to have disappeared in the char materials, showing the occurrence of thermal degradation (Fig. 4.9).

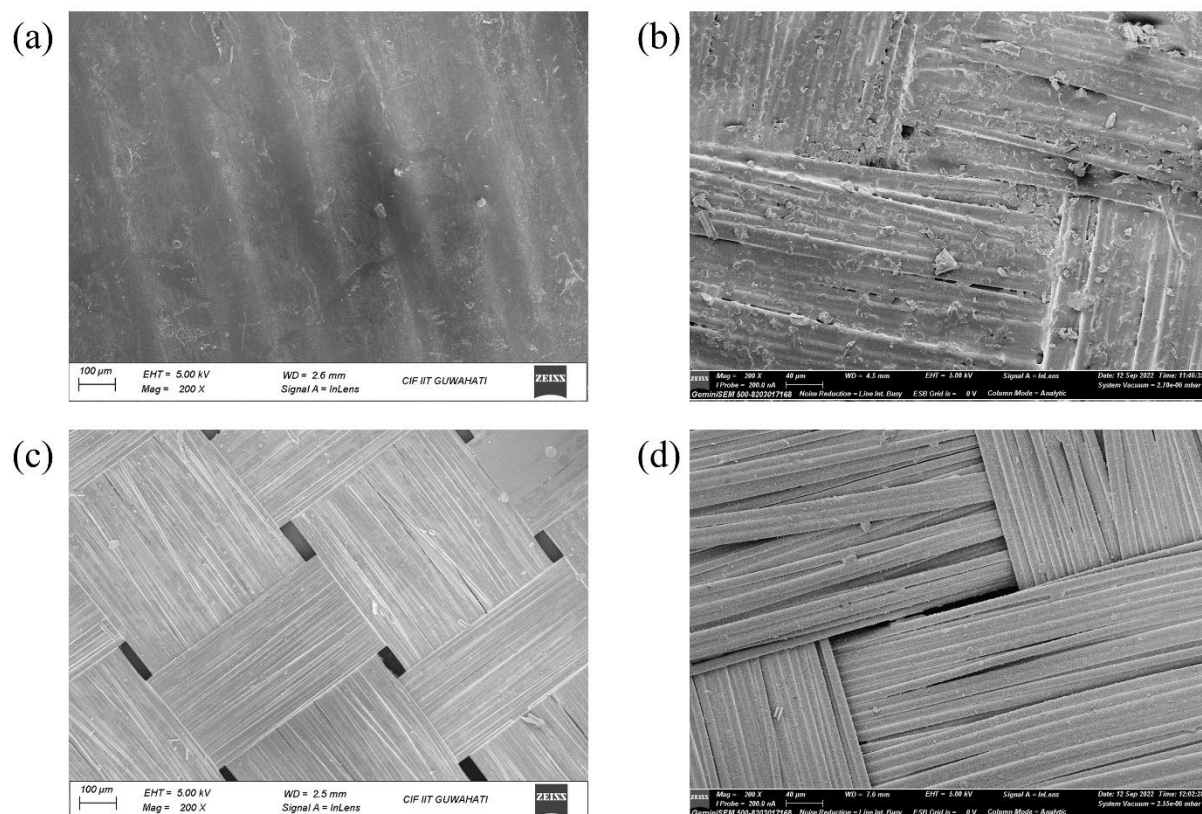
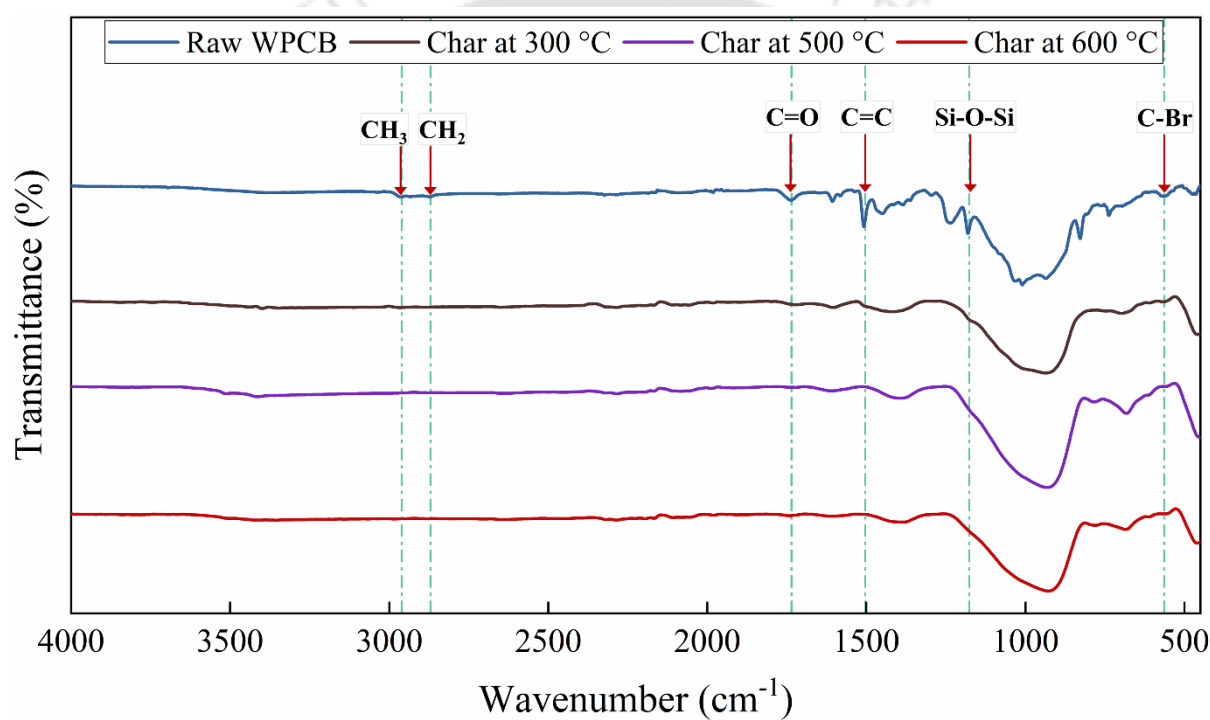


Fig. 4.8 FESEM images (top view) of (a) raw WPCB, (b) char at $300\text{ }^{\circ}\text{C}$ (c) char at $500\text{ }^{\circ}\text{C}$ and (d) char at $600\text{ }^{\circ}\text{C}$

Table 4.10 CHNS analysis of the WPCB pyrolysis char at 300, 500 and 600 °C

Pyrolysis temperature (°C)	Elemental composition (wt%) of			
	C	H	N	S
300	11.73	0.97	0	1.59
500	4.30	0.29	0	1.07
600	3.73	0.22	0	1.05

**Fig. 4.9** FTIR spectra for the raw WPCB and char obtained at pyrolysis temperatures of 300, 500 and 600 °C

4.4. Summary

Waste printed circuit board consists of organic and inorganic fractions. To recover the organic fraction in the form of oil and gas, pyrolysis of WPCB cut pieces (RW-cut) was studied and optimization of process parameters was performed. The independent parameters temperature, heating rate, and hold time were investigated for the responses char, and oil yields (wt%) to obtain maximum oil and minimum char yields using RSM. Additionally, the qualitative analysis of the product fractions was investigated based on the increasing pyrolysis temperature. The following conclusions can be drawn from this chapter.

- The quadratic model is the best-fit model for the relationship between the independent parameters and the responses. Temperature is the most significant parameter that influences the distribution of WPCB pyrolysis products.
- The oil fraction characterization inferred that it consists mainly of aromatics (mainly phenolic compounds) and a lower fraction of aliphatic and brominated compounds. This was confirmed by the FTIR, GC-MS, and NMR analyses (^1H and ^{13}C). A minor amount of metals transferred into the oil fraction upon direct pyrolysis of the WPCB samples. The pyrolytic oil exhibited high calorific value (30–35 MJ/kg), low viscosity (5–11 cP), and low density (1.07–1.13 kg/m³) values, depicting its potential for energy generation applications.
- The increase in pyrolysis temperature decreased the aromatic and alkyl content, whereas it increased the olefin content in the oil fraction. The calorific value showed a decreasing trend, whereas the viscosity and density increased with the increase in pyrolysis temperature.
- The GC analysis using TCD and FID showed the presence of high calorific value gases, low concentrations of CO and CO₂, and minimal concentrations of C₂–C₅ gases. The amount of H₂, CH₄, and CO₂ increased with pyrolysis temperature.

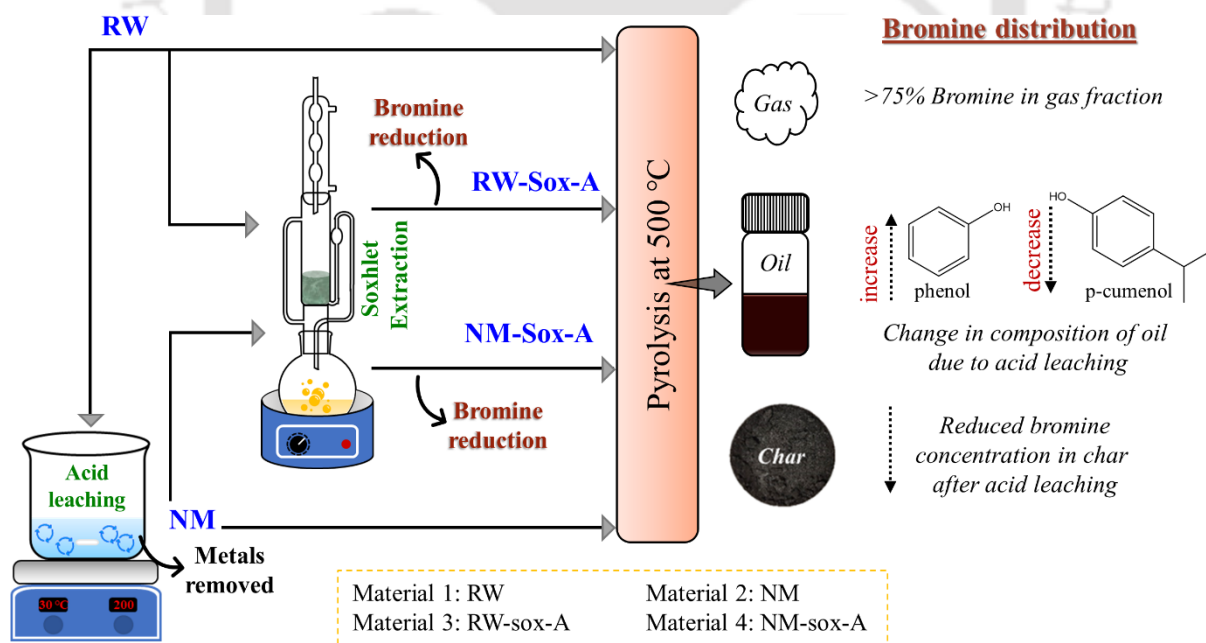
- The maximum amount of the organic fraction gets degraded up to 500 °C, and clean glass fibers were obtained at higher pyrolysis temperatures (500–600 °C).

The study provides an insight into sustainable E-waste management and its significant potential for practical applications in waste treatment, resource recovery, and clean energy generation. Translating lab-scale results to industrial-scale applications might require further validation and cost analyses. Additional work might be needed to refine the quality of the recovered products, particularly the oil fraction, to enhance their market value. The large amount of char produced during the pyrolysis process, containing metals and glass fibers, has a great potential for application to increase the profit. After the pyrolysis, the metal recovery is made easier as the organic part gets removed in the pyrolysis process, and the remaining glass fibers can be used for construction purposes. Hence, a complete utilization of the WPCB components or resource recovery is achieved.

Chapter 5

Reduction of bromine in pyrolytic oil produced from WPCB

- Brominated flame retardant
- Pyrolysis
- Metals
- Waste printed circuit board
- Acid leaching
- Soxhlet extraction



Publication: B. Boro and P. Tiwari, “Effects of pre-treatment on product characteristics and bromine behavior during pyrolysis of waste printed circuit boards for resource recovery”, *Journal of Analytical and Applied Pyrolysis*, 193, 107375, 2026.

5. Reduction of bromine in pyrolytic oil produced from WPCB

Pyrolysis presents a viable route for resource recovery from waste printed circuit boards (WPCBs); however, brominated flame retardants (BFRs) poses significant challenges due to their toxicity and the potential contamination of recovered products. The transfer of bromine into the volatiles released during pyrolysis can be mitigated through two primary approaches: (i) pre-treatment of the feedstock, and (ii) the use of catalysts or additives during pyrolysis. This chapter investigates both approaches to minimize bromine content in the pyrolytic oil fraction. Soxhlet extraction was incorporated as the pre-treatment technique to reduce the bromine content of WPCB prior to pyrolysis, while the embedded metals present within the WPCB matrix were examined for the catalytic effect to reduce bromine transfer into the oil phase. Accordingly, four feedstocks were prepared: raw WPCB (RW), nonmetallic fraction obtained post-acid leaching (NM), and their Soxhlet-extracted counterparts (RW-sox-A, NM-sox-A). Pyrolysis experiments were conducted at the previously optimized conditions (Chapter 4). The product fractions (char, oil and gas) obtained from pyrolysis of these feedstocks were analyzed to assess both quantitative and qualitative variations, with specific emphasis on bromine distribution. Characterization techniques such as FTIR, ^1H NMR, GC-SimDist and GC-MS were performed on the oil samples. Gas chromatography (GC-TCD/FID) analysis was performed for the gas fractions produced. Bomb calorimeter-ion chromatography analysis was mainly used for the examination of the bromine distribution across different product fractions for different feedstocks. This chapter presents a study on the reduction of bromine content in oil by means of Soxhlet extraction of feed material and the action of embedded metals during pyrolysis. This systematic approach enables a comprehensive assessment of the individual and combined effects of the pre-treatment steps and embedded metals' presence on brominated compound formation during WPCB pyrolysis.

5.1. Selection of solvent for Soxhlet extraction

Metal removal via acid leaching and bromine reduction through Soxhlet extraction modified the thermal degradation profiles and kinetic parameters in WPCB samples (Chapter 3). Although acid leaching effectively removed metals, Soxhlet extraction using toluene was inadequate for significant bromine reduction. Consequently, other organic solvents DCM, acetone and 2-propanol were explored to further reduce the bromine content from RW before pyrolysis experiments. The bromine reducing efficiency of these solvents was compared using X-ray fluorescence (XRF) analysis (Fig. 5.1). The matrix composition of all the samples remained unchanged across all the extractions thus, XRF analysis provided adequate data for comparing bromine reduction efficiency. The analysis identified acetone as the most effective solvent, achieving an approximate bromine reduction of 16 wt%. Similar bromine reduction efficiencies (15–19%) were achieved using toluene and 2-propanol for Soxhlet extraction of WPCB samples, as reported by Evangelopoulos et al. [158]. Hence, acetone was selected as the extraction solvent for preparing the reduced-bromine feedstock RW-sox-A. Similarly, Soxhlet extraction of the metal-free, acid leached sample (NM) using acetone produced the corresponding sample, NM-sox-A.

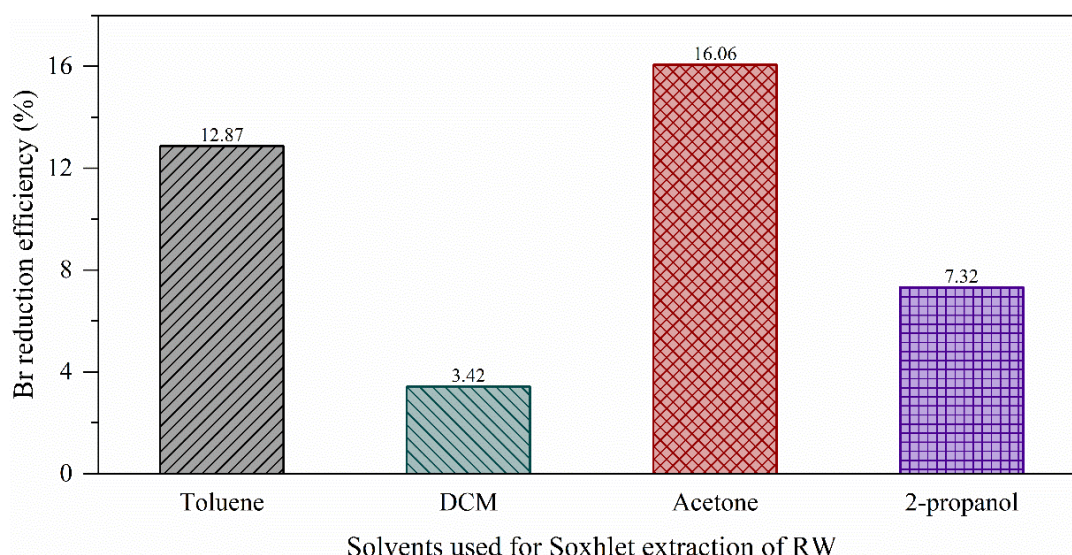


Fig. 5.1 Bromine reduction efficiency obtained after 24 h Soxhlet extraction using different solvents: toluene, DCM, acetone, and 2-propanol

5.2. Characterization of the feedstocks

5.2.1. Elemental composition of feedstocks using XRF analysis

The relative elemental compositions of the prepared feedstock materials (RW, NM, RW-sox-A, and NM-sox-A) were determined using XRF analysis. The analysis revealed that elements such as Si, Al, and Ca were present in significant amounts, which can be attributed to the glass fiber component of the WPCBs (Table 5.1). Furthermore, the acid leaching treatment using HCl-HNO₃ mixture resulted in the removal of several metallic elements, specifically Cr, Ni, Cu, Sn, and Pb [100]. Partial reduction of elements such as Fe and Mg was also observed, while elements including Na, K, Ti, Sr, and Ba remained largely unaffected by the acid treatment.

Table 5.1 Inorganic elemental composition of the materials RW, NM, RW-sox-A (acetone) and NM-sox-A (acetone) using XRF analysis

Elements	Elemental composition (wt%)			
	RW	NM	RW-sox-A	NM-sox-A
Si	43.78	50.5	35.14	52.39
Al	10.71	11.56	9.47	12.12
Fe	2.17	0.59	0.75	0.37
Mg	1.15	0.56	6.15	0.52
Ca	20.98	23.03	12.04	23.9
Na	0.36	0.37	0.40	0.43
K	0.16	0.15	0.12	0.17
Ti	0.67	0.66	0.34	0.70
S	1.42	0.84	0.95	0.85
Br	8.47	8.73	7.11	4.57
Sr	0.18	0.20	BDL	0.20
Ba	1.50	1.23	1.14	1.34
F	BDL	0.43	BDL	0.45
Cl	BDL	0.82	0.12	0.98
Cr	0.44	BDL	BDL	BDL
Cu	4.45	BDL	21.94	BDL
Sn	2.72	BDL	3.58	BDL
Ni	0.29	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL
Zn	BDL	BDL	BDL	BDL

*BDL = below detection limit

5.2.2. Material composition, proximate and CHNSO analyses

The compositions of polymer, metal and ceramic components in a WPCB vary according to the type, application and other factors [26, 184]. According to the type of substrate, WPCBs can be classified into FR-4 (superior quality, glass-reinforced epoxy-based) and FR-2 (inferior quality, phenolic-based substrate). Other types of printed circuit board are single-sided, double-sided, or multi-layered. The WPCBs used in the current study are of multi-layered FR-4 type [38]. Hence, the current study can be a representative for a similar kind of WPCBs. The compositional analysis provided the distribution of polymer, metal and ceramic fractions in the acid-treated and Soxhlet-extracted samples. The WPCB powder sample without any treatment (RW) consisted of approximately 22% polymers, 33% metals and 45% ceramics. The polymer fraction was found to be 51%, 22% and 44% for the NM, RW-sox-A and NM-sox-A materials, respectively (Fig. 5.2). Due to the acid leaching, the NM and NM-sox-A have negligible metal content ($\sim 1\%$), which shows that the metal extraction step was efficient. As a result, these materials have increased polymer content as compared to the RW and RW-sox-A materials.

The proximate analysis showed a similar trend of low moisture and fixed carbon content, along with high ash content for all the feedstock materials (Table 5.1). The NM and NM-sox-A samples showed higher volatile matter content due to the removal of the metallic fraction in the acid leaching process. On comparing RW-sox-A with RW, the volatile matter was slightly reduced from 23.80 wt% (for RW) to 21.77 wt% (RW-sox-A). A small amount of the polymer fraction might have been leached out into acetone during extraction. A similar reduction in the volatile matter is noticeable for the NM and NM-sox-A; however, the reduction is higher for the latter. The CHNSO analysis for RW (reported in Chapter 4) was compared with the other three materials [132]. The sample analyses showed an overall trend of low N and S content. The C and H contents for the NM and NM-sox-A are higher than those of the RW and RW-

sox-A samples, respectively. This was also supported by the higher volatile matter and polymer content obtained in the proximate and material compositional analyses, respectively.

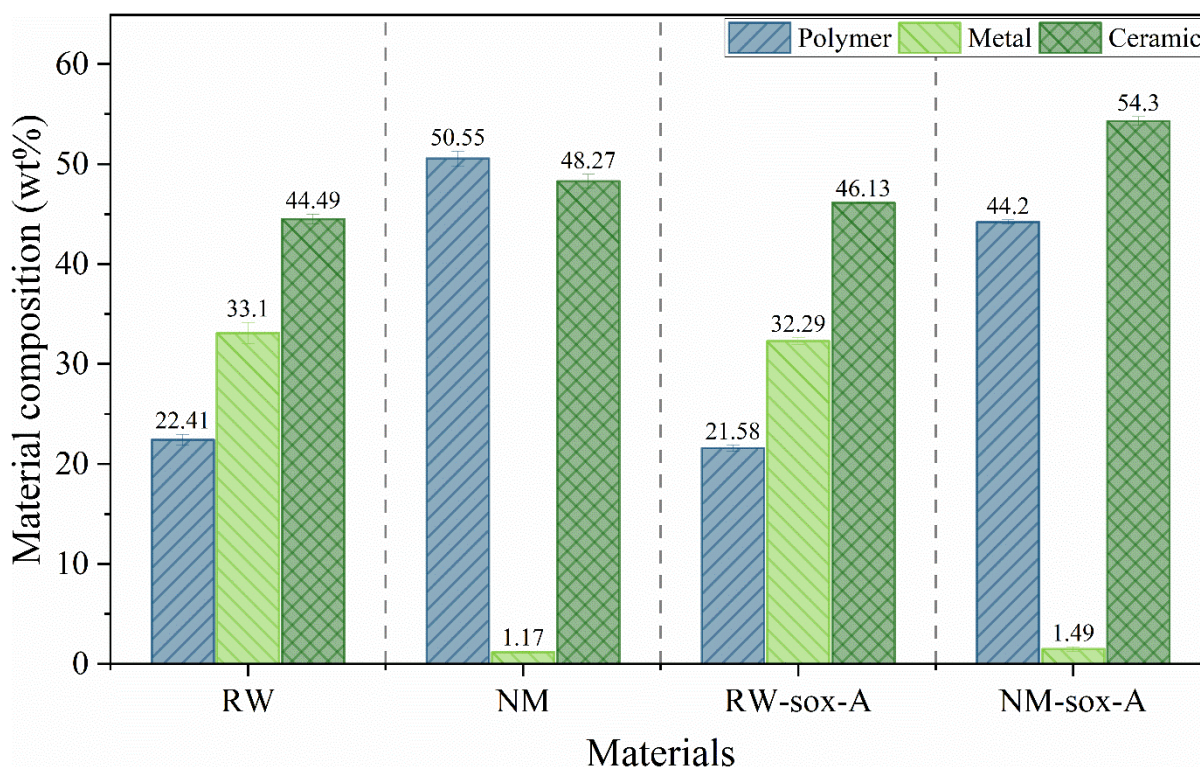


Fig. 5.2 Compositional analysis (wt%) of the materials RW, NM, RW-sox-A and NM-sox-A in terms of polymer, metal and ceramic fractions

Table 5.2 Proximate and CHNSO analyses of the feedstock materials RW, NM, RW-sox-A and NM-sox-A

Material	Proximate analysis* (wt%) $\pm$ S.D.				CHNSO analysis** (wt%) $\pm$ S.D.				
	Moisture	VM	AC	FC	C	H	N	S	O [#]
RW	0.72 $\pm$ 0.18	23.80 $\pm$ 0.74	75.36 $\pm$ 0.78	0.12 $\pm$ 0.05	17.44 $\pm$ 0.12	1.50 $\pm$ 0.02	0.47 $\pm$ 0.01	0.90 $\pm$ 0.58	4.33 $\pm$ 1.20
NM	1.60 $\pm$ 0.28	49.83 $\pm$ 0.40	47.71 $\pm$ 0.98	0.87 $\pm$ 0.59	25.61 $\pm$ 0.11	2.25 $\pm$ 0.15	0.94 $\pm$ 0.01	0.14 $\pm$ 0.02	23.37 $\pm$ 0.99
RW-sox-A	1.00 $\pm$ 0.18	21.77 $\pm$ 0.48	77.08 $\pm$ 0.21	0.14 $\pm$ 0.03	18.34 $\pm$ 0.51	1.53 $\pm$ 0.11	0.50 $\pm$ 0.02	0.09 $\pm$ 0.00	2.45 $\pm$ 0.56
NM-sox-A	1.43 $\pm$ 0.23	44.06 $\pm$ 0.55	54.01 $\pm$ 0.40	0.49 $\pm$ 0.43	24.45 $\pm$ 0.17	2.19 $\pm$ 0.10	0.83 $\pm$ 0.02	0.18 $\pm$ 0.03	18.33 $\pm$ 0.45

by difference, *wet basis, **dry basis

O content (wt%) = $100 - \sum(\text{wt\% of C, H, N, S, ash})$

5.2.3. Thermal degradation study

The thermal degradation behavior of the feedstock materials (RW, NM, RW-sox-A, and NM-sox-A) was investigated prior to the lab-scale pyrolysis experiments using thermogravimetric-derivative thermogravimetric (TG-DTG) analysis (Fig. 5.3). All samples exhibited a similar degradation pattern characterized by three distinct stages. However, differences in residual mass and mass loss contents were observed, attributed to variations in their organic and inorganic content. The acid-leached samples (NM and NM-sox-A) showed lower residual masses compared to RW, indicating a reduction in ash forming components due to the removal of metallic fractions and a corresponding increase in volatile content. In contrast, Soxhlet-extracted samples (RW-sox-A and NM-sox-A) demonstrated higher residual masses relative to their respective untreated counterparts (RW and NM). The overall degradation profile can be divided into three stages. The minimal mass loss in stage I can be attributed to the minor moisture contents, and the degradation of epoxy resin can be connected to stage II. The mass loss of the organic material in stage II is in the order of $NM > NM\text{-}sox\text{-}A > RW > RW\text{-}Sox\text{-}A$. This agrees with the organic/volatile matter fraction obtained for the four different materials prepared. The stage III can be attributed to the formation of char.

Furthermore, the acid leaching and Soxhlet extraction treatments affected the thermal degradation profile. Acid leaching predominantly affected the final degradation temperature (T_{offset}), resulting in an increase, while the initial degradation temperature (T_{onset}) showed relatively minor shifts. The presence of metals was found to lower the T_{offset} , consistent with catalytic effects that facilitate thermal degradation at lower temperatures. Additionally, the temperature with maximum degradation rate (T_{max}) was elevated for the acid-leached sample (NM), whereas a reduction in T_{max} was observed for the Soxhlet-treated samples (RW-sox-A and NM-sox-A) compared to the untreated RW sample [100].

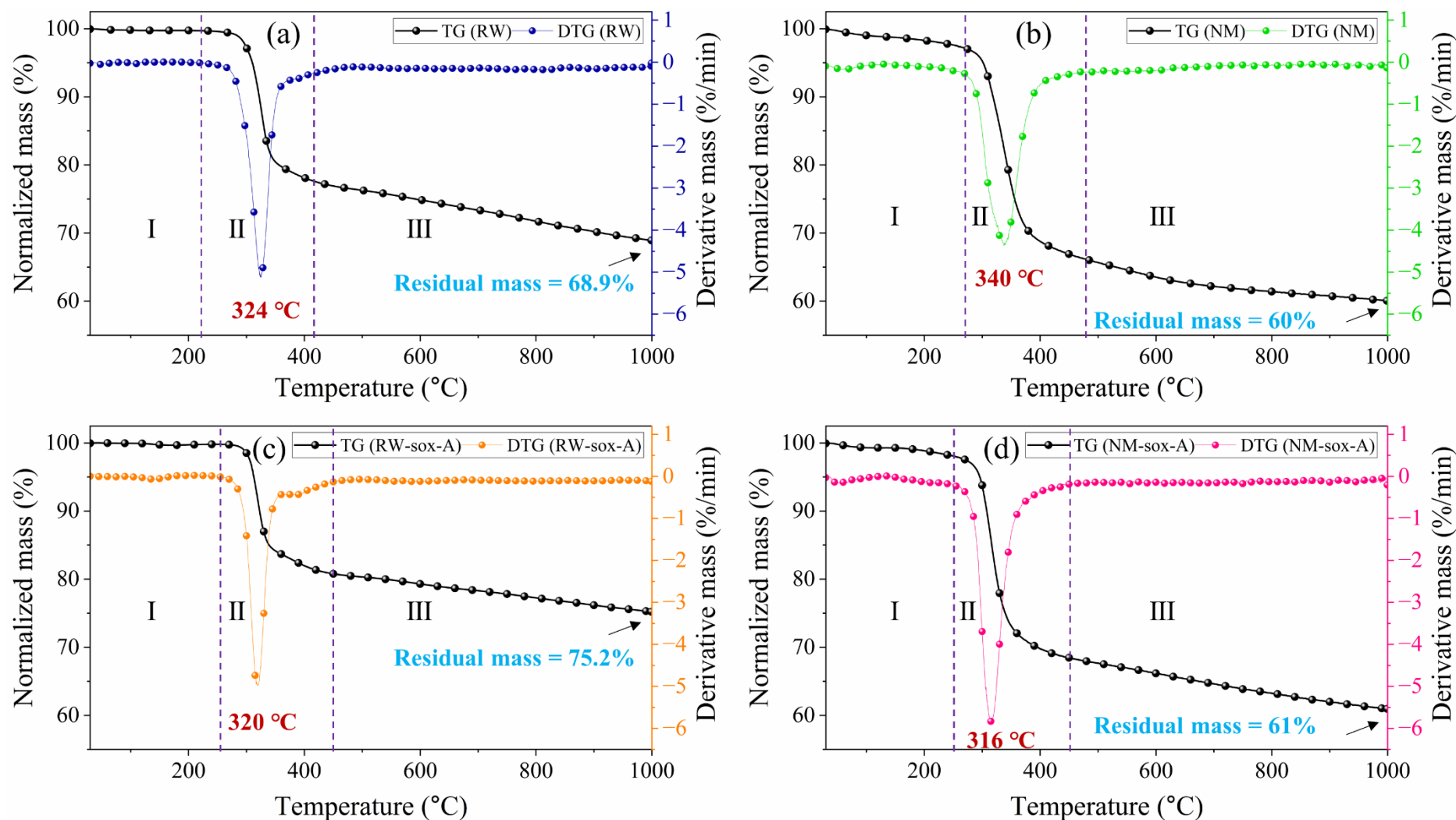


Fig. 5.3 TG-DTG study of (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A at 10 °C/min from 30 to 1000 °C under N₂ environment

5.3. Lab-scale pyrolysis: product yield distribution

The lab-scale pyrolysis experiments at optimized conditions of 500 °C, 30 °C/min and 156 min hold time have produced three product fractions: char, oil and gas [132]. The char content ranged from 64% for NM to 77.3% for RW-sox-A (Fig. 5.4 (a)). The oil content was found to be lowest for RW-sox-A (6.5%) and highest for the NM (14.5%). This could be traced back to the lowest and highest volatile matter in the RW-sox-A and NM samples, respectively. Thus, the recovery of metals from WPCB before pyrolysis is favorable for obtaining a higher oil yield. However, since the pre-treatment steps have changed the material composition of the feed materials, understanding the contribution of the organic fraction to oil and gas yields is important. Thus, the product yields of oil and gas have been recalculated based on the organic fraction (OF) using Eq. 5.1 and Eq. 5.2, and the results are given in Fig. 5.4 (b). In this case, the presence of metals has increased oil yield as compared to the acid leached residues. This may be attributed to the change in thermal degradation range (section 5.2.3). A few more perspectives, such as the economic and environmental perspectives, must be considered before deciding the best process. Hence, the product fractions were characterized extensively to understand their compositions.

$$\text{Oil yield}_{\text{OF}}(\text{wt}\%) = \frac{\text{Wt. of oil produced (g)}}{\text{Wt. of OF (g)}} \times 100\% \quad (5.1)$$

$$\text{Gas yield}_{\text{OF}}(\text{wt}\%) = 100 - \text{Oil yield (wt}\%) \quad (5.2)$$

where, OF refers to organic fraction

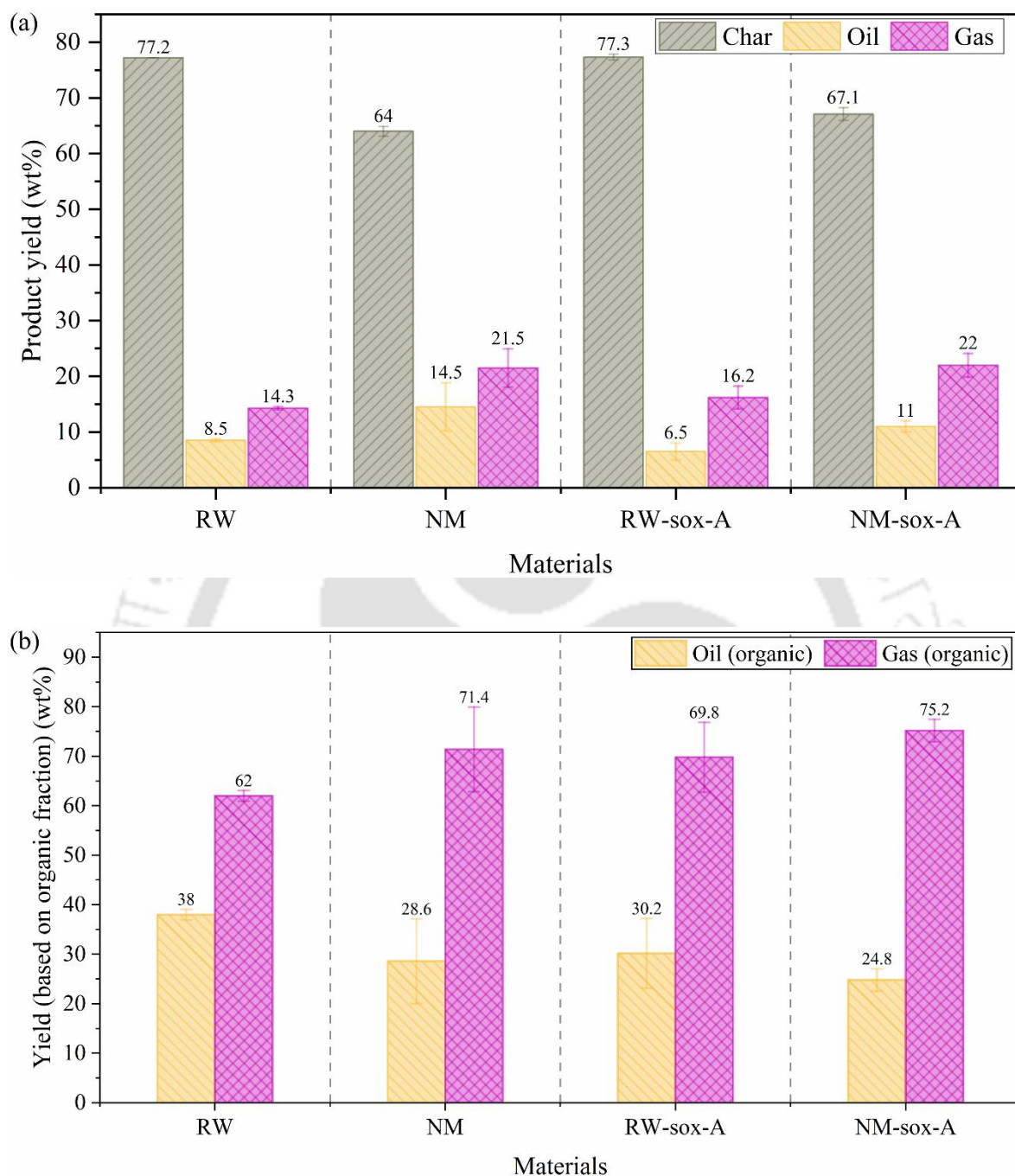


Fig. 5.4 Pyrolytic product yield distribution obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A materials based on (a) total feed and (b) organic fraction

5.4. Characterization of pyrolytic oil and gas fraction

5.4.1. FTIR analysis of pyrolytic oil

The pyrolytic oil samples were analyzed for the functional groups present using FTIR to observe the effect of change in feedstock composition on its quality. All the oil samples depicted similar functional groups consisting of phenolic, methyl, methylene and aromatic compounds (Fig. A. 2). The prominent peak around 3300 cm^{-1} can be attributed to the -OH group, and the peaks at the fingerprint region ($1596, 1470, 1361, 1224, 1069, 814, 745\text{ cm}^{-1}$) depicted the strong presence of a benzene ring in various forms (in-plane and out-of-plane vibrations) at wavenumbers 1224 and 1069 cm^{-1} , respectively [99, 132]. Additionally, C=C bond (stretching) can be attributed from the peaks at $1596, 1470, 1361\text{ cm}^{-1}$. The peaks at 2960 and 2868 cm^{-1} also depicted the presence of -CH₃ and CH₂ groups. The peak near 506 cm^{-1} depicted the presence of C-Br bond, which is crucial and needs further investigation. Since the FTIR analysis could not identify any significant change in its quality, the oil samples obtained from the pyrolysis of four materials were subjected to NMR and compositional analysis using GC-MS.

5.4.2. ¹H NMR of oil samples

The ¹H NMR analysis depicted the presence of aromatic, olefin and aliphatic compounds [170, 185]. The polymer content of the WPCB is epoxy-based, which consists of mainly aromatic groups, hence high amount of aromatic content is expected. The aliphatic might have resulted from the branch attached to the aromatic compounds. Hence, from the ¹H NMR analysis, the structure of oil can be identified as aromatic compounds with branched alkyl groups (Fig. A. 3). Quantification of the chemical groups showed higher aromatic contents for the acid treated samples (NM and NM-sox-A) (Table 5.3). To further understand the chemical composition, GC-MS analysis was performed (section 5.4.3).

Table 5.3 ^1H NMR chemical shift integral regions and area% for the pyrolytic oil obtained from RW, NM, RW-sox-A and NM-sox-A materials

Chemical shift (ppm)	Proton assignments	Peak area (%)			
		RW	NM	RW-sox-A	NM-sox-A
8.0–6.8	Aromatic ring	47.56	55.41	43.42	53.62
6.4–4.2	CHO, *ArOH, HC=C-(nonconjugated)	17.07	21.26	17.11	18.84
3.0–2.2	CH ₃ C=O, CH ₃ -Ar*, -CH ₂ -Ar*	12.20	9.46	14.47	10.14
1.6–0.0	-CH ₂ , -CH ₃	23.17	13.51	25.00	17.39

*Ar = aromatic ring

5.4.3. GC-MS of oil samples

The chemical compounds in the pyrolytic oil samples were determined using GC-MS analysis. The NIST library search provided the probable list of compounds, and the compounds were selected based on the parameters search index (SI), reverse search index (RSI) and probability. The compounds detected based on the normalized area% were reported for all the feedstocks in Table 5.4. The effect of metals and Soxhlet extraction (before pyrolysis) on the pyrolytic oil chemical compounds can be observed. Moreover, the formation of brominated compounds in the oil fraction, depending on the type of feedstock used, was elaborated. Phenol and its derivatives are the major compounds detected along with minor quantities of furans, ketones, and halogenated compounds. However, the presence of metals (or acid leaching) profoundly impacted the composition of the compounds formed in the pyrolytic oil. The value of area% for phenol compound in RW (28.14%) and RW-sox-A (27.08%) materials was lower than that of NM (35.99%) and NM-sox-A (32.75%). The higher production of p-cumenol compensated for the lower production of phenol content in the presence of metals. This indicates the formation of more alkylated phenolic compounds in the absence of metals, which was also observed in ^1H NMR analysis (Table 5.3).

The production of brominated compounds in the oil hinders its application. Hence, monitoring the formation of these compounds was investigated under different circumstances (acid leaching and/or Soxhlet extraction). It was observed from the GC-MS analysis that a minor quantity of brominated compounds was detected in all the samples, but the amount is higher in the case of oil fractions produced from feedstocks without metals (NM and NM-sox-A). The compounds having greater than or equal to 0.5 GC-MS area% are listed and considered for analysis. At retention time (RT) = 5.14, phenol, 4-bromo was detected in the pyrolytic oil obtained from NM and NM-sox-A (Fig. 5.5 (a)). Other brominated compounds were also detected between RT 6 to 8 (Fig. 5.5 (b)). Thus, the presence of metals has reduced the transfer

of bromine into the pyrolytic oil, whereas the Soxhlet extraction showed minimal impact/change.

5.4.4. SimDist analysis of oil samples

This study highlights the carbon fraction distribution of the pyrolytic oil. The light distillate (C_7 – C_{11}), middle distillate (C_{12} – C_{20}) and heavy (C_{20+}) fractions were identified in the oil samples obtained from the pyrolysis of RW, NM, RW-sox-A and NM-sox-A materials by comparing area% of the peaks obtained with that of the standards [185]. Since, the chemical composition was already identified using GC-MS analysis, the purpose of simDist using GC analysis has been limited to determination of the carbon fraction distribution of the straight chain hydrocarbon compounds. However, as it is evident from the 1H NMR and GC-MS analysis, that the chemical composition is mainly aromatic type, the usage of alkane standards will result in some inaccuracy, however, it is considered acceptable as, the GC-FID analysis was not meant for identification of the compounds, but a range of compounds were examined. The analysis depicted the dominance of light fraction in all the samples [186]. However, higher wt% of light, middle and heavy fractions was detected for the oil from RW, RW-sox-A and NM, respectively (Fig. 5.6).

Table 5.4 List of compounds detected using GC-MS analysis in the pyrolytic oil samples obtained from feedstock materials RW, NM, RW-sox-A and NM-sox-A

Compounds	Area%			
	RW	NM	RW-sox-A	NM-sox-A
Phenol	28.14	35.99	27.08	32.75
Benzofuran	0.99	BDL*	BDL	BDL
Phenol, 2-chloro	BDL	BDL	BDL	5.03
3-Methylpyridazine	BDL	7.20	BDL	BDL
Phenol, 2-methyl	3.71	2.42	2.45	2.17
p-Cresol	1.83	1.90	1.14	1.65
Phenol, 4-bromo	BDL	2.40	BDL	1.37
Benzofuran, 2-methyl	6.30	2.23	4.93	1.48
Phenol, 4-ethyl	1.89	0.81	1.41	0.93
Phenol, 2-ethyl	0.87	BDL	0.53	BDL
Phenol, 2-propyl	0.75	0.54	BDL	BDL
Phenol, 4-propyl	0.68	BDL	0.58	0.72
p-Cumenol	26.14	11.82	25.32	16.09
Phenol, 2,4-dichloro	BDL	2.03	BDL	0.63
Phenol, 2,6-dichloro	BDL	2.18	BDL	1.39
Ethanone, 1-(2,3-dihydro-1H-inden-5-yl)-	1.09	BDL	0.99	BDL
Biphenyl	BDL	0.68	0.66	0.54
Phenol, 4-chloro-2-(1-methylethyl)-	BDL	4.23	BDL	4.65
Phenol, 4-bromo-2-chloro	BDL	0.59	BDL	BDL
Ethanone, 1-(3-bromo-4-hydroxyphenyl)-	BDL	2.29	0.87	2.32
1-LInden-1-one, 2,3-dihydro-3,3,6-trimethyl-	2.70	BDL	2.17	BDL
3-Hydroxybiphenyl	4.21	7.00	5.11	10.76
Cyclopentadecanol	BDL	2.96	BDL	BDL

*BDL = below detection limit (<0.5 area%)

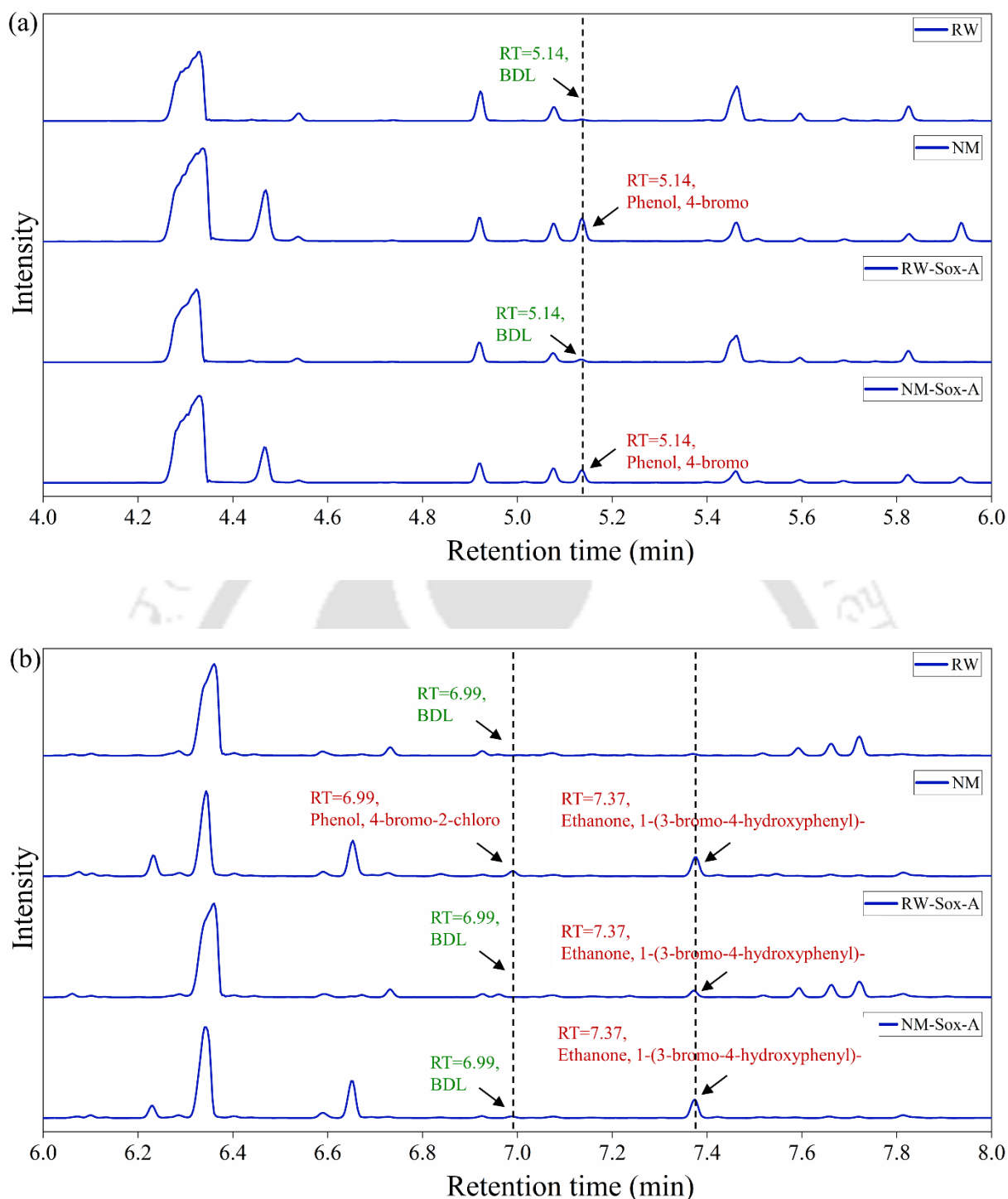


Fig. 5.5 GC-MS chromatograms for the retention time (a) 4 to 6 min, and (b) 6 to 8 min, to show the presence of brominated compounds in the pyrolytic oil from the feedstocks RW, NM, RW-sox-A and NM-sox-A

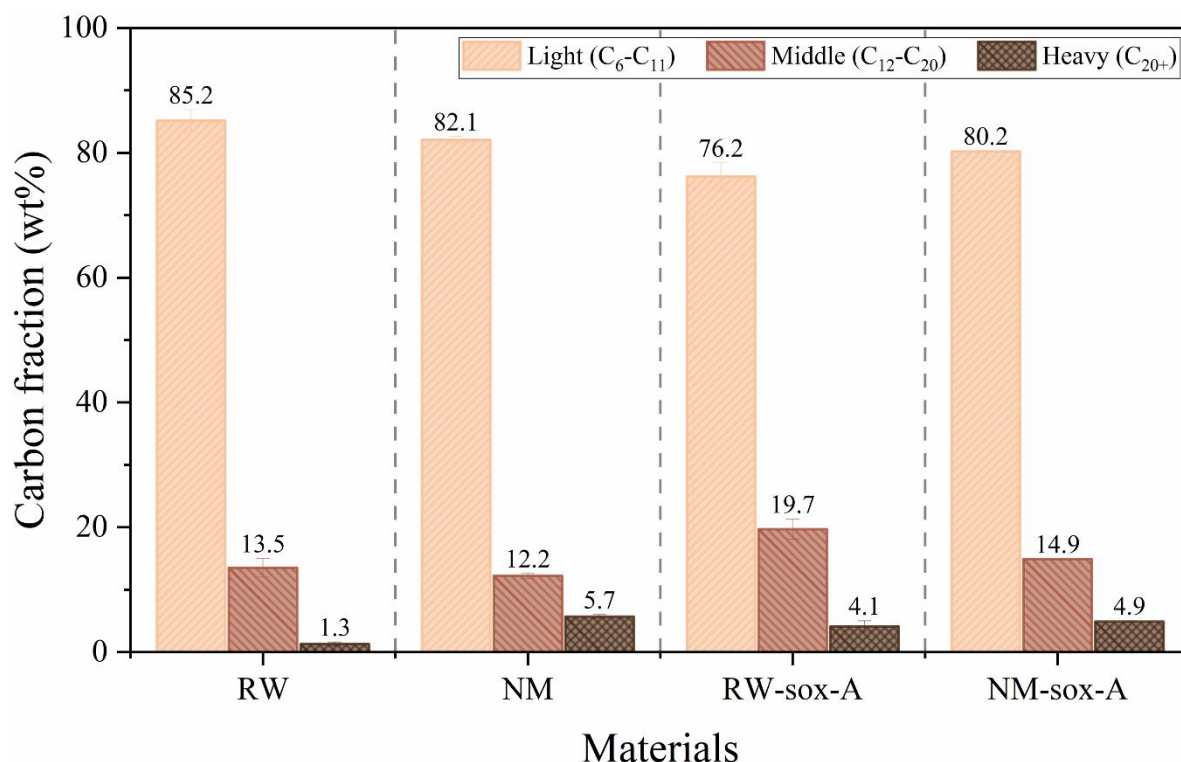


Fig. 5.6 SimDist analysis of the pyrolytic oil samples obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A materials

5.4.5. Calorific values of the feedstock, pyrolytic char and oil

The energy content in a sample is understood by its calorific value. Commonly, WPCB is used to produce heat in pyrometallurgical processing, where the polymer fraction is burnt, which supplies the energy required to generate high temperature required in the process. During pyrolysis, the occurrence of thermal cracking results into generation of lighter fraction of compounds. Thus, higher energy content products are generated (Table 5.5). Moreover, the calorific values were found to be dependent on the material composition of the WPCB feedstock, such as, the NM and NM-sox-A samples exhibited higher calorific values due to the presence of higher volatile matter contents. The char samples with reduced volatile matter content, showed reduced calorific values across all the samples RW, NM, RW-sox-A and NM-sox-A. The calorific values of the oil fraction increased significantly. Thus, the pyrolytic oil fraction is a potential resource for energy generation. However, the pyrolytic oil produced from

RW and RW-sox-A showed higher calorific values as compared to the pyrolytic oil produced from NM and NM-sox-A. This can be attributed to the lower concentrations of brominated compounds in the pyrolytic oil produced from WPCB samples with metals intact (GC-MS analysis, section 5.4.3). This perfectly aligns with the studies the work done by Zhu et al. [26], that was mentioned in section 4.3.1.2 in Chapter 4. Thus, metals have significant role in increasing the calorific value as well as reducing bromine content in the pyrolytic oil fraction produced from WPCB.

Table 5.5 Calorific values of feedstock, pyrolytic oil and char fractions produced from the WPCB samples RW, NM, RW-sox-A and NM-sox-A

Particulars	Calorific values (MJ/kg) of the materials			
	RW	NM	RW-sox-A	NM-sox-A
Feed	8.0	9.3	7.6	9.5
Char	3.9	6.6	3.7	4.6
Oil	36.3	29.5	31.7	28.8

5.4.6. Gas chromatography of gas fraction

The GC-TCD analysis of the pyrolytic gas fractions collected at 500 °C showed the presence of H₂, CH₄, CO and CO₂ gases [91]. The presence of metals (RW and RW-sox-A) promoted the production of H₂ and CO gases (Fig. 5.7), which showed the occurrence of dehydrogenation reactions [99]. The concentrations of CO and CH₄ were reduced, and that of CO₂ increased for the gas produced from the acid-leached materials (NM and NM-sox-A). The GC-FID analysis confirmed the presence of light hydrocarbon gases (<C₅) (Fig. 5.8) [132]. Among the hydrocarbon gases, n-butane was the highest and that of other gases was minimal (<0.5 vol%). Thus, the gases produced during the WPCB pyrolysis also serve as an energy resource.

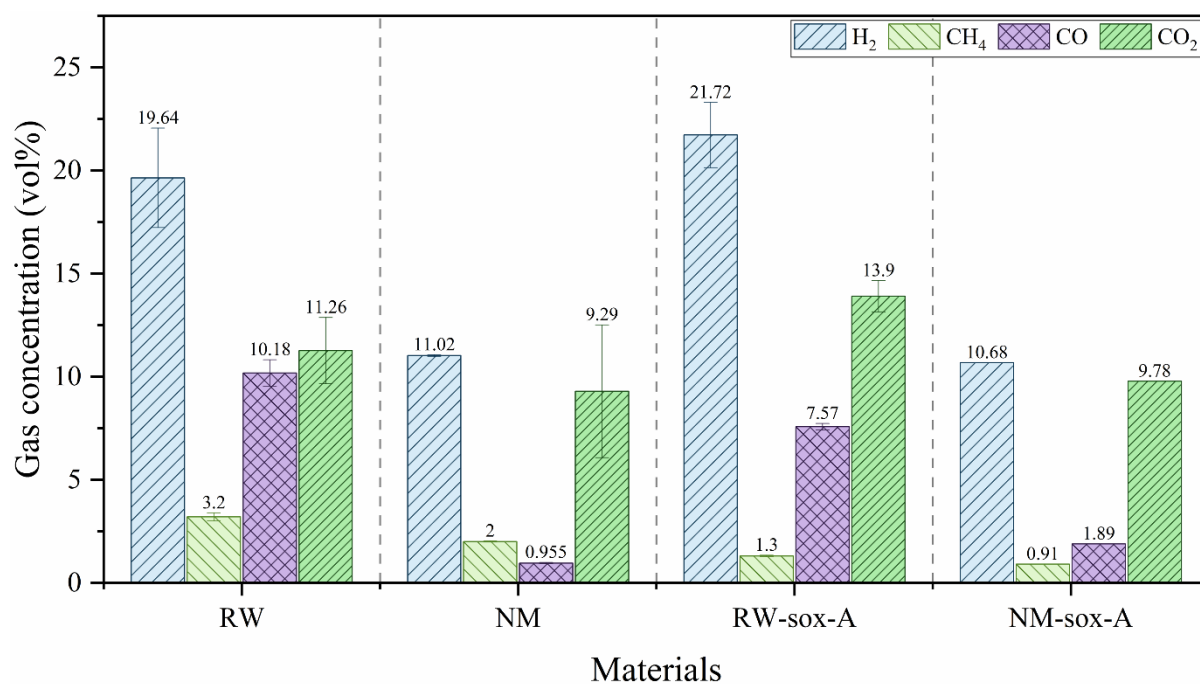


Fig. 5.7 Compositional analysis of pyrolytic gas using GC-TCD, produced at 500 °C for the materials RW, NM, RW-sox-A and NM-sox-A

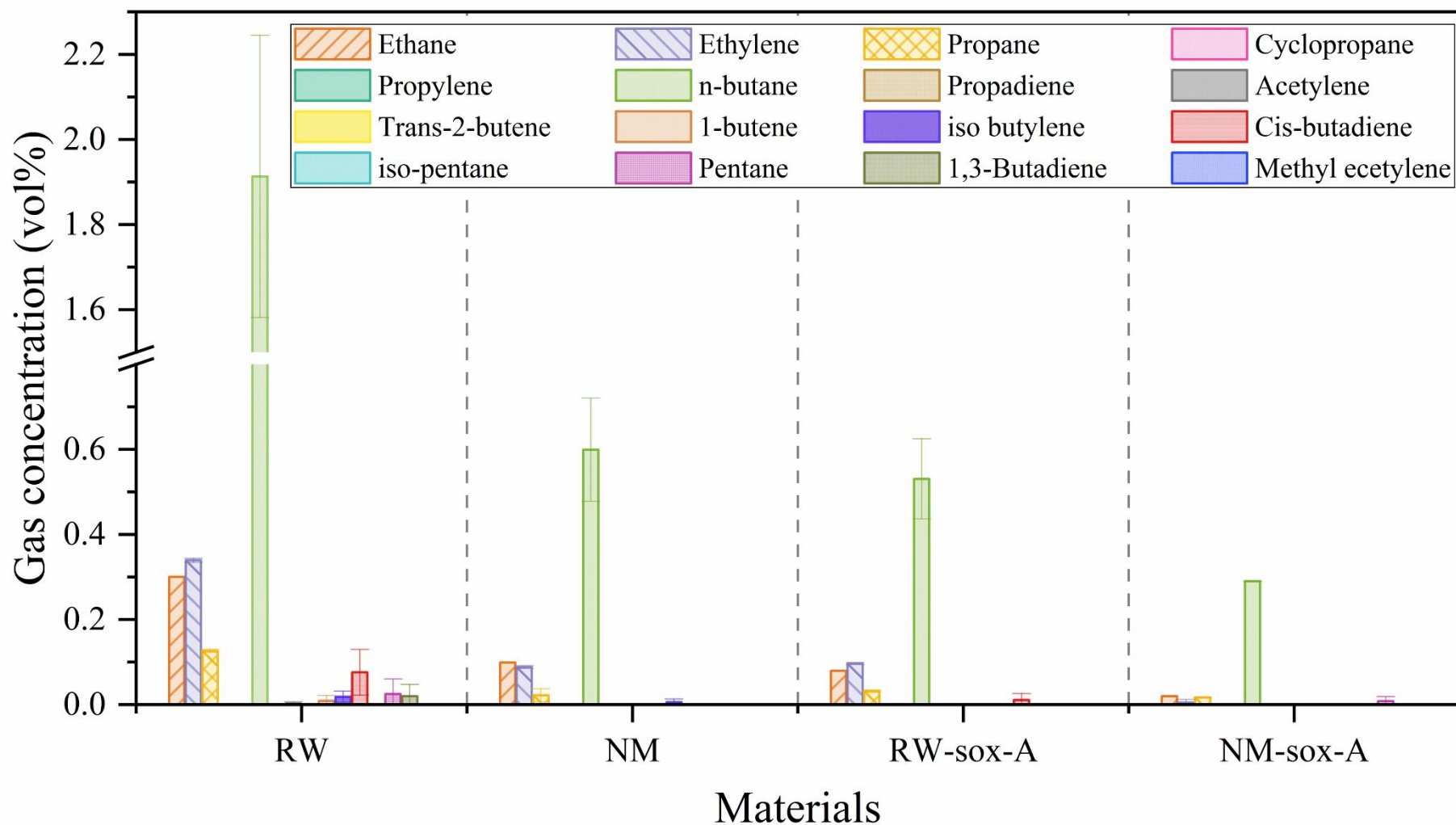


Fig. 5.8 Compositional analysis of pyrolytic gas using GC-FID, produced at 500 °C for the materials RW, NM, RW-sox-A and NM-sox-A

5.5. Characterization of char to examine the effect of pyrolysis

5.5.1. CHNS analysis of char

The char fractions produced at 500 °C were analyzed for the elemental compositions of C, H, N and S. In comparison with the feedstock materials, the char fractions had lower values of C, H, N, and S (Fig. 5.9) due to thermal degradation. The C and H wt% reduced to a greater extent as compared to the elements N and S. The value of C reduced by 7.3, 8.61, 9.76, 10.13 wt% for the RW, NM, RW-sox-A and NM-sox-A materials, respectively. The H was reduced by 1.21, 1.72, 1.34, and 1.69 wt% for the RW, NM, RW-sox-A and NM-sox-A materials, respectively. These reduced concentrations of C and H have contributed to the production of the oil and gas fractions. It is also certain that the oil and gas fractions will not contain sulphur compounds, as it is trapped in the char fraction. The high wt% of C for NM (17%) and NM-sox-A (14.32%) may be due to the increase in T_{offset} (section 5.2.3) for the acid leached WPCBs as compared to the RW and RW-sox-A WPCBs. Besides, this can also be related to the lower oil yield for the acid leached materials as compared to raw samples.

5.5.2. FTIR analysis of char

The FTIR analysis of the char and feedstock materials supports the occurrence of thermal degradation during pyrolysis. Fig. 5.10 depicts the removal of the functional groups in the char fractions compared to the feedstock materials [187]. The WPCB materials depicted the presence of a series of functional groups, such as -OH, alkanes, alkene, benzene ring, C-Br, etc. However, the broad peak in the wavenumber 1177 cm^{-1} remained unchanged because it depicts the Si-C or Si-O-Si group [99]. This peak represented the glass fibers in the WPCB, which remained in the char. The XRF analysis also confirmed the presence of Si in the feedstocks (Table 5.1).

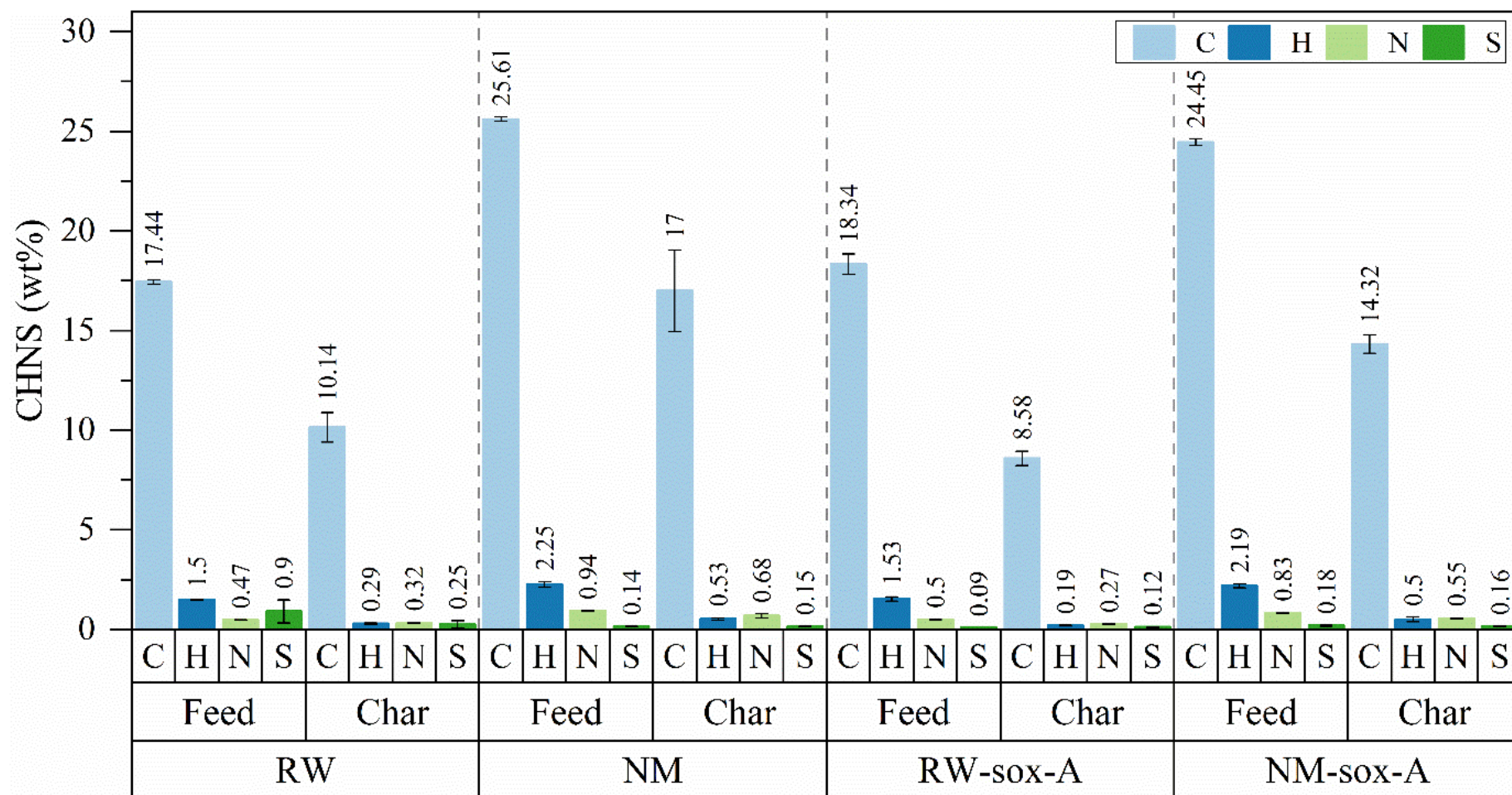


Fig. 5.9 Comparison of CHNS values in feed and char of the materials RW, NM, RW-sox-A and NM-sox-A

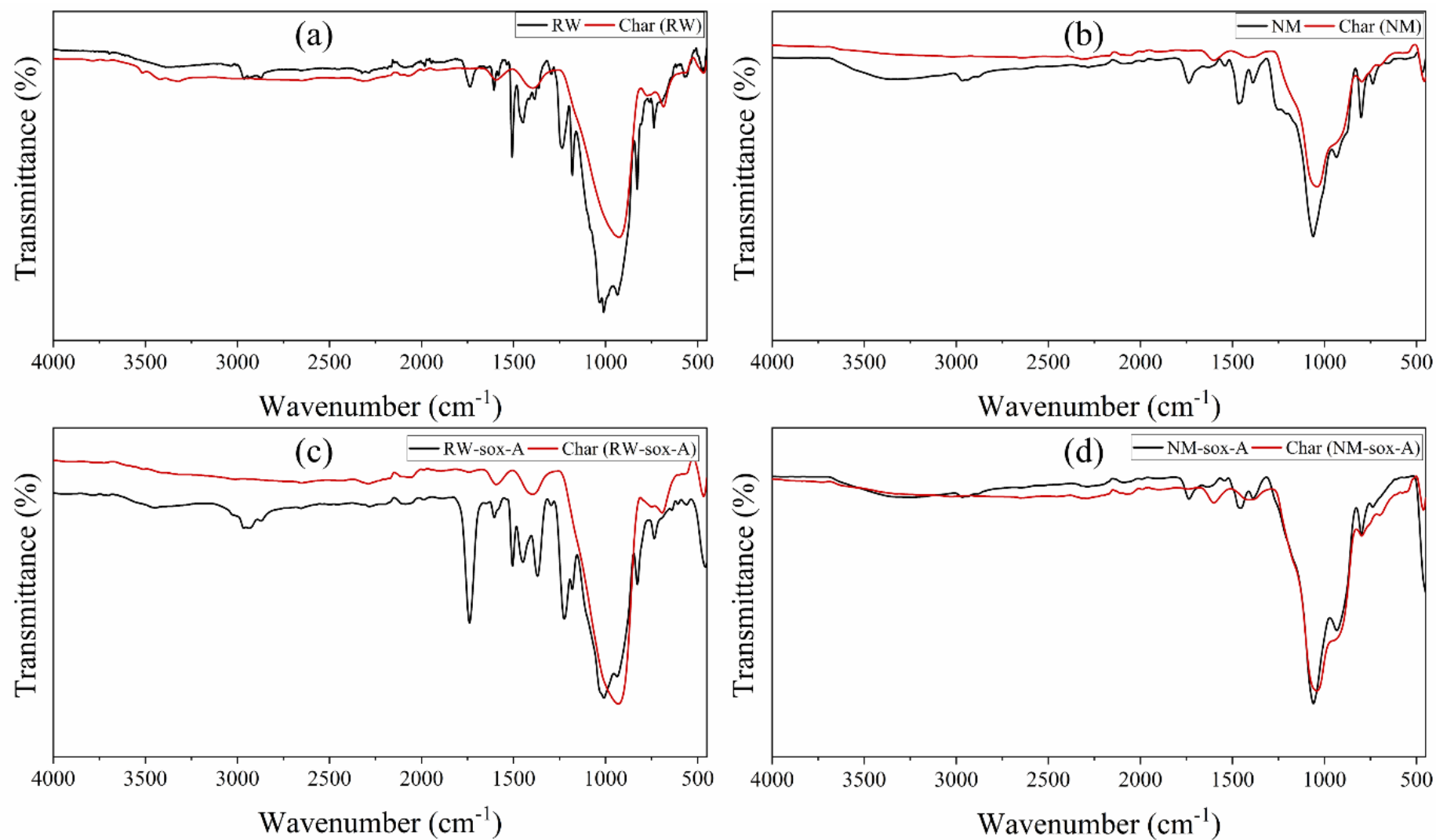


Fig. 5.10 FTIR comparison for the feedstock and char samples produced from pyrolysis of (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A

5.6. Distribution of bromine among pyrolysis product fractions using oxygen bomb-ion chromatography

The presence of BFRs in WPCBs results in the formation of brominated compounds in pyrolytic product fractions. Previous studies have reported the occurrence of such compounds in both the gas phase (e.g., HBr) and the oil phase (e.g., 4-bromophenol) [162, 166, 175, 188, 189]. The distribution of bromine among the pyrolysis product fractions was assessed using a combined analysis of bomb calorimeter and ion chromatography for the feed, and products fractions (char and oil). Bromine concentrations in the char and oil fractions were calculated based on the initial bromine content in the feedstock, and that in gas samples were calculated by difference. The char samples produced from RW and RW-sox-A exhibited higher bromine concentrations than those from acid-leached samples, indicating that embedded metals contribute to bromine retention in the solid phase during pyrolysis. Conversely, lower bromine concentrations in the char samples produced from NM and NM-sox-A suggests a greater release of bromine into the volatile phase in the acid leached materials. An elevated bromine concentration was also observed in the pyrolytic oil derived from the acid leached samples, consistent with the findings from the GC-MS analysis [190]. These results suggest that the embedded metals present in the WPCB retain bromine in the char, thereby eliminating the need for external catalysts or metal oxides. Fig. 5.11 shows the distribution of bromine from the feed materials into the product fractions. More than 75% of the bromine from feed has transferred into the gas phase. This observation is similar to the study reported by Chien et al. [186]. Evangelopoulos et al. [191] also reported that most of the bromine gets transferred into the gas phase and minimal bromine remained in the oil phase during the pyrolysis of waste electrical and electronic equipment plastics. Brominated compounds in the gas phase can be removed by passing the gas through an alkaline solution before release into the environment or use in downstream applications [110]. Zhu et al. [91] used 0.5 mol/L NaOH solution to absorb the

brominated gases produced during the WPCB pyrolysis. However, the removal of brominated compounds from the oil fraction remains challenging. Hence, the current study investigated the reduction of brominated compounds in oil. In summary, the embedded metals present in WPCB appear sufficient to facilitate the regulation of bromine species away from the oil fraction, in contrast to the pre-treatment method Soxhlet extraction.

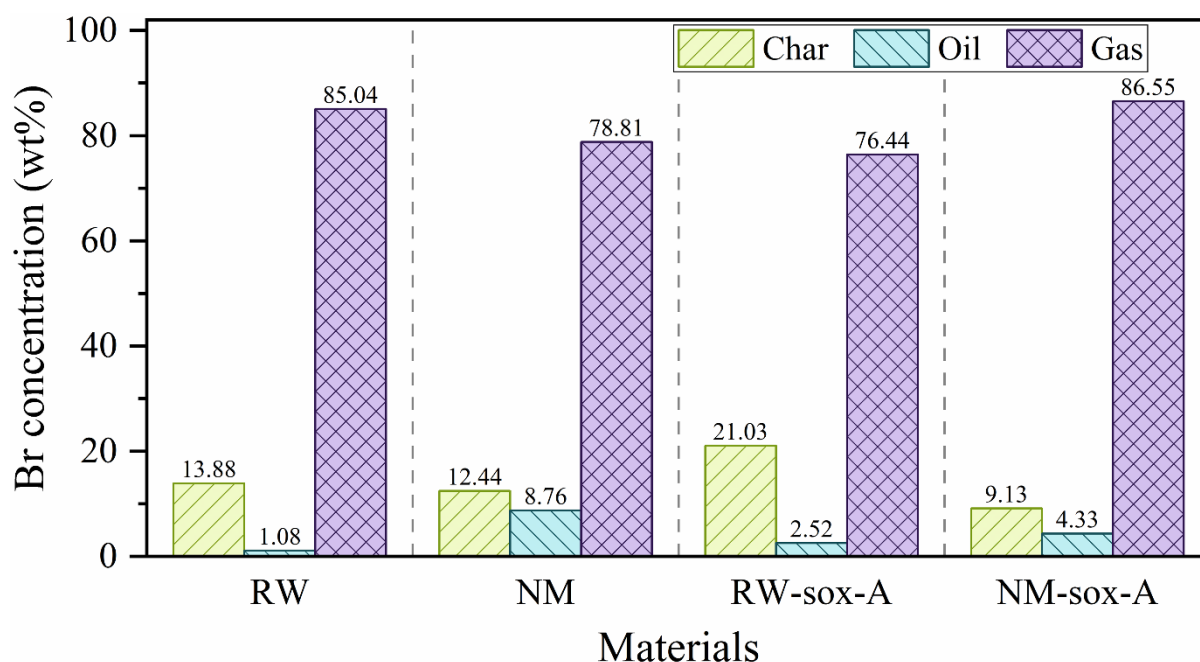


Fig. 5.11 Distribution of bromine into pyrolytic products produced from different feedstock materials (RW, NM, RW-sox-A and NM-sox-A) using oxygen bomb-ion chromatography method

5.7. Summary

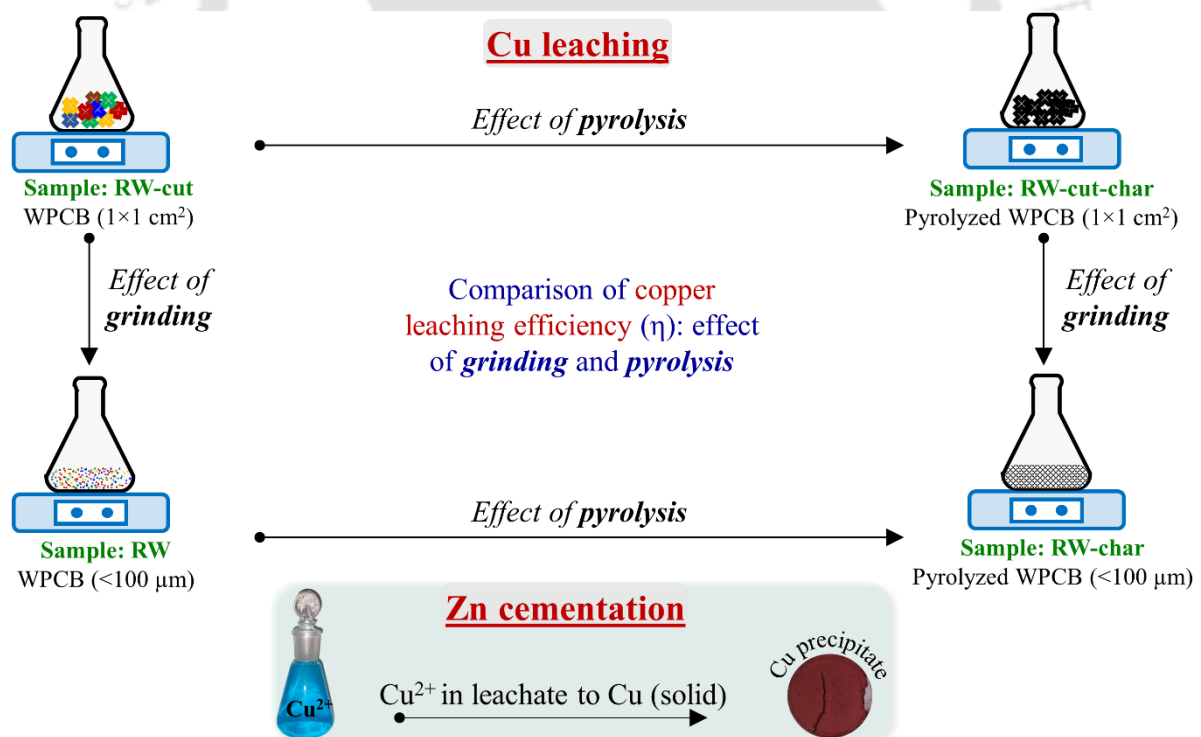
WPCB powder (<100 μm) samples were prepared under four conditions: raw (RW), acid-leached (NM), and their Soxhlet extracted forms using acetone (RW-sox-A, NM-sox-A), and pyrolyzed separately at previously optimized 500 $^{\circ}\text{C}$ to determine a viable route for obtaining pyrolytic oil with reduced bromine content. The product fractions were characterized to determine its quality, and distribution of bromine was emphasized. The FTIR and ^1H NMR analyses depicted that the oil is primarily of aromatic type, irrespective of the material

preparation technique(s) utilized. However, GC-MS analysis showed that the oil composition was dependent on the presence of metals. The acid-leached samples (NM and NM-sox-A) produced a higher fraction of phenol, whereas those without acid leaching (RW and RW-sox-A) produced oil containing more p-cumenol. Moreover, a higher amount of bromine was found in the volatile (oil and gas) fraction for acid-leached materials. The Soxhlet extraction reduced bromine content in the WPCB samples; however, the presence of metals was more efficient in reducing the transfer of bromine into the oil phase. The pre-treatment using solvents might prove a better solution for E-waste plastics (like keyboard, computer casing, etc.) that do not contain in-situ metals then again, the generation of solvent waste needs to be considered. The oil, being aromatic in nature, can be utilized to produce aromatic chemicals or as an energy resource. The gas fraction containing gases like H_2 and CH_4 is suitable for energy generation; however, it needs scrubbing for the removal of bromine before being used. The char fraction containing metals can be used for metal recovery using physical or hydrometallurgical methods. The recovered glass fibers can be used as reinforcement material in construction, as an insulating wool, etc. Moreover, bromine in char needs to be considered, as it might leach out, posing a danger to the aquatic life. Hence, when comparing the pyrolytic product characteristics (quantitatively and qualitatively), it is recommended that the WPCB pyrolysis be performed without any pre-treatment for higher yield of oil and reduced bromine content in oil. Thus, the valorization of organic fraction using pyrolysis and recovery of inorganic fraction, including copper and glass fibers using hydrometallurgy technique has been presented in Chapter 6.

Chapter 6

Recovery of copper from WPCB using hydrometallurgy

- Acid leaching
- Pyrolysis
- Copper recovery
- Cementation



Publication: B. Boro and P. Tiwari, “Effect of pyrolysis and comminution on copper extraction and techno-economic assessment for resource recovery from waste printed circuit board”, *Journal of Environmental Management*, 397, 128365, 2026.

6. Recovery of copper from WPCB using hydrometallurgy

Waste printed circuit board is one of the richest sources of copper in E-waste. Copper provides the electrical connectivity among the electronic components (ECs) present in WPCB. Among other metals present in E-waste, copper holds the highest wealth contribution of \$19 billion. Copper (or other metals) in the WPCBs can be recovered via pyrometallurgical, hydrometallurgical and bio-metallurgical approaches. Due to the release of toxic gases, the pyrometallurgical method is not an environmentally friendly process, and the infrastructure cost is also high; the bio-metallurgical approach is time-consuming and has less potential for commercialization. The hydrometallurgical approach provides higher selectivity of metals and has a lesser economic burden. The efficiency of copper leaching is influenced by several factors, including the type and concentration of the leaching agent, leaching time, temperature, mixing rate, and, the extent of contact between the material and the leaching agent. The solder mask forms a protective laminate over the surface of the WPCB, shielding it from environmental degradation; however, it also impedes the penetration of the leaching agent, thereby reducing the leaching efficiency. Thus, to increase the exposure of metals, powder form of WPCB is commonly used. However, grinding generates dust and material loss while handling. The dust particles containing heavy metals, brominated flame retardants (BFRs) and glass fiber particles are detrimental to human health. In the case of larger pieces, delamination/removal of solder masks using chemicals or thermal treatment prior to leaching has been reported. However, a comparative analysis of leaching efficiencies influenced by grinding and thermal pre-treatment (pyrolysis) remains unreported in the literature. This chapter compares the leaching efficiencies of copper from WPCB using H_2SO_4 and H_2O_2 for different sizes and their pyrolyzed versions. The zinc cementation of copper after acid leaching has been presented.

6.1. Leaching of copper

This chapter includes recovery of copper from WPCB using acid leaching and cementation processes. Furthermore, the influence of pre-treatment methods, including grinding and pyrolysis of WPCB, on subsequent leaching was investigated. For this purpose, the samples RW-cut, RW, RW-cut-char, and RW-char were prepared. The RW-cut-char and RW-char are the pyrolyzed versions of the samples with the size ranges of approximately $1 \times 1 \text{ cm}^2$ (RW-cut), and $<100 \text{ }\mu\text{m}$ (RW). The detailed sample preparation methodology has been discussed in section 2.8. The pyrolysis was performed using the optimized conditions obtained in Chapter 4. Thus, four WPCB samples RW-cut, RW, RW-cut-char and RW-char were subjected to acid leaching to evaluate the effects of grinding and pyrolysis on the leaching efficiency of copper. The leaching performance was examined under varying concentrations of H_2O_4 and H_2O_2 , as well as different leaching times. The efficiency was calculated using Eq. 6.1, and the corresponding results are presented in Figs. 6.1 and 6.2.

$$\text{Leaching efficiency, } \eta(\%) = \frac{\text{Cu}_L \times V_L}{\text{Cu}_o \times W_i} \times 100\% \quad (6.1)$$

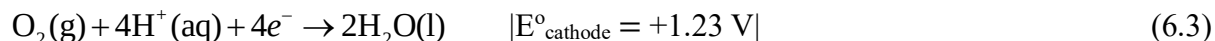
where, Cu_L is the copper concentration (mg/L) in the leachate, V_L is the volume of leachate (L), Cu_o is the concentration (wt%) of copper in the material RW-cut, RW, RW-cut-char or RW-char and W_i is the weight (mg) of material taken for leaching.

The leaching efficiencies exhibited an overall increasing trend with both H_2SO_4 concentration and leaching time irrespective of sample type (Fig. 6.1). However, the efficiency achieved using diluted H_2SO_4 alone remained unsatisfactory due to its limited oxidizing capacity. The metallic copper present in WPCB is oxidized to Cu^{2+} in the presence of H^+ ions from H_2SO_4 and dissolved oxygen. Eqs. 6.2, 6.3, and 6.4 represent the corresponding anodic, cathodic, and overall reactions of the leaching process, along with their standard electrode potential values.

Anode (oxidation reaction):



Cathode (reduction reaction):



Overall reaction:

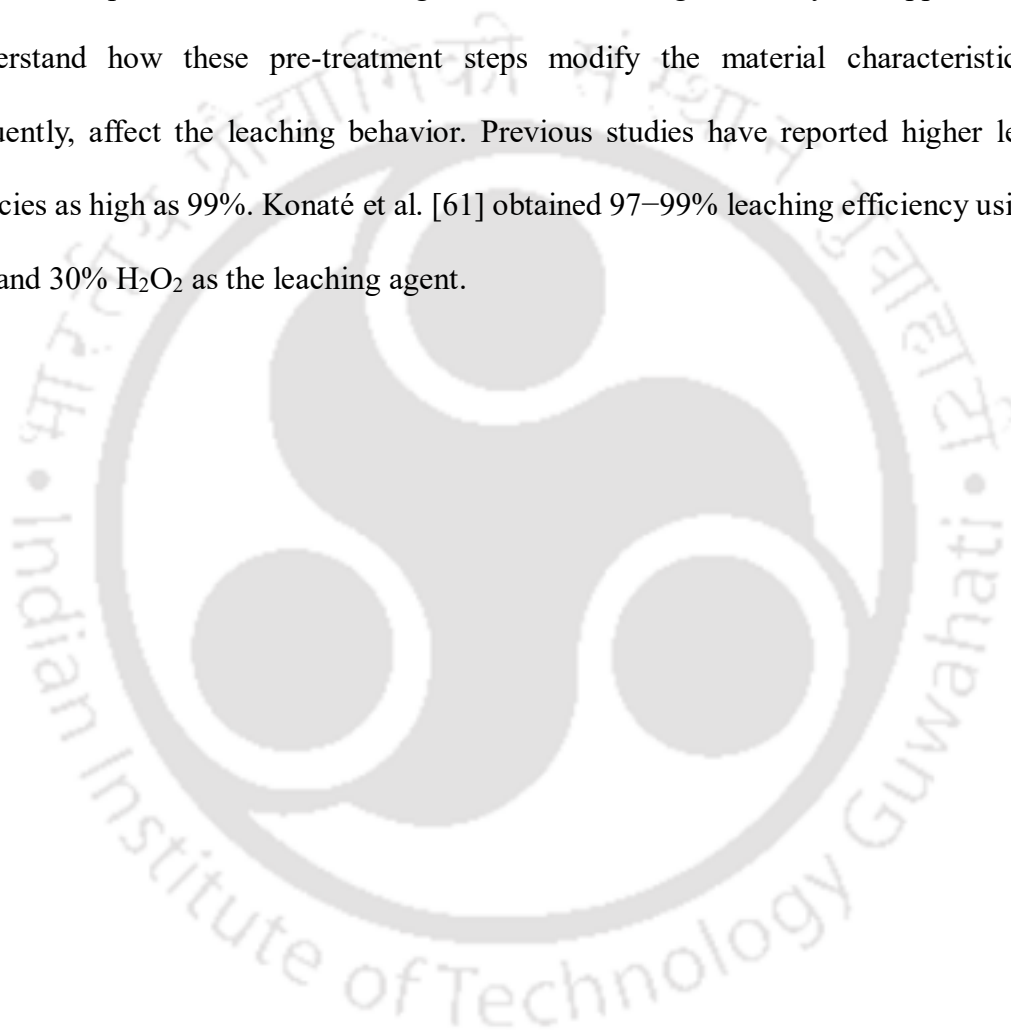


6.1.1. Effect of addition of oxidant on copper leaching efficiency

A maximum copper leaching efficiency of 12% was achieved using H_2SO_4 alone as the leaching agent, specifically for the RW-char sample at 4 M H_2SO_4 concentration and 1.5 h leaching time. Further increasing the H_2SO_4 concentration include risks, such as corrosion, and occurrence of exothermic reactions. Moreover, such highly acidic conditions can degrade common grade reactor construction materials, necessitating costly specialized alloys and increasing operational complexity. Consequently, the lowest concentration of 1 M H_2SO_4 was fixed, and then H_2O_2 , an oxidizing agent, was incorporated as a supplementary oxidizing agent to enhance the leaching efficiency (section 2.8) [44]. The H_2O_2 , being a strong oxidizing agent (in acidic media) with a reduction potential value of approximately +1.77 V, makes the reaction thermodynamically spontaneous, thus increasing the copper leaching efficiency (Fig. 6.2) [192]. The efficiency increased with an increase in H_2O_2 concentration from 5 vol% to 10 vol% and with leaching time. However, a decrease in efficiency was observed at a reaction time of 2 h compared with 1.5 h, which may be attributed to the decomposition of H_2O_2 over time. Zhang et al. [193] also obtained similar results.

An analysis on the copper leaching efficiency data across all sample types and operating conditions revealed a maximum efficiency of approximately 96%, achieved for the RW-cut-

char and RW-char samples, at 1 M H_2SO_4 with 10 vol% H_2O_2 after a leaching duration of 1.5 h. The leaching efficiency is expected to improve further with an increase in H_2SO_4 concentration, such as 2 M. However, the current chapter primarily focuses on evaluating the influence of grinding and pyrolysis as pre-treatment steps, both individually and combined, on the leaching efficiency of copper from WPCB. The objective is not to determine the best combination of parameters for achieving maximum leaching efficiency of copper, but rather to understand how these pre-treatment steps modify the material characteristics, and consequently, affect the leaching behavior. Previous studies have reported higher leaching efficiencies as high as 99%. Konaté et al. [61] obtained 97–99% leaching efficiency using 2 M H_2SO_4 and 30% H_2O_2 as the leaching agent.



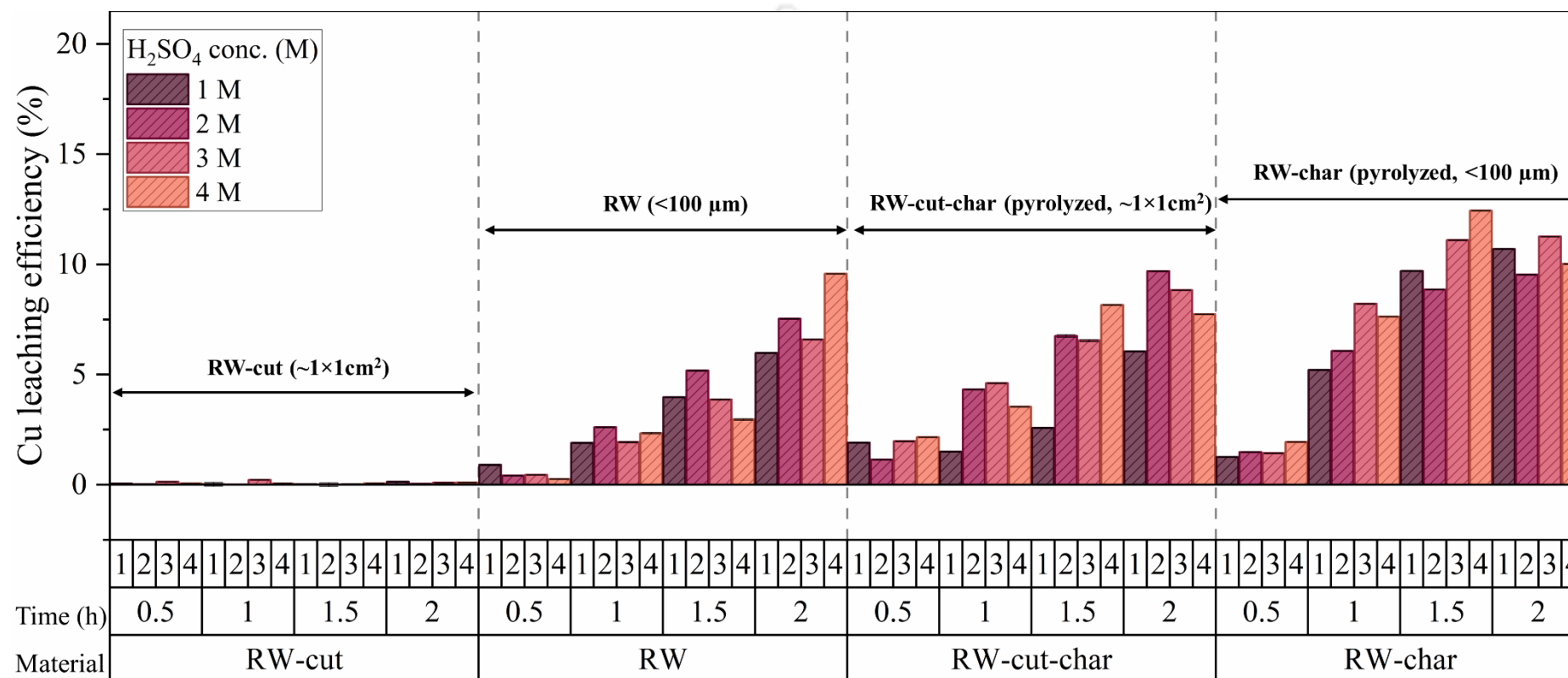


Fig. 6.1 Copper leaching efficiencies at increasing H₂SO₄ concentrations and time depending on cut pieces (RW-cut) and powder (RW) form of WPCBs and their pyrolyzed versions (RW-cut-char and RW-char)

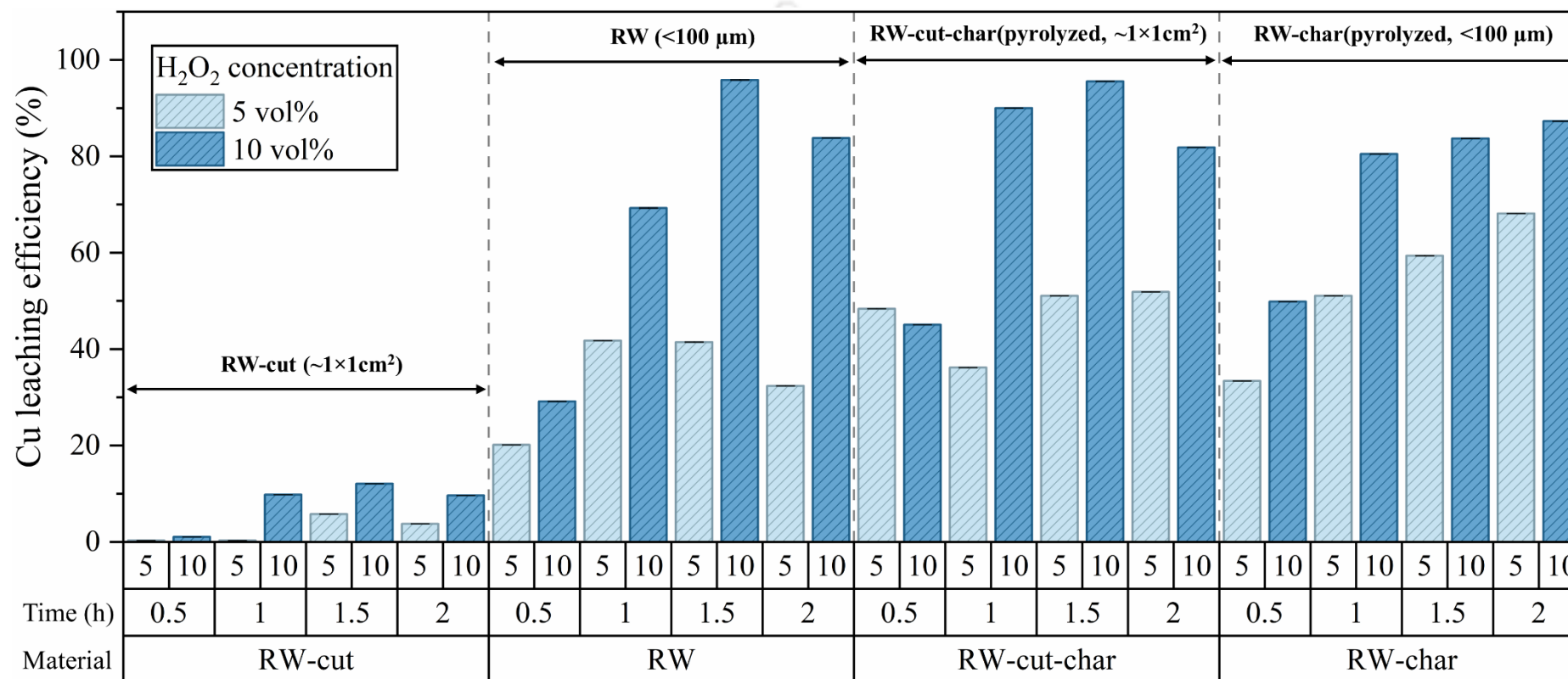


Fig. 6.2 Copper leaching efficiencies at 1 M H₂SO₄ and increasing H₂O₂ concentrations (5 vol% and 10 vol%) and time depending on cut pieces (RW-cut) and powder (RW) form of WPCBs and their pyrolyzed versions (RW-cut-char and RW-char)

6.1.2. Effect of grinding and pyrolysis on copper leaching efficiency

When comparing the leaching efficiencies for different samples but under the same experimental conditions, the effect of grinding and pyrolysis was observed. For instance, the leaching efficiency of RW-cut was less than 1% and that of RW ranged from 0.18 to 10% (Fig. 6.1). The observed enhancement in the leaching efficiency can be attributed to the increased surface area of the powdered samples (RW) compared to the cut samples (RW-cut). As reported by Birloaga et al. [70], smaller particle sizes enhance metal recovery by increasing the surface area for reaction and thus improving the contact area between the solid particles and the leaching agent.

To examine the influence of pyrolysis alone as a pre-treatment step, the RW-cut sample and its pyrolyzed version (RW-cut-char) were compared. For the pyrolyzed sample, the leaching efficiency exhibited an improvement of up to 10% when leached with H_2SO_4 alone for a duration of 2 h. Similarly, in case of the powdered samples, RW-char exhibited higher leaching efficiency than its non-pyrolyzed form RW, although the improvement was less significant. This reduced difference can be attributed to the fact that the RW sample was already in powdered form, thereby limiting the additional effect of pyrolysis on surface exposure and, consequently, the leaching efficiency.

The effect of pyrolysis can be clearly observed in the side-view microscopic images (Empspira 3 Digital Microscope, Leica, Germany) of the cut pieces before (RW-cut) and after (RW-cut-char) pyrolysis (Fig. 6.3 (a) and 6.3 (b)). The WPCB pieces delaminated and the solder mask was thermally degraded resulting in improved leaching efficiency. This was further confirmed by EDX mapping analyses of the same samples RW-cut and RW-cut-char (Fig. 6.3 (c) and 6.3 (d)). The swelling allowed the leaching agent to move inside the glass fiber layers and contact the copper lining. The minimal leaching efficiency observed for the raw WPCB cut pieces

(RW-cut), regardless of the addition of the oxidizing agent H_2O_2 , can be attributed to the limited contact between the copper lining and the leaching agent. In the pyrolyzed versions of both cut pieces (RW-cut-char) and powdered samples (RW-char), similar extent of leaching efficiencies were achieved. However, considering the additional energy requirements, material losses and potential human health risks associated with grinding, the direct use of cut pieces is recommended. Consequently, further techno-economic assessments were conducted specifically on the RW-cut-char samples, with detailed discussions presented in Chapter 7.

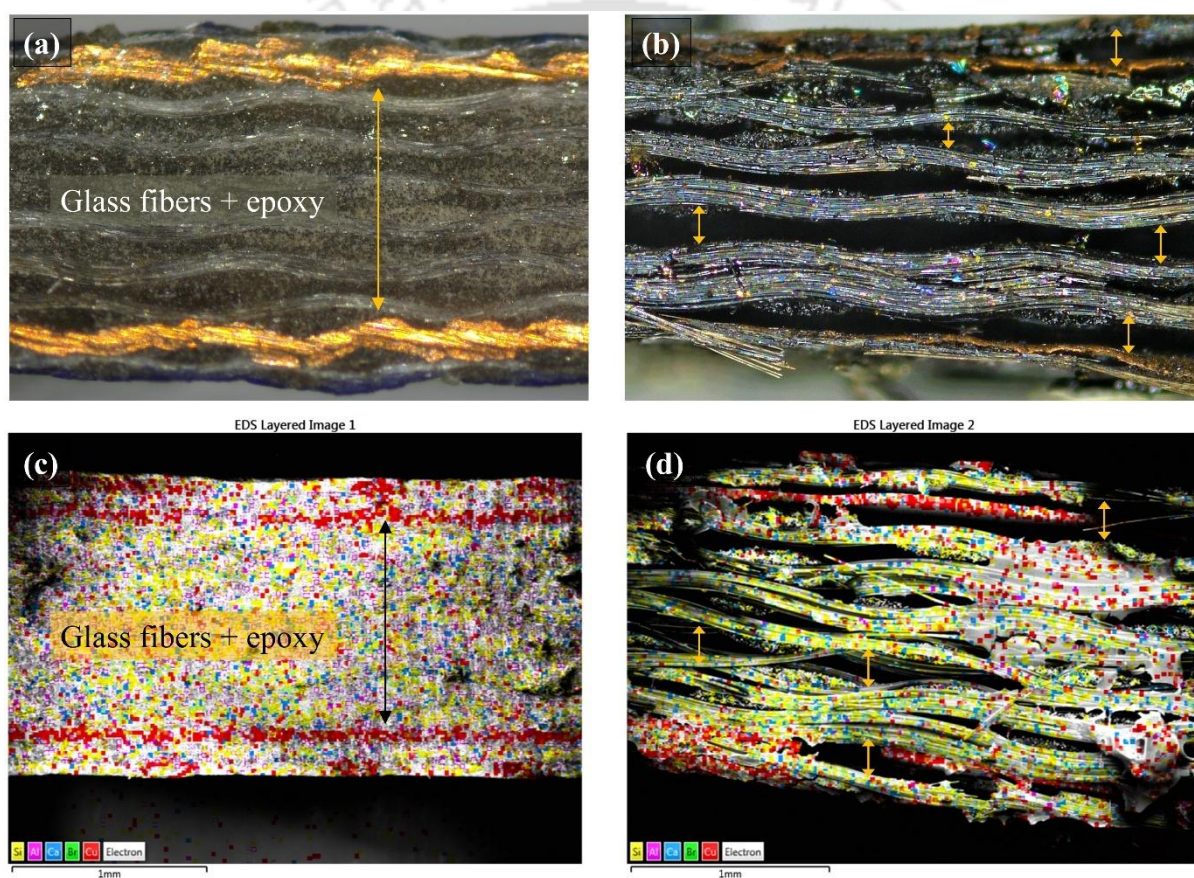


Fig. 6.3 Side-view microscopic images of a WPCB cut piece (a) before pyrolysis, (b) after pyrolysis showing delamination of the glass fiber layers in substrate, and their respective EDX mapping images (c) and (d)

6.2. Cementation using zinc powder

During the leaching experiments, the metallic copper present in RW-cut-char sample is converted into its ionic form and subsequently leached into the solution. It is essential to recover and convert dissolved copper into a solid phase. This conversion is crucial for enabling subsequent utilization of the recovered copper in various applications. Zinc has a negative standard electrode potential (E°), while copper has a positive one, making zinc suitable for the cementation process. Similarly, other types of metal (such as iron) in the electrochemical series that have lower electrode potentials than copper can be used in the cementation process [61]. However, the difference in the electrode potential between zinc and copper is very high, thus making the reaction highly efficient. The copper ions (Cu^{2+}) are reduced on the surface of the zinc powder, producing copper powder. The leachate color changed from blue to colorless, denoting the occurrence of a displacement reaction and formation of ZnSO_4 (Fig. 6.4 (a) and 6.4 (b)). Additionally, the formation of copper precipitate (reddish color) was visibly distinguishable from the zinc powder (grey color) because of their color difference (Fig. 6.4 (c)). To confirm the formation of copper, the precipitate was subjected to compositional analysis using EDX (area and mapping). The composition of the precipitate was 97.4 wt% copper and 2.6 wt% zinc (Table 6.1). These values were obtained from the average values for different areas/spectra selected (Fig. 6.5 (a) and 6 (b)). The precipitate was also analyzed using a mapping technique, showing the copper and zinc distribution in the sample. The mapping analysis also clearly suggested that the precipitate is rich in copper; however, some amount of zinc was also observed (Fig. 6.5 (c)–(e)). The remaining colorless solution after the precipitation was further investigated using ICP-MS for zinc and copper concentrations, and it was found that only 1.5 ppb of copper was left, which accounts for 0.01% of the zinc concentration (11090 ppb). These showed successful recovery of copper in solid form.

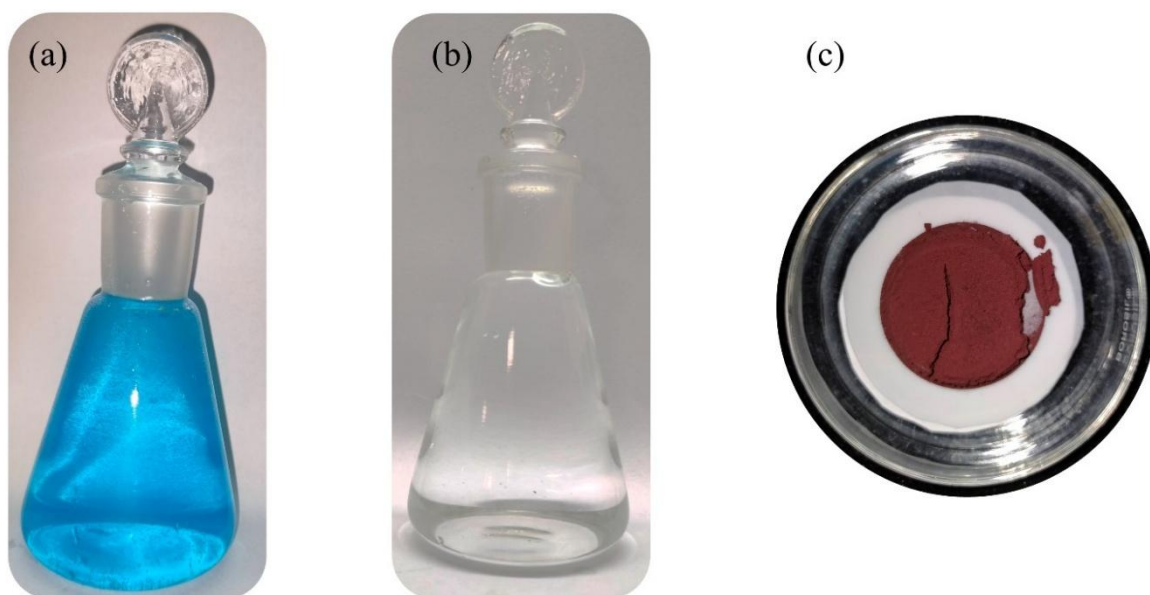


Fig. 6.4 Photographs showing (a) leachate (blue color) after acid leaching, (b) solution (colorless) after zinc cementation and separation of the precipitate, and (c) precipitate obtained after zinc cementation

Table 6.1 Concentrations of copper and zinc in precipitate obtained and the remaining solution after the zinc cementation process

Metals	Metal concentrations in	
	Precipitate obtained in cementation process (EDX analysis, average wt%)	Solution after cementation reaction (ICPMS analysis, ppb)
Cu	97.4 ± 3.8	1.5 ± 1.1
Zn	2.6 ± 3.8	11090.8 ± 0.2

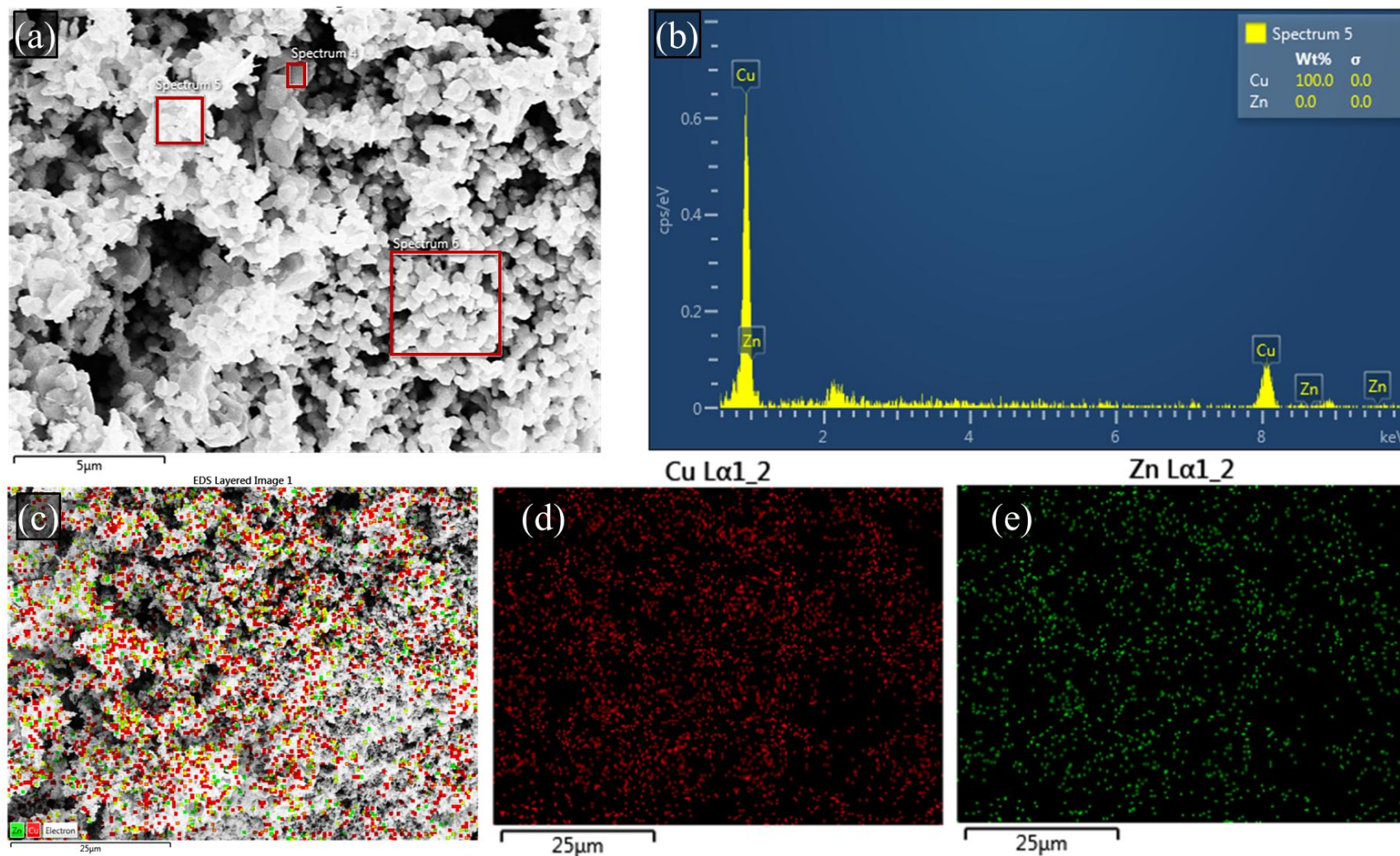


Fig. 6.5 EDX area analysis for the precipitate showing (a) selection of area and (b) composition (average wt%) of selected area of the precipitate and mapping analysis showing (c) overall mapping, (d) mapping for copper and (e) mapping for zinc

6.3. Summary

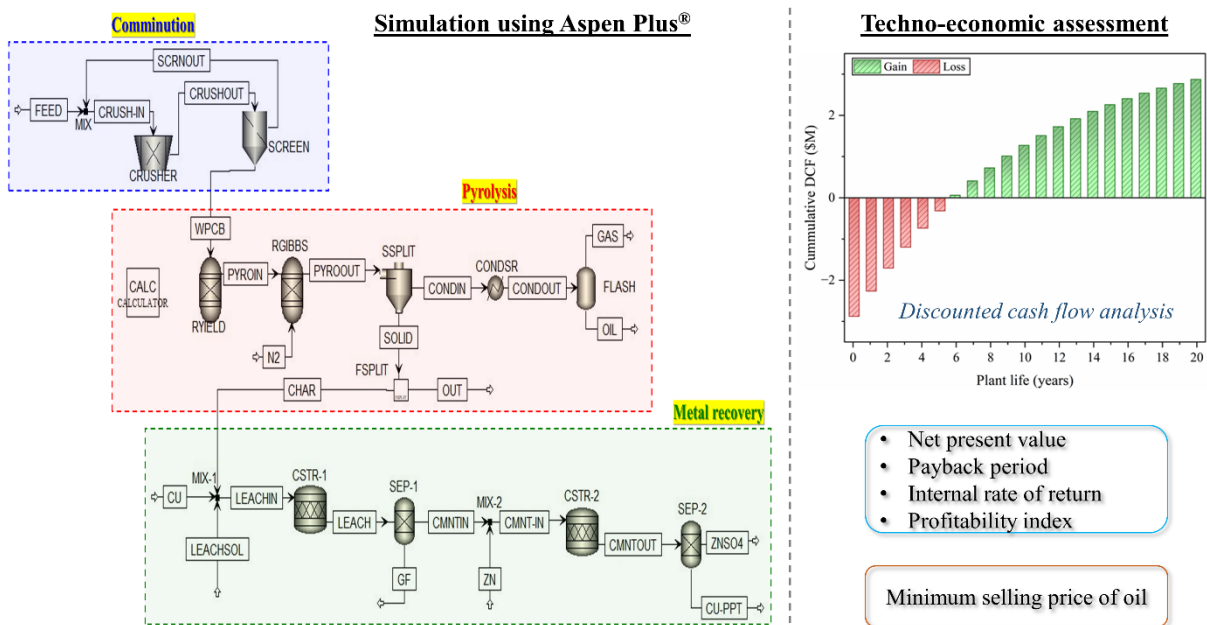
This chapter explored the copper recovery processes corresponding to various WPCB preparation techniques, including mechanical (grinding) and/or thermal (pyrolysis) pre-treatment methods. The WPCB samples of different sizes, RW-cut ($\sim 1 \times 1 \text{ cm}^2$) and RW ($< 100 \mu\text{m}$) and their pyrolyzed versions, RW-cut-char and RW-char were prepared to study the influence of grinding and pyrolysis as pre-treatment step(s), on the leaching efficiency of copper from WPCB. The RW, RW-cut-char and RW-char samples exhibited higher leaching efficiencies than RW-cut due to enhanced copper exposure to the leaching agent consisting of H_2SO_4 and H_2O_2 . However, the pyrolyzed sample without grinding (RW-cut-char) minimizes material loss and dust generation that would otherwise occur during the grinding process. A maximum leaching efficiency of 96% was achieved for RW-cut-char while using 1 M H_2SO_4 and 10 vol% H_2O_2 for 1.5 h leaching time. Cementation experiments using zinc powder produced copper particles with a concentration of 97.6 wt% copper and 2.6 wt% zinc.

Thus, combining the Chapters 3, 4 and 5, a proper route for the recovery of the organic and inorganic fraction of materials from WPCB has been achieved. The use of cut samples of WPCB and recovery of copper after pyrolysis showed multiple benefits: reduction of waste generation and material loss from grinding operations, reduced brominated compounds in the pyrolytic oil and better leaching efficiency of copper. The next chapter presents simulation for a proposed plant consisting of an integrated process with pyrolysis and hydrometallurgy at industrial scale, followed by the techno-economic assessment of the plant.

Chapter 7

Simulation using Aspen Plus[®] and techno-economic assessment

- Resource recovery
- Pyrolysis
- Aspen Plus[®]
- Techno-economic
- Minimum selling price of oil



Publication: B. Boro and P. Tiwari, “Effect of pyrolysis and comminution on copper extraction and techno-economic assessment for resource recovery from waste printed circuit board”, *Journal of Environmental Management*, 397, 128365, 2026.

7. Simulation using Aspen Plus® and techno-economic assessment

For a newly developed process, a comprehensive assessment of economic feasibility is essential prior to industrial implementation. In this chapter, an integrated comminution, pyrolysis and hydrometallurgical process for the recovery of materials from WPCB has been modelled using Aspen Plus® software (v14), followed by techno-economic assessment of the plant. The simulation parameters were taken from the preceding chapters. To the best of our knowledge, a combined simulation and techno-economic assessment of a plant combining comminution, pyrolysis and hydrometallurgical techniques has never been reported. The economic performance of the proposed plant was presented based on the values of the net present value (NPV), internal rate of return (IRR), profitability index (PI), and payback period (PBP) using discounted cash flow (DCF) analysis. These parameters were calculated based on the revenue generated from copper and glass fibers, and the minimum selling price (MSP) of oil was calculated for different scenarios.

This study provides a systematic methodology for the Aspen Plus® simulation of the hybrid process consisting of feedstock preparation, pyrolysis and hydrometallurgy to recover polymers, metals, and glass fibers from WPCB, followed by assessment of the economic performance of the simulated plant. Thus, it identifies key parameters influencing the economic viability and optimal recycling pathways for valorizing WPCBs.

7.1. Simulation of an integrated comminution-pyrolysis-hydrometallurgy plant using Aspen Plus®

The preceding chapters established the material recovery process from WPCB consisting of polymers, metals (copper), and glass fibers to maximize resource recovery while minimizing bromine transfer to the oil fraction. This include the following steps:

- I. Use of cut pieces of WPCB (RW-cut) over powder samples for pyrolysis to avoid material loss and reduce human health hazards.
- II. Pyrolysis of the RW-cut samples with embedded metals intact to convert the polymer fraction into oil with reduced bromine content, and gas phases.
- III. Recovery of copper from the pyrolyzed RW-cut samples (RW-cut-char) by employing hydrometallurgical approach using H_2SO_4 and H_2O_2 mixture in ambient atmosphere.
- IV. Recovery of copper in solid phase using zinc cementation
- V. Recovery of glass fibers from the residue left post pyrolysis and hydrometallurgical extraction.

This proposed route was simulated using Aspen Plus® software for a plant with 500 kg/h feed capacity. The plant has been divided into three sections: (i) Comminution, (ii) Pyrolysis, and (iii) Metal extraction (Fig. 7.1) [34]. The **comminution section** consists of a crusher and a screen with 1 cm opening, which produced WPCB samples that represented the RW-cut samples. In the **pyrolysis section**, the RW-cut samples were simulated to pyrolyze at the optimized temperature (500 °C) in a RGibbs reactor to produce char, oil and gas fractions. In the **metal extraction section**, copper leaching and cementation processes were simulated to obtain high purity copper precipitate. The detailed methodology of the simulation process has been discussed in section 2.9.

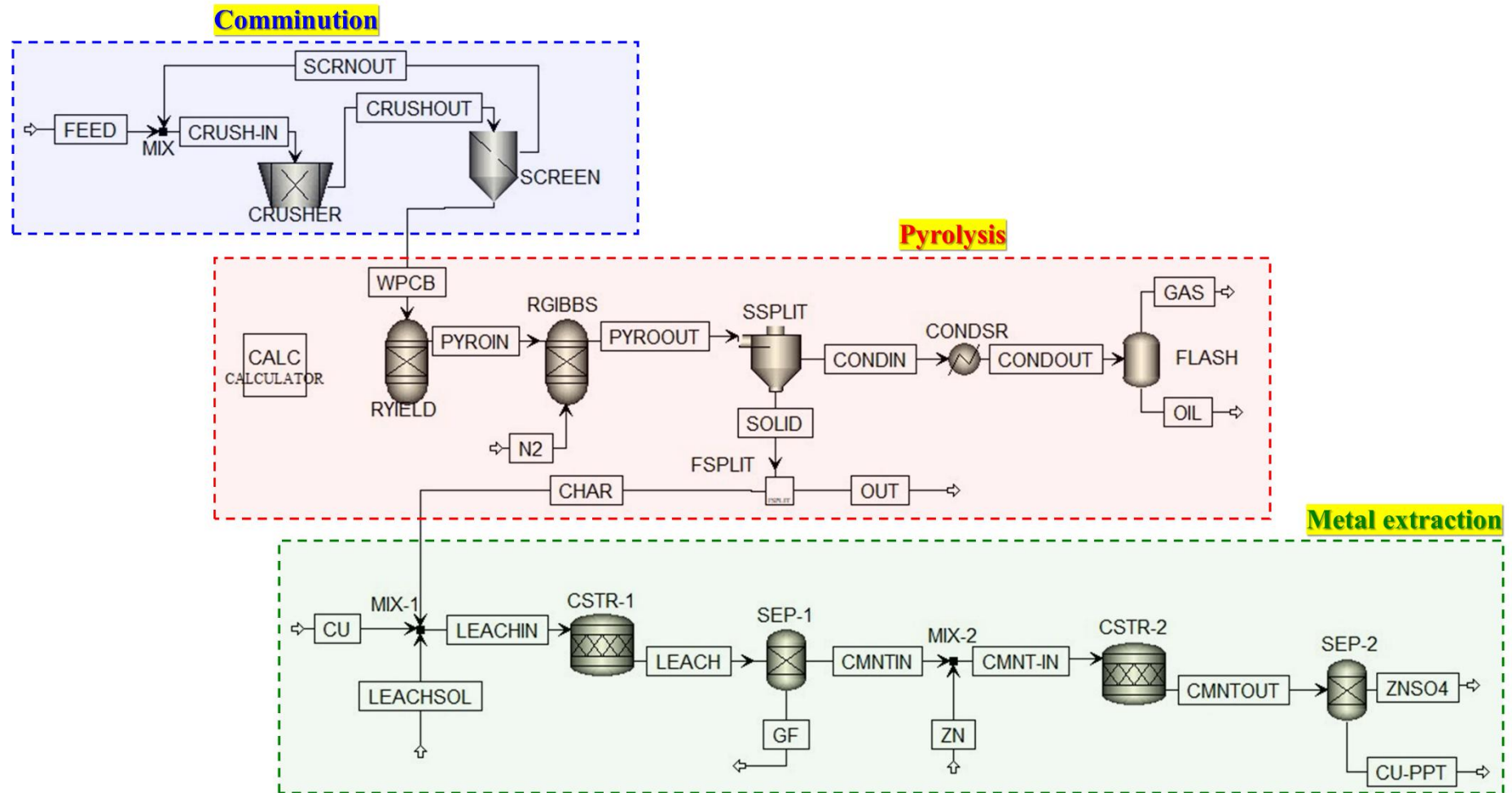


Fig. 7.1 Aspen Plus® simulation flowsheet of WPCB pyrolysis and metal extraction considering three different steps: comminution, pyrolysis and metal extraction

The proposed plant was successfully simulated (no error message) using Aspen Plus[®] software, from which the overall and component mass balance were obtained (Fig. 7.2 (a), 7(b), and Fig. A. 4). In the pyrolysis section, WPCB feed rate of 500 kg/h was thermally degraded to produce approximately 71% char, 14% oil and 15% gas fractions. The lower value of char yield obtained from simulated process may result from minimal heat resistance in the reactor model. WPCBs contain brominated flame retardants (BFRs), with most bromine transferring to the gas fraction during pyrolysis [186, 190]. However, the presence of BFRs in the feed was not accounted for in the simulations, resulting in lower predicted gas yields and correspondingly higher oil yields compared to experimental values. This exclusion of brominated compounds thus accounts for the reduced gas yield and increased the oil yield observed in simulation.

In the metal extraction section, the glass fibers and copper precipitate were obtained using zinc cementation. A higher purity (98.5%) of copper precipitate was obtained in simulation, as compared to the EDX analysis of the experimentally obtained precipitate of 97.4% Cu. Detailed stream compositions for major equipment, including SSPLIT and FLASH in the pyrolysis section, and SEP-1 and SEP-2 in the metal extraction section are provided in the Appendix B (Fig. A. 5 to A. 8).

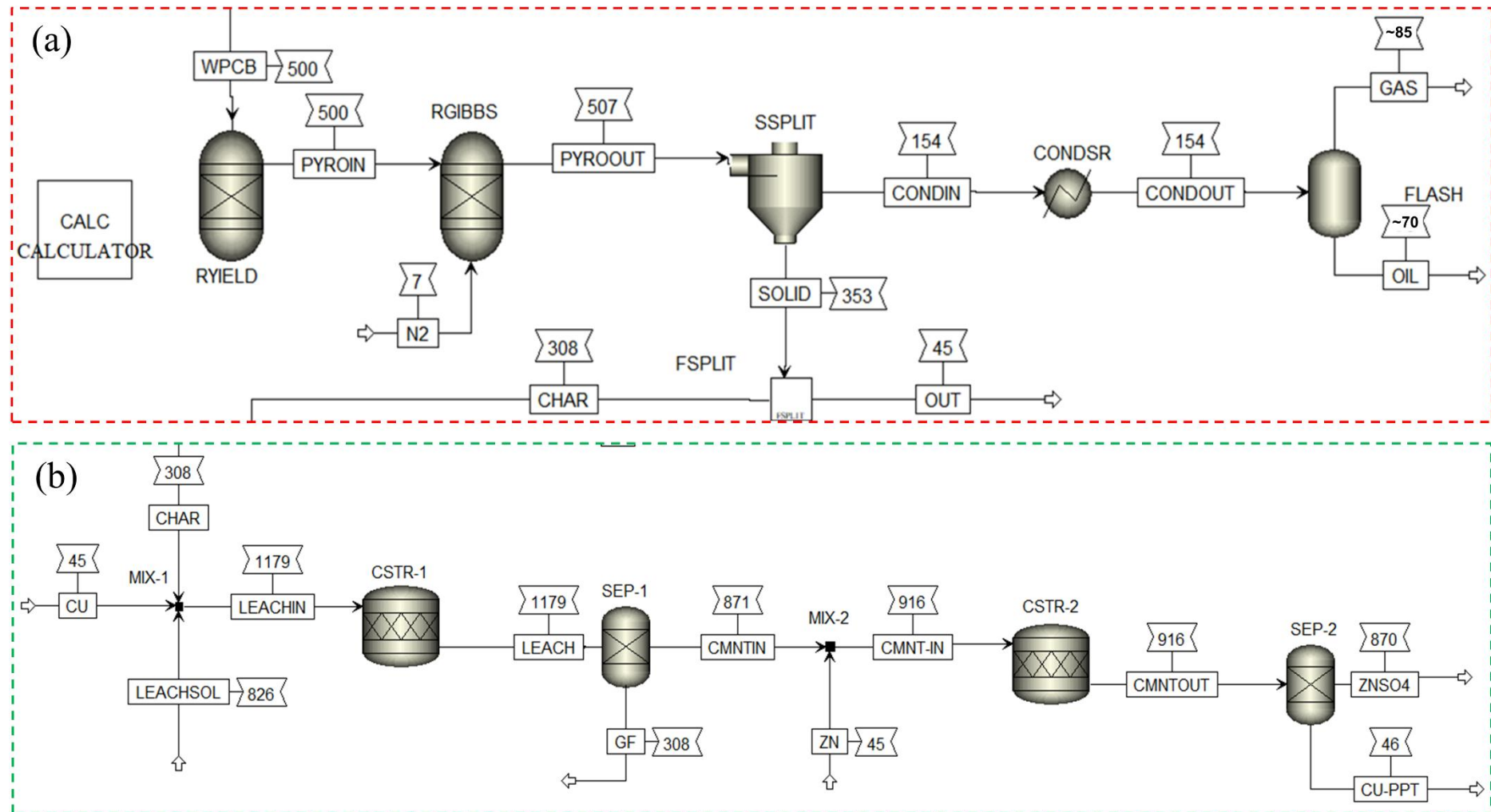


Fig. 7.2 Material balance for the (a) pyrolysis and (b) metal extraction processes

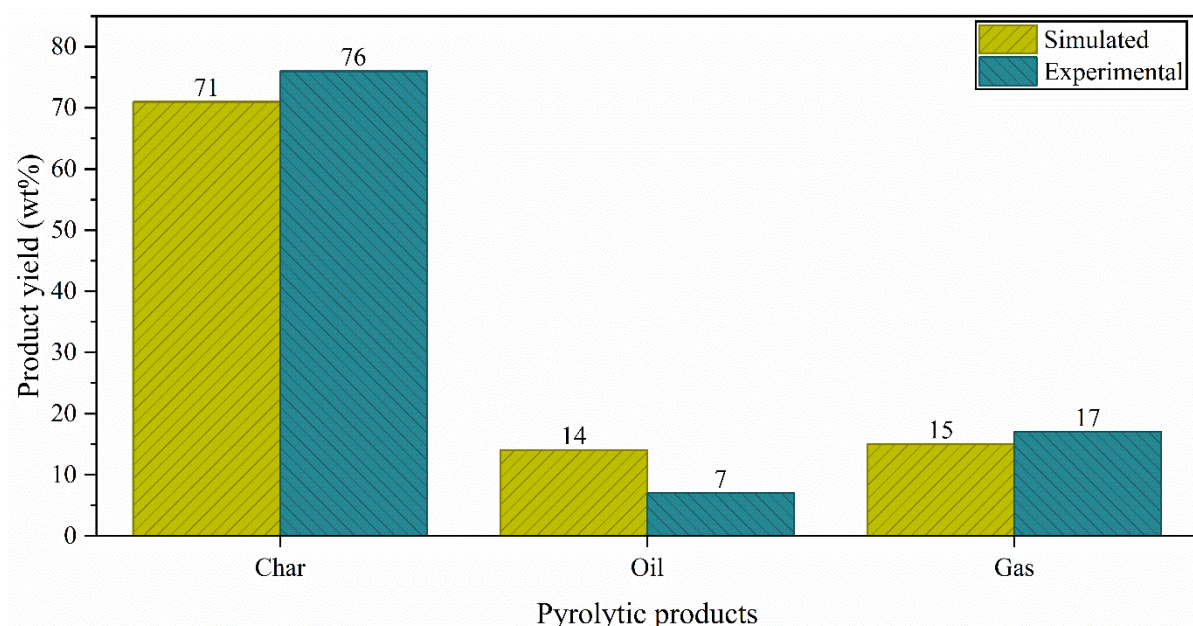


Fig. 7.3 Comparison of simulated and experimental pyrolytic product yields

7.2. Techno-economic assessment of the proposed plant

The detailed methodology for the techno-economic assessment of the proposed plant has been discussed in section 2.10. Few assumptions were made to design the proposed plant and perform the economic analysis (Table 7.1). The proposed plant was planned to be situated in India.

7.2.1. Capital and operating expenses

The capital expenditure (CAPEX) and the operating expenditure (OPEX) are the key components of techno-economic assessment of a plant. The detailed list of components associated with the CAPEX and OPEX have been listed out in Table 2.3. The Aspen Plus Economic Analyzer (APEA) sizes, maps and provides the price of the equipment based on the database available (year 2022). The equipment cost has been updated for the recent year 2024 from the base year 2022 using the CEPCI cost index (Eq. 2.25). Detailed cost of the equipment at the industrial scale has been elaborated in Table. 7.2. A total estimate of \$ 0.35M was required

to purchase the equipment to be used for comminution, pyrolysis and metal extraction processes.

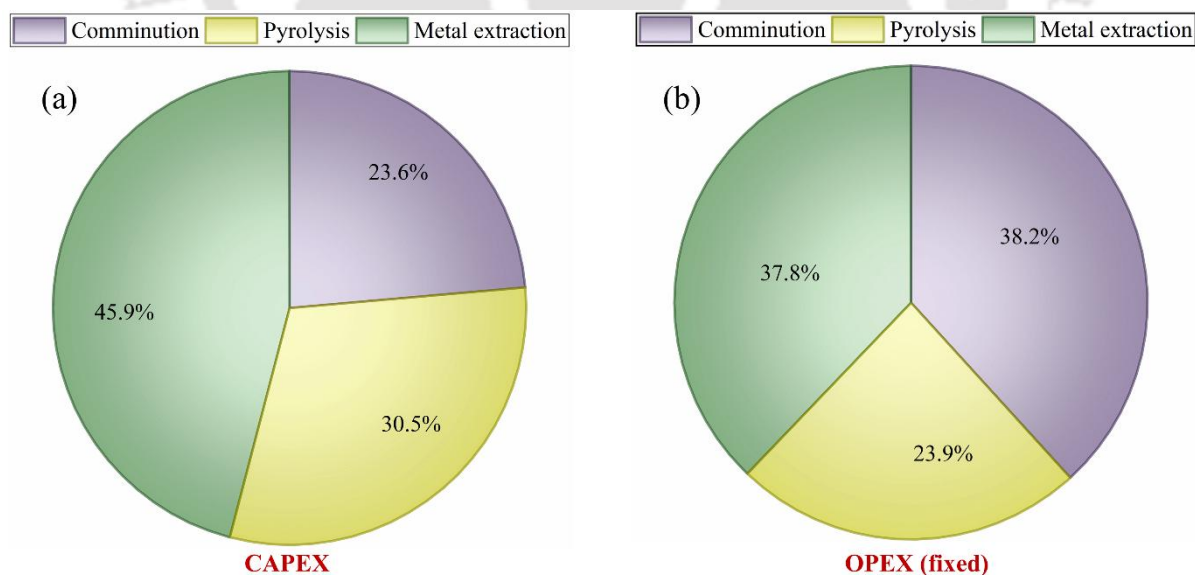
To determine the cost contribution of different processes: comminution, pyrolysis and the metal extraction towards CAPEX and OPEX (fixed) components, the share for each of these operations/processes has been compared (Fig. 7.3). The metal extraction process had the highest contribution of about 45.9% of the total capital cost, followed by pyrolysis and comminution (Fig. 7.3 (a)). This can be attributed to the high cost of CSTR reactors used for the leaching and cementation processes. In case of the fixed operating expenses, the cost contribution of comminution section is the highest (38.2%). It is because of the requirement of a higher number of labors in handling the solids (Fig. 7.3 (b)).

Table 7.1 Parameters assumed for the techno-economic assessment of the proposed plant

Parameters	Assumptions
Plant location	India
Currency	\$
Conversion (₹)	85.76
Plant lifetime	20 years
Working h per year	8000
Depreciation method	Straight line
Tax rate	15%
Raw material cost	Nil + transportation charges

Table 7.2 Cost of equipment used in the proposed plant updated to year 2024

Operations	Equipment	Cost _{aspen} (\$)	Cost ₂₀₂₄ (\$)
Comminution	Crusher	57800	56667
	Screen	26400	25882
Pyrolysis	RGibbs	34400	33725
	Ssplit	22300	21863
	Flash Sep	22300	21863
	Cooler	29600	29020
Metal extraction	2×Rstoic	2×59600	86275
	2×Separator	2×22300	43725
Total equipment cost (\$)		356600	349608 (= 0.35 M)

**Fig. 7.4** Contribution of the comminution, pyrolysis and metal extraction sections towards (a) CAPEX and (b) OPEX (fixed)

7.2.2. Discounted cash flow analysis

The discounted cash flow analysis of the material recovery from WPCB using the combination of pyrolysis and hydrometallurgy proved that it is economically sound with a cumulative profit of \$2.87M. Detailed inflow and outflow of cash throughout the useful life of the plant can be tracked from Fig. 7.5. An attractive return with a PBP (discounted) of 5.4 years could be achieved from the revenue generation from copper and glass fibers. The economic behavior of the WPCB recycling plant depends on the capacity, metal content, and optimization of the plant. For an optimized plant that processes high-grade WPCB, the payback period can be as low as one year [162]. The current DCF analysis has been performed considering the revenue generated by copper and glass fiber (GF) recovery, but it did not consider the sale of oil and gas. Since most of the recyclers concentrate on the recovery of copper, the DCF analysis was checked considering revenue generation from copper alone, but the discounted PBP extended beyond the plant's useful life (Fig. 7.6). Hence, it is necessary to sell glass fibers along with copper to make a profit. Moreover, recovery of copper alone will lead to the generation of secondary wastes (glass fibers and polymers), and a landfill charge might be incurred, which will further add to the losses. Tran et al. [140] obtained an NPV of \$5.94 M and a PBP of 3.9 years for a hydrometallurgical plant to recover copper and gold from WPCB. The favorable performance of the plant can be attributed to the recovery of precious metal gold and a higher amount of copper (34.1%) than in the present study (9%).

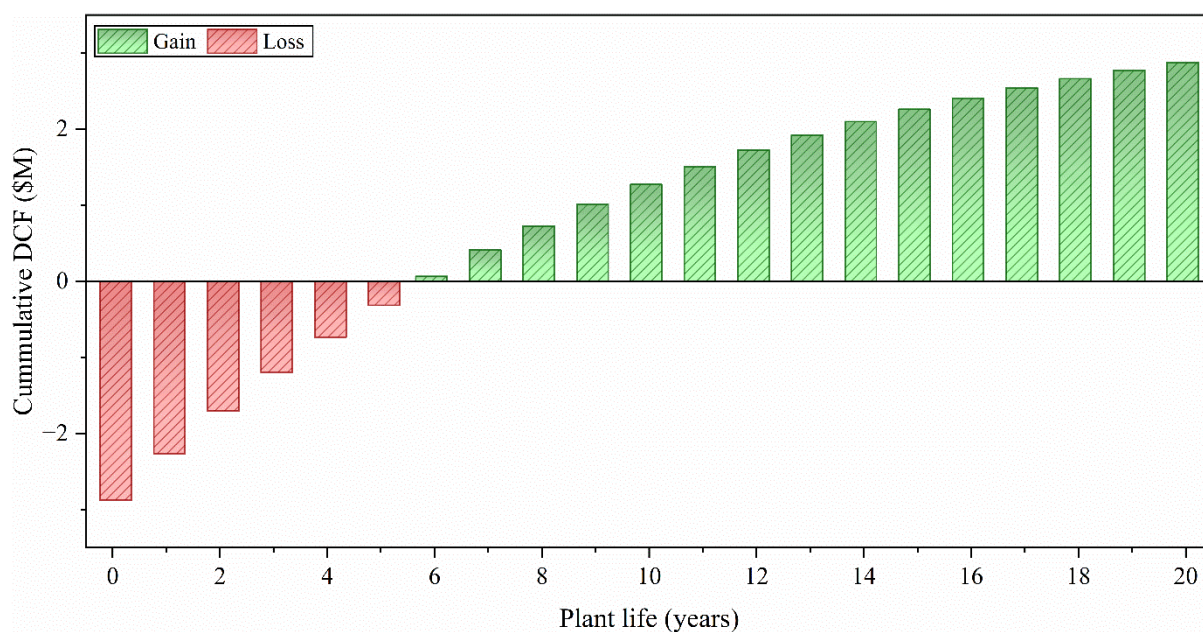


Fig. 7.5 Discounted cash flow analysis for the recovery of polymer, copper and glass fibers from WPCB using an integrated comminution-pyrolysis-hydrometallurgical processes

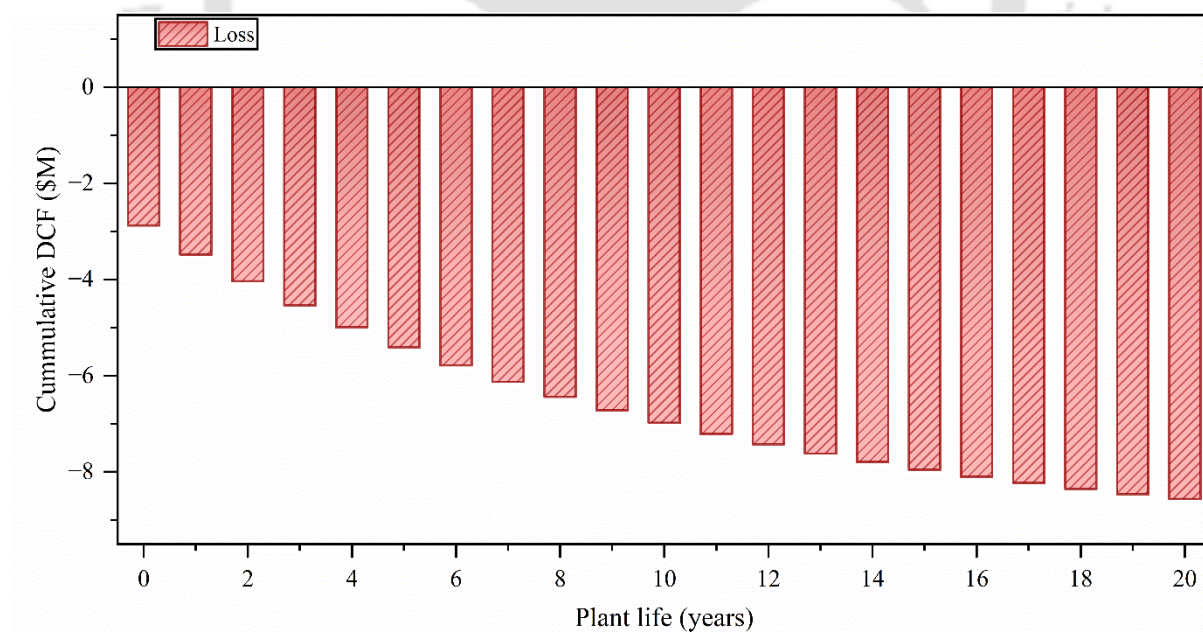


Fig. 7.6 Discounted cash flow analysis for the recovery of copper from WPCB using comminution-hydrometallurgical processes

7.2.3. Economic evaluation and minimum selling price of oil

The economic performance of the plant was assessed by comparing the obtained values to the minimum economic feasibility thresholds outlined in the 'Criteria' column in Table 7.3, thereby determining the extent to which the plant satisfies the established benchmark requirements for feasibility (Table 7.3). The results confirmed that the proposed plant is economically viable based on the NPV, IRR, PI, and discounted PBP values. For the proposed plant, four products: oil, gas, copper, and glass fibers were generated. Therefore, revenue generation will depend on all these products, and so will the value of the MSP of oil. To account for this situation, four different MSPs (defined below) were calculated.

- I. MSP_i : Copper and GF were sold
- II. MSP_{ii} : Only GF was sold
- III. MSP_{iii} : Only copper was sold
- IV. MSP_{iv} : neither copper nor GF were sold (only oil was sold)

The MSP of oil was determined using the 'Goal Seek' tool within the 'What if Analysis' in Microsoft Excel. The goal for NPV was set as zero for the changing value of the selling price of oil per unit. For the MSP_{ii} and MSP_{iii} , the selling price was considered zero for copper and GF, respectively. Similarly, for MSP_{iv} , the selling prices of both copper and GF were taken as zero. However, in this case, the metal extraction part has been omitted; thus, the components in the CAPEX and OPEX related to the hydrometallurgical part were also removed. For example, the equipment prices and the cost of chemicals were not taken as zero. The MSP of the pyrolytic oil in different scenarios is reported in Table 7.3. It is reflected that the MSP values are sensitive to the revenue generated from copper and GF. For MSP_i , the value is zero, which means that the oil can be sold at a minimal price, provided the copper and GF were also sold. The $MSP_{ii} > MSP_{iii}$, shows that the revenue generated from the sale of copper is higher than that

of GF, even though the amount of GF production is higher than that of copper. To conclude, the WPCB recycling plant should incorporate both pyrolysis and hydrometallurgical sections to achieve a higher return and complete recovery of the metallic and non-metallic components present in WPCB. Moreover, consideration of the gas fraction would lead to a higher return; however, the removal of brominated compounds from the gas phase needs to be addressed. The current study did not consider the presence of brominated compounds. Hence, the gas fraction was not discussed.

Table 7.3 Economic performance of the proposed plant

Economic parameters	Criteria	Value
Net present value	≥ 0	\$2.87 M
Internal rate of return	$\geq$ discount rate (=10%)	29%
Profitability Index	≥ 1	2.25
Discounted Payback period	$\geq$ plant life (=20 years)	5.4 years
MSP _i	-	0 \$/kg
MSP _{ii}	-	4.42 \$/kg
MSP _{iii}	-	2.11 \$/kg
MSP _{iv}	-	1.57 \$/kg

7.3. Summary

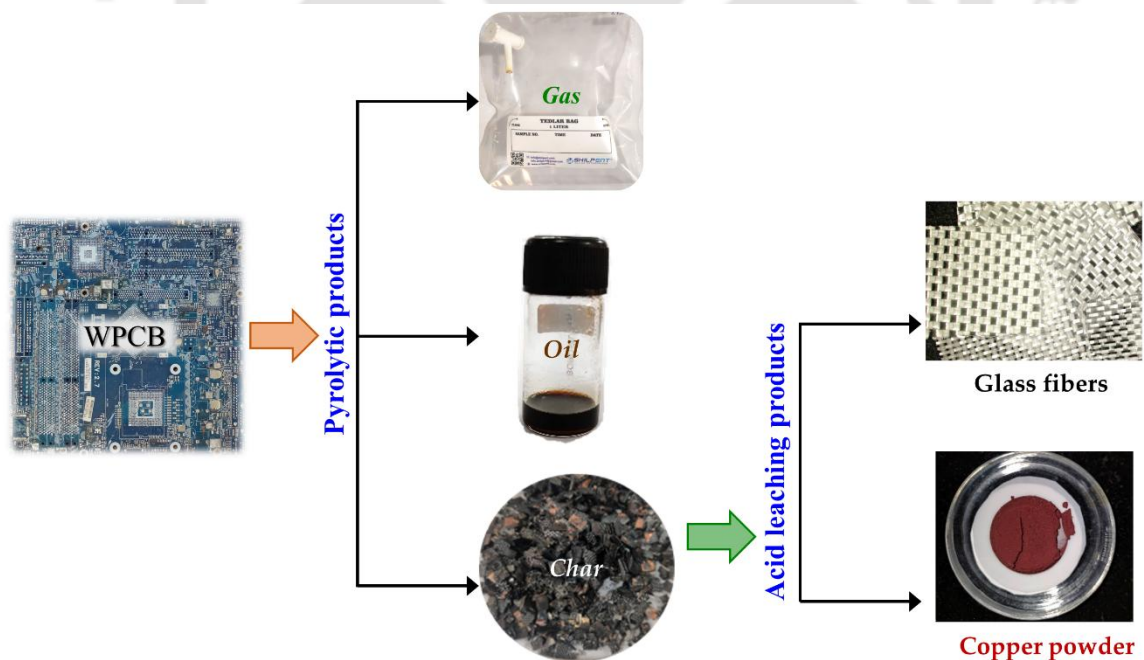
This study developed an integrated process for recovering the most abundant metal in WPCB, copper, along with non-metallic components such as polymers and glass fibers. A techno-economic assessment was subsequently conducted for a proposed plant simulated in Aspen Plus® comprising comminution, pyrolysis and metal extraction sections. The process flowsheet, integrating comminution, pyrolysis, and metal extraction, was simulated in Aspen Plus® for techno-economic evaluation. The discounted cash flow analysis revealed a payback period of 5.4 years based on the sale of copper and glass fibers. Since the selling price of oil was uncertain, its MSP was determined separately. The proposed plant demonstrated economic feasibility even without considering the oil revenue.

Nevertheless, certain modifications are necessary for practical implementation, particularly in terms of environmental considerations. For instance, a gas scrubbing unit is necessary to remove brominated compounds from the pyrolytic gas fraction. There is also scope for modifying the process flow sheet to include the recovery of Zn from ZnSO₄ solution and the recycling of water/energy streams for an optimized process. Overall, this study provides a foundation framework for future in-depth techno-economic analyses and process optimization in the R&D industry sector.

Chapter 8

Overall conclusion and future recommendations

- Overall conclusion
- Summary
- Future work



8. Overall conclusion and future recommendations

This thesis presents a comprehensive study on material recovery from WPCB through an integrated pyrolysis-hydrometallurgical approach. The target of this approach is to recover all major components: polymers, metal (copper), and glass fibers, while effectively reducing the bromine content in the pyrolytic oil. This chapter summarizes the previous chapters and provide future recommendations to improvise the WPCB recycling process.

8.1. Overall conclusion of the thesis

With rapid technological advancements and changes in lifestyle, the excessive consumption of materials has led to significant resource depletion, a surge in waste generation, and thus, expansion of landfills. The era of information technology, in particular, has witnessed a remarkable rise in the use of EEE. However, inadequate policy agendas that address the issues of increasing waste materials, and inefficient waste recycling facilities have failed to cope with the growing volume of discarded electronics, resulting in the accumulation of large quantities of waste EEE (E-waste). It has emerged as one of the fastest-growing solid waste streams. Owing to the presence of heavy metals and toxic compounds (BFRs), E-waste is classified as hazardous; nonetheless, it is also a valuable secondary source of various precious, base and critical metals.

Waste printed circuit boards represent one of the most valuable constituents of E-waste, comprising a complex mixture of polymers, metals, and ceramics. This thesis presented a comprehensive study on material recovery from WPCBs through integrated pyrolysis and hydrometallurgical processing. The research aimed at achieving maximum resource recovery, minimizing bromine transfer to the pyrolytic oil, and conducting a detailed techno-economic evaluation of the developed process. Accordingly, the thesis was structured into seven chapters. Chapters 1 and 2 provided an extensive review of relevant literature and the methodologies

employed throughout the study. Chapters 3 to 7 incorporated the kinetic parameter investigations, experimental work such as pyrolysis and metal extraction, characterization of products obtained from pyrolysis and metal extraction, process simulation using Aspen Plus[®] software, and techno-economic analysis. Together, these chapters presented a complete exploration of sustainable recovery pathways for WPCB recycling and a potential contribution to circular economy advancement.

The thermal degradation kinetics of WPCBs were investigated to understand the influence of their complex composition consisting of organic and inorganic fractions on degradation behavior. Kinetic parameters were determined from TGA data acquired at multiple heating rates (5, 10, 20 and 50 °C/min) providing insights into the decomposition mechanism under non-isothermal conditions. The key kinetic parameters: activation energy, reaction model and pre-exponential factor, were determined using various isoconversional methods, Criado master plot, and the concept of compensation effect, respectively. The results were further validated through the reconstruction of conversion profiles, which revealed that the Starink method provided the best overall fit to the experimental data. The thermal degradation profiles and Starink derived kinetic parameters were compared to assess the effects of embedded metals and bromine content. The presence of embedded metals lowered the final degradation temperature, reduced the activation energy, and modified the reaction mechanism, whereas bromine reduction via Soxhlet extraction slightly decreased the initial degradation temperature, had a negligible impact on the activation energy, likely due to the limited extent of bromine reduction, whereas altered the reaction model.

Lab-scale pyrolysis experiments using WPCB cut pieces (RW-cut, $\sim 1 \times 1 \text{ cm}^2$), combined with response surface methodology (RSM) optimization of key parameters, temperature, heating rate and hold time, to minimize char yield and maximize oil yield were performed. Temperature emerged as the most significant parameter (p-value < 0.0001), with optimized conditions

identified as 500 °C, 30 °C/min heating rate and 156 min hold time. Pyrolytic products obtained at 300 °C, 500 °C, and 600 °C were characterized to interpret the influence of the most significant parameter, temperature. Elemental (CHNS) analysis of char samples revealed optimal organic matter removal at 500 °C, supported by FESEM morphological studies showing clear images of glass fibers. The pyrolytic oil was predominantly aromatic with high phenol content, with a calorific value of 30–35 MJ/kg, density of 1.07–1.13 g/cm³, and viscosity of 5–11 cP, depending on the pyrolysis temperature. Thus, making it a viable energy source and feedstock for production of phenolic based chemicals. Gas analysis confirmed the presence of C₁–C₅ hydrocarbon gases, and non-hydrocarbon gases H₂, CO, and CO₂, confirming the energy potential of gas fraction as well. However, brominated compounds were detected in the oil fraction, highlighting the need for further debromination strategies.

The brominated compounds detected in the pyrolytic oil limits its applicability. Two debromination strategies were examined: bromine reduction via Soxhlet extraction before pyrolysis, and influence of catalytic action of the metal fraction in WPCBs. Pyrolysis experiments conducted under previously optimized conditions (500 °C, 30 °C/min, 156 min hold time) demonstrated that the metal fraction was more effective in minimizing bromine transfer to the oil. However, over 75% of the bromine content was consistently transferred to the gas fraction, regardless of metal presence or pretreatment methods.

Recovery of copper, the most abundant and valuable metal in WPCBs, through hydrometallurgical processing using H₂SO₄ and H₂O₂ as leaching agent has been discussed. Hydrometallurgy was selected for its economic viability, and high metal selectivity. Leaching efficiency was systematically evaluated for various WPCB pretreatment methods, grinding (to enhance surface area), and pyrolysis (to degrade the lamination effect provided by solder mask). Direct comparison of the leaching efficiencies demonstrated better copper leaching efficiencies for pyrolyzed cut WPCB samples (RW-cut-char), ground samples (RW) and its

pyrolyzed version (RW-char). However, considering the additional energy requirement associated with grinding, RW-cut-char was subjected to leaching and cementation experiments. The leachate processed via zinc cementation, produced high-purity copper precipitate (97.4%). These results confirmed that pyrolysis of cut WPCB pieces, followed by direct char leaching for copper and glass fiber recovery, optimizes the integrated process by minimizing losses, dust, and bromine contamination in the oil fraction.

The techno-economic evaluation of an integrated plant comprising of comminution, pyrolysis, and metal extraction sections in Aspen Plus[®] software, incorporating the experimental results from preceding chapters has been discussed. Pyrolysis was modeled at the optimized 500 °C temperature and with 96% leaching efficiency was taken for the hydrometallurgical section. The techno-economic assessment showed favorable results with NPV of \$2.87 M, IRR of 29%, discounted PBP of 5.4 years, and PI of 2.25, considering copper and glass fibers as primary products. Determination of MSP of oil at different scenarios suggested its dependency on the process flowsheet.

In conclusion, this thesis established an integrated pyrolysis-hydrometallurgical framework for comprehensive recovery of polymers, copper, and glass fibers from WPCBs, achieving maximal resource valorization while minimizing bromine contamination in oil, and environmental impacts. Key findings highlight pyrolysis optimization at 500 °C as superior pretreatment over grinding, for producing high oil yield, reduced bromine contamination in oil, and high purity (97.4%) copper yield. Techno-economic analysis confirms commercial viability, positioning the process as a sustainable alternative to conventional E-waste management.

8.2. Future recommendations

This thesis presented a comprehensive study for the material recovery from WPCB. That include, the thermal degradation characteristics, kinetic parameter determination, optimization of the lab-scale pyrolysis process, reduction of brominated compounds in the oil fraction, comparison of various pre-treatment methods to identify the best technique for maximum copper recovery, simulation of an integrated comminution-pyrolysis-hydrometallurgy process and performance of techno-economic assessment of the simulated plant. However, further research is needed to address environmental concerns and to investigate the applications of the recovered products. Hence, the following future work and recommendations have been presented:

1. Life cycle assessment studies for the proposed material recovery process from WPCB using pyrolysis and metal extraction need to be performed.

The proposed material recovery process from WPCB containing integrated pyrolysis and hydrometallurgical approach proved to be economically viable and effective in material recovery. However, the waste streams generated during the process, such as the pyrolytic gas containing high bromine concentrations, and the chemical residues from metal extraction need to be considered.

2. Development of a membrane to selectively remove the brominated compounds from gas phase need to be studied.

During pyrolysis, most of the bromine content is transferred into the gas phase. A membrane could be developed to capture these brominated compounds and produce Br-free gas. This Br-free gas can subsequently be utilized for energy generation within the pyrolysis process.

3. Application-based studies on the pyrolytic product fractions: oil and recovered glass fibers need to be performed.

The products recovered from WPCB were: oil, gas, copper and glass fibers. The gas phase can be utilized for energy generation within the pyrolysis plant, while copper has wide established applications. However, there is currently no established market for the pyrolytic oil derived from WPCB pyrolysis, and its potential applications in various fields require further investigation. Similarly, the application of recovered glass fibers calls for broader study. Glass fiber is an integral part of WPCB and it constitutes the major fraction, hence its recovery and application cannot be ignored.

4. Optimization of the material recovery plant in Aspen Plus[®] software by enabling energy and material reuse by integrating recycle streams, and effectively removing brominated compounds from the targeted product fraction, thereby improving overall process efficiency and economic viability.

A more realistic model could be developed by incorporating treatment processes for brominated compounds and considering the disposal of chemical streams generated during the metal extraction stage. Furthermore, optimization of the recycling plant should address the reusability of materials and energy, which would provide a more practical representation of the plant and strengthen the reliability of the economic analysis.

Appendix



Appendix A

Table A. 1 GC-MS compound table for WPCB pyrolysis liquid fraction obtained at pyrolysis conditions of 500 °C

Retention Time	Compounds	GC-MS
		Area%
10.339	1,6-heptadiene-3-yne	0.02
11.92	pyridine, 2-methyl-	0.06
15.566	phenol	62.08
17.445	phenol, 2-methyl	0.90
17.9	phenol, 3-methyl	0.22
18.465	phenol, 4-bromo	0.11
19.216	2-allylphenol	0.21
20.131	phenol, 3-ethyl	0.29
21.577	p-cumenol	28.90
21.967	ethyl-2-benzofuran	0.07
24.918	2-bromo-n-formylaniline	0.14
30.825	benzene, 1-(1-carboxyethyl)-4-(1-formylethyl)-	0.05
32.306	p-hydroxybiphenyl	6.17
33.707	1,1'-biphenyl, 3-methoxy-	0.43
	Others	0.34

Table A. 2 Components for Aspen Plus® simulation of WPCB pyrolysis and metal extraction

Component ID	Type	Component name	Alias	CAS number
WPCB	Nonconventional			
H2O	Conventional	WATER	H2O	7732-18-5
N2	Conventional	NITROGEN	N2	7727-37-9
O2	Conventional	OXYGEN	O2	7782-44-7
S	Conventional	SULFUR	S	7704-34-9
H2	Conventional	HYDROGEN	H2	1333-74-0
ASH	Nonconventional			
C	Solid	CARBON-GRAPHITE	C	7440-44-0
CH4	Conventional	METHANE	CH4	74-82-8
CO	Conventional	CARBON-MONOXIDE	CO	630-08-0
CO2	Conventional	CARBON-DIOXIDE	CO2	124-38-9
C2H6	Conventional	ETHANE	C2H6	74-84-0
PHENOL	Conventional	PHENOL	C6H6O	108-95-2
M-CRE-01	Conventional	M-CRESOL	C7H8O-4	108-39-4
CUMENOL	Conventional	PHENOL,-P-ISOPROPYL-	C9H12O-N2	99-89-8
CU	Solid	COPPER	CU	7440-50-8
ZN	Solid	ZINC	ZN	7440-66-6
CUSO4	Conventional	COPPER-SULFATE	CUSO4	7758-98-7
ZNSO4	Conventional	ZINC-SULFATE	ZNSO4	7733-02-0
H2SO4	Conventional	SULFURIC-ACID	H2SO4	7664-93-9
H2O2	Conventional	HYDROGEN-PEROXIDE	H2O2	7722-84-1
C7H8O	Conventional	O-CRESOL	C7H8O-3	95-48-7

Appendix B

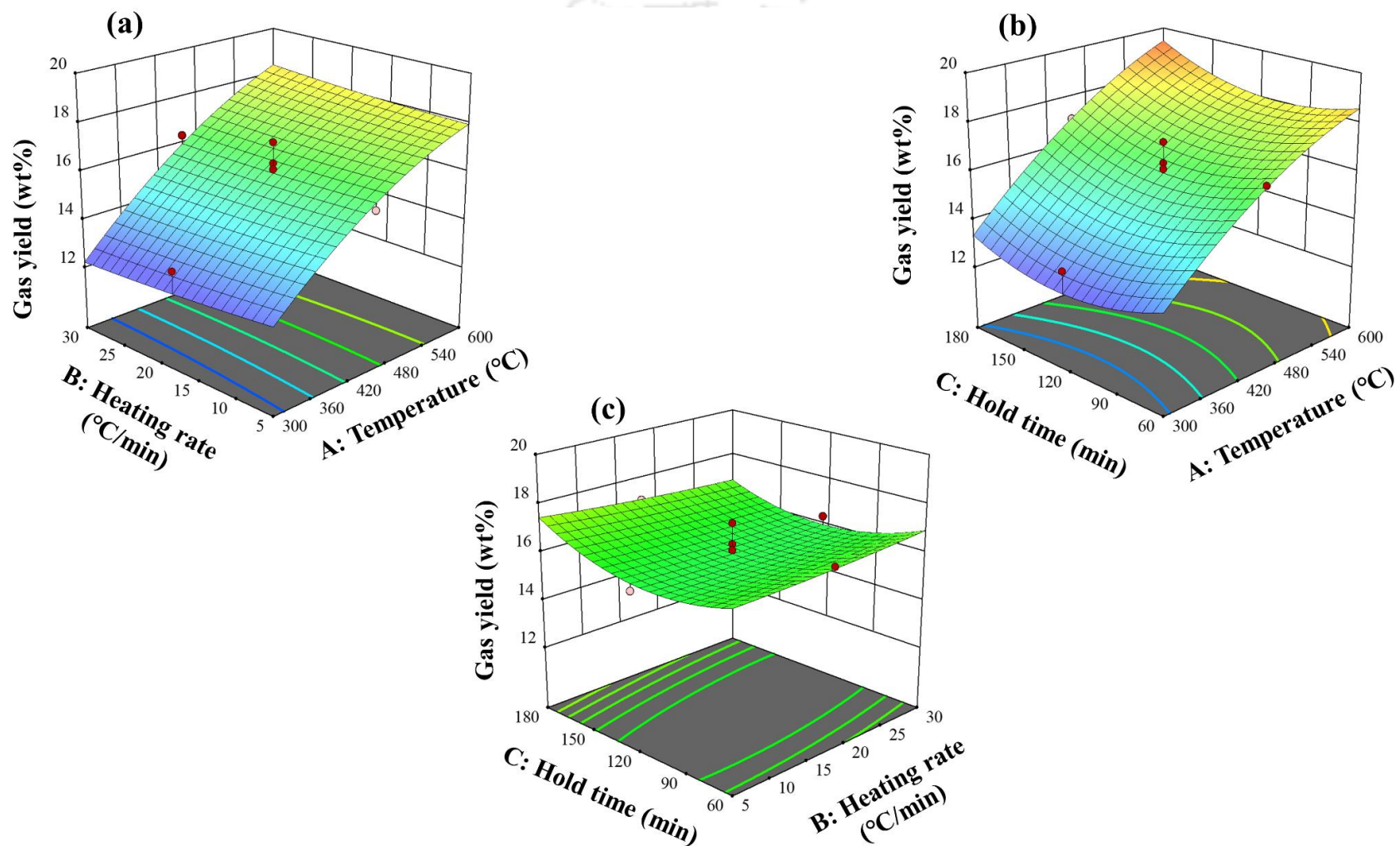


Fig. A. 1 3D response surface plots for the WPCB pyrolysis gas yield (wt%) with varying (a) A and B, (b) A and C, and (c) B and C

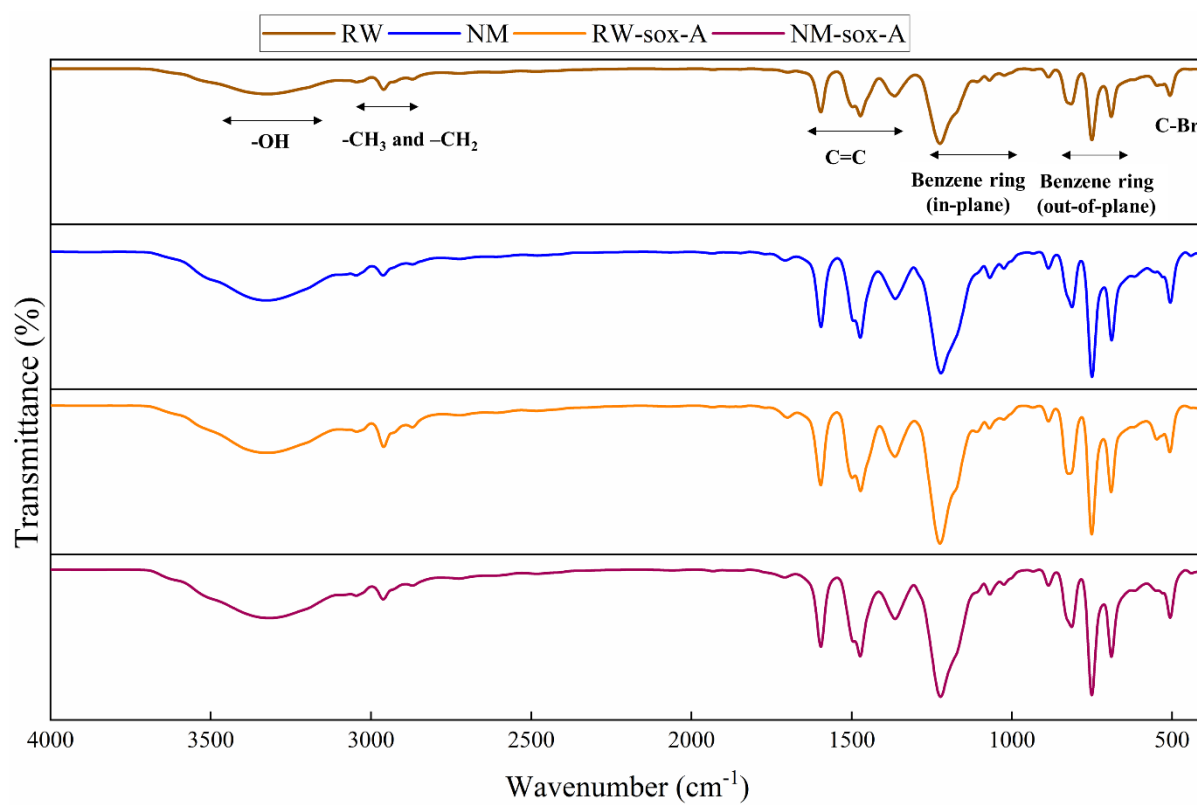


Fig. A. 2 FTIR analysis of pyrolytic oil obtained from pyrolysis of RW, NM, RW-sox-A and NM-sox-A

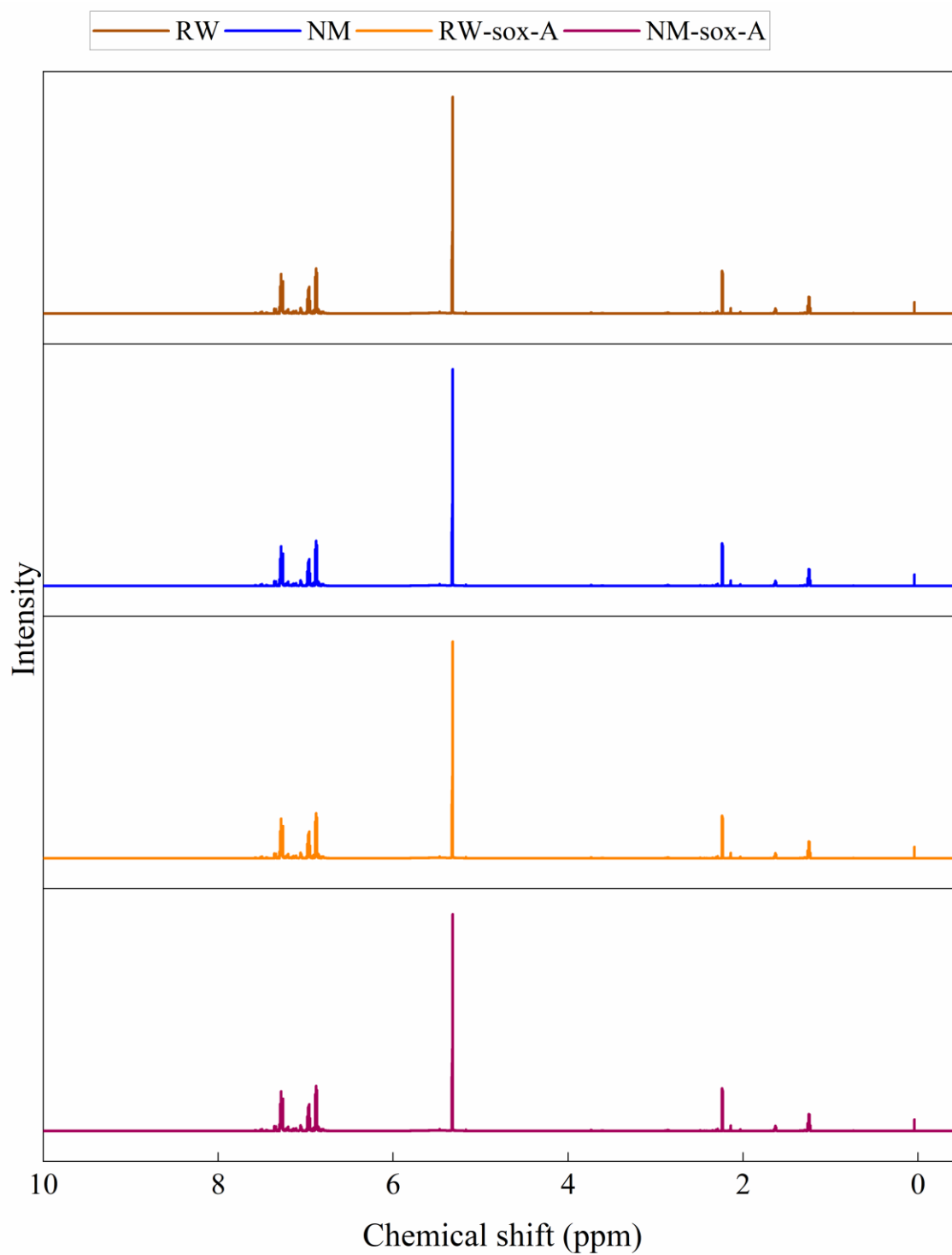


Fig. A. 3 ^1H NMR analysis of the pyrolytic oil produced using materials (a) RW, (b) NM, (c) RW-sox-A and (d) NM-sox-A

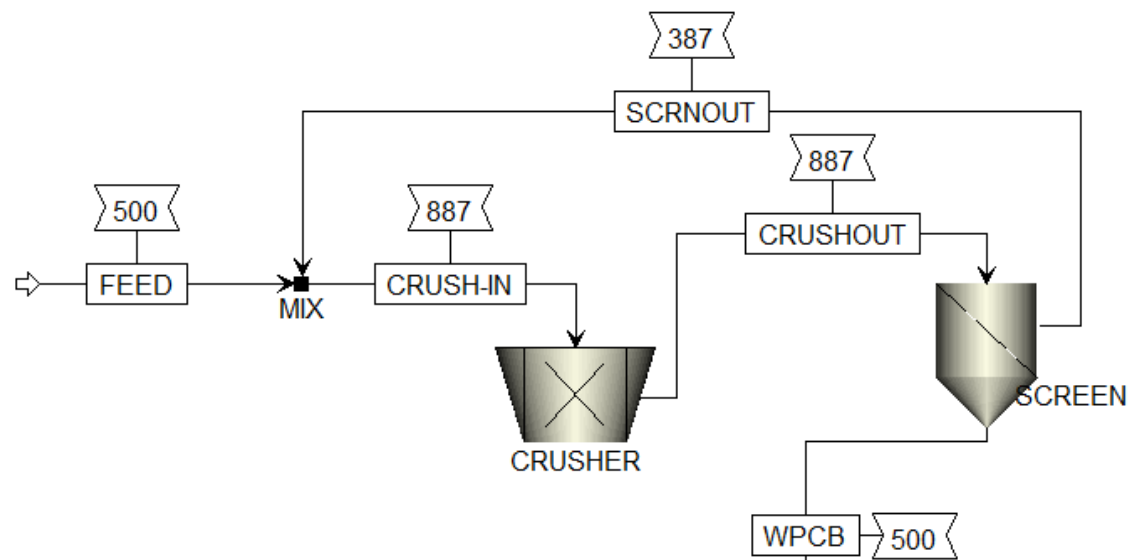


Fig. A. 4 Material balance for the comminution section

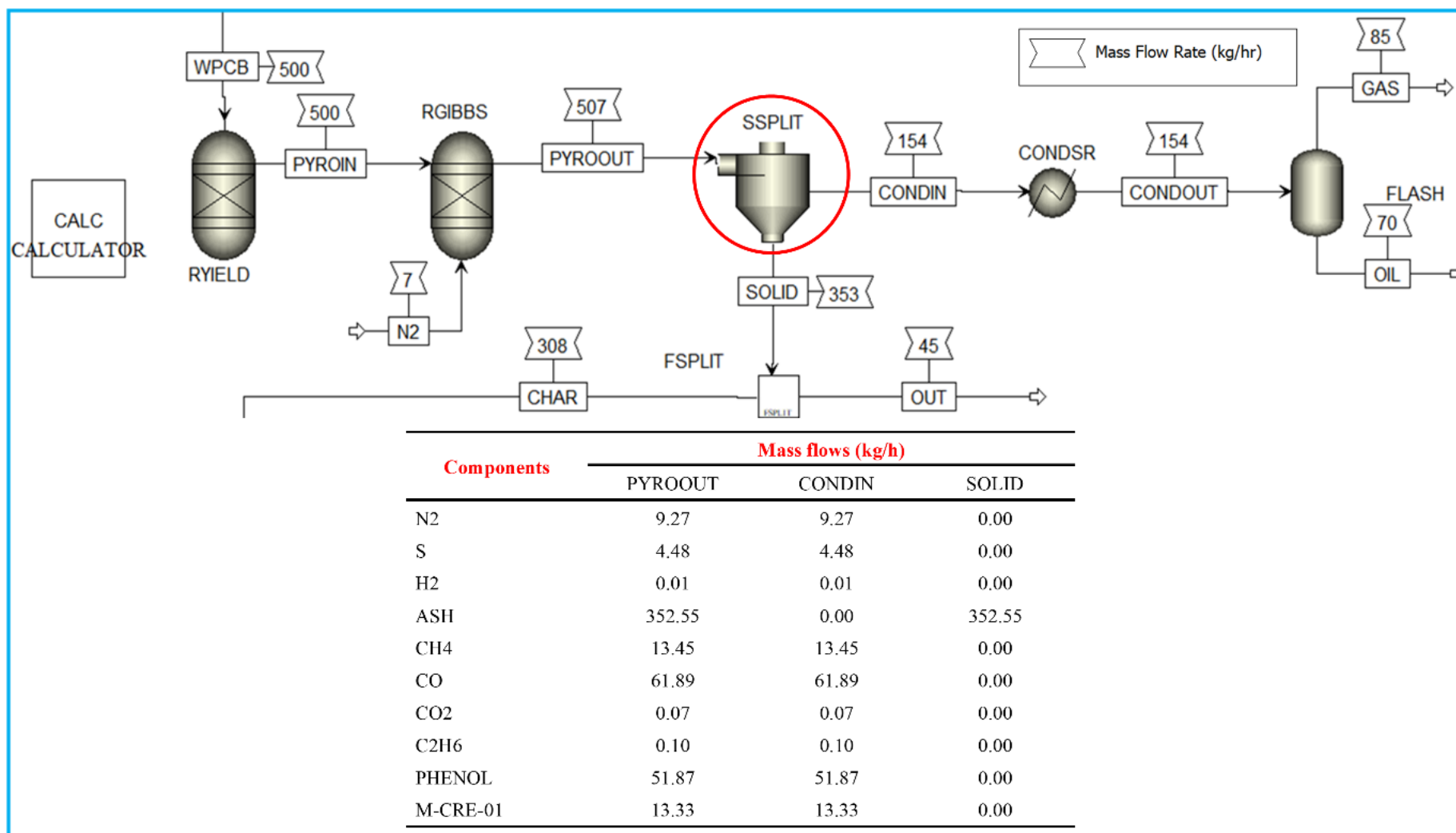


Fig. A. 5 Stream results showing the total and component mass flow around the equipment SSPLIT in the pyrolysis section

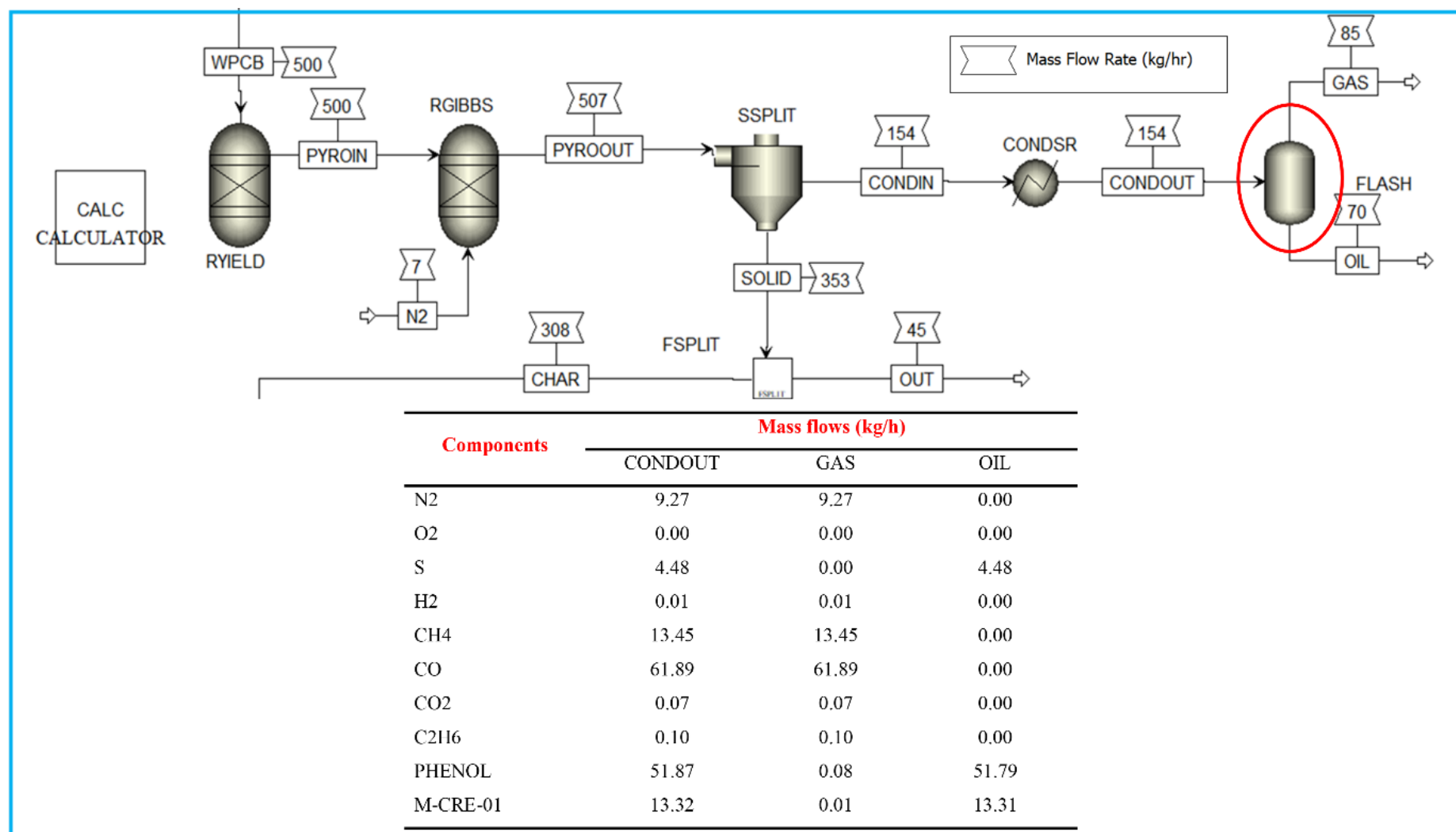


Fig. A. 6 Stream results showing the total and component mass flow around the equipment FLASH in the pyrolysis section

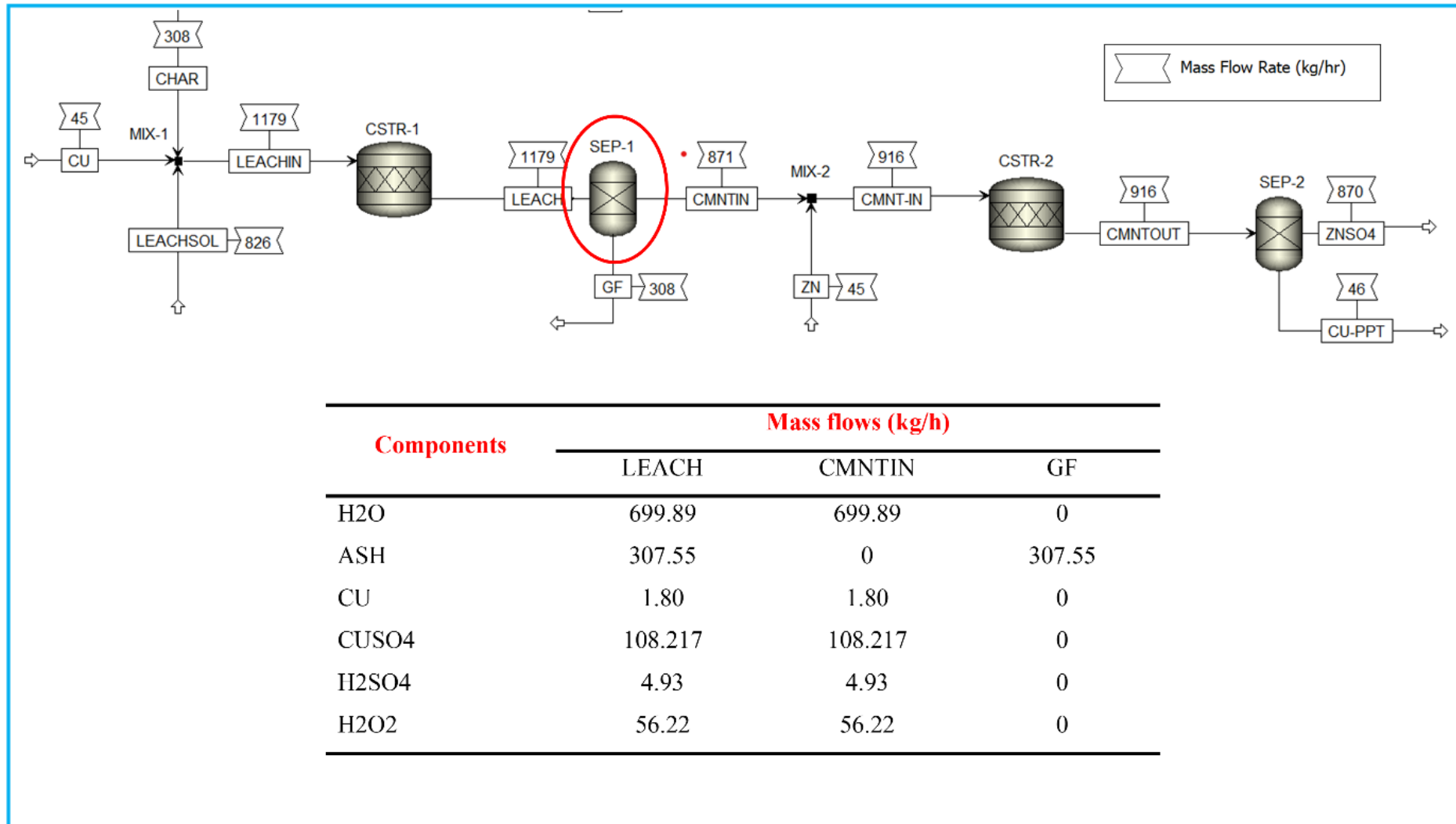


Fig. A. 7 Stream results showing the total and component mass flow around the equipment SEP-I in the metal extraction section

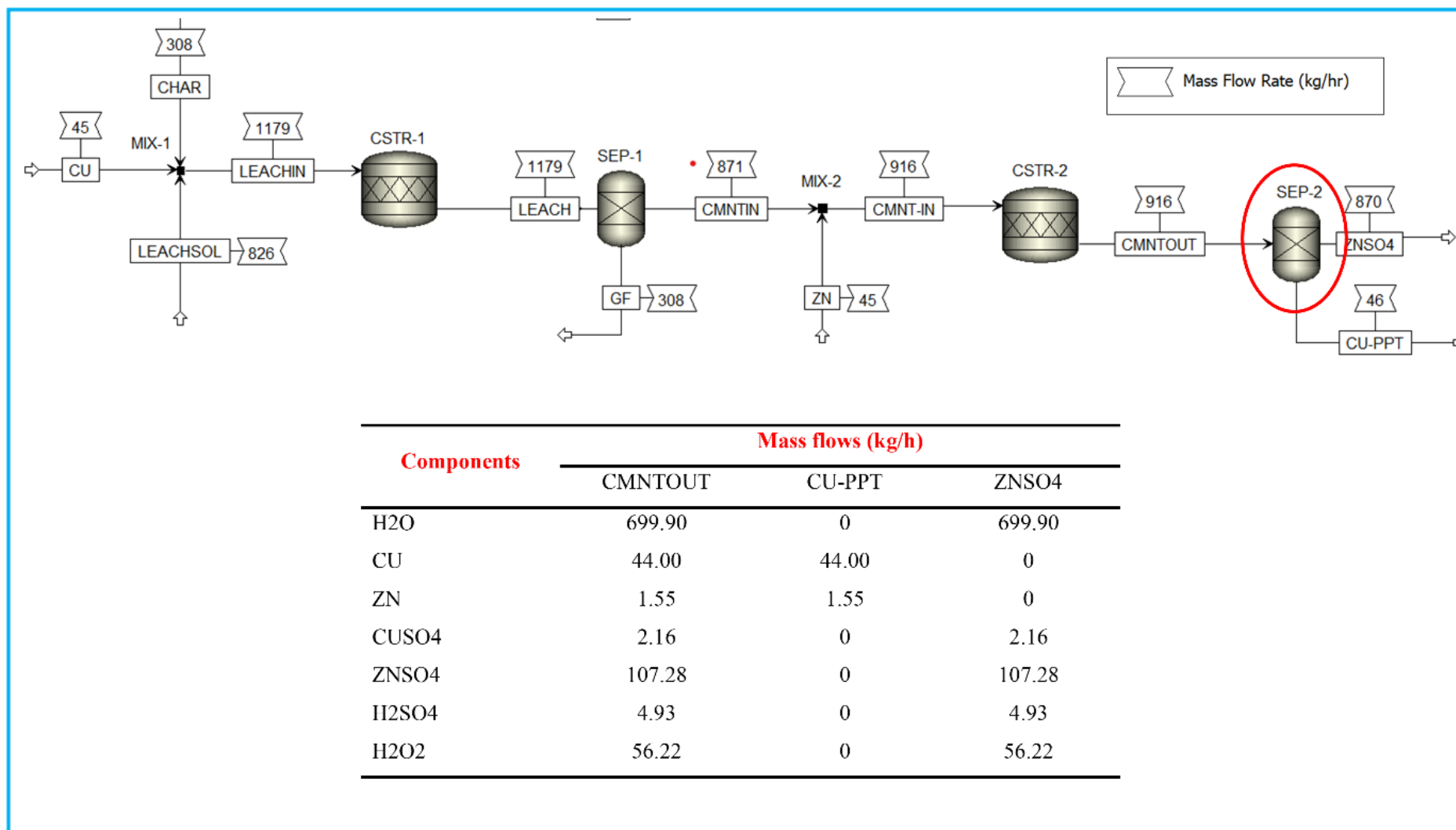


Fig. A. 8 Stream results showing the total and component mass flow around the equipment SEP-II in the metal extraction section

Appendix C

C. 1 FORTRAN code

FACT is the factor to convert the CHNSO analysis to a wet basis.

$$\text{FACT} = (100 - \text{WATER})/100$$

$$\text{H}_2\text{O} = \text{WATER}/100$$

$$\text{ASH} = \text{ULT}(1)/100*\text{FACT}$$

$$\text{CARB} = \text{ULT}(2)/100*\text{FACT}$$

$$\text{H}_2 = \text{ULT}(3)/100*\text{FACT}$$

$$\text{N}_2 = \text{ULT}(4)/100*\text{FACT}$$

$$\text{SULF} = \text{ULT}(6)/100*\text{FACT}$$

$$\text{O}_2 = \text{ULT}(7)/100*\text{FACT}$$

C. 2 WPCB recycling plant capacity

E-waste generation annually in India = 4100 million kg (Source: Global E-waste monitor 2024)

WPCB contribution = 5% of total E-waste = 205 million kg

Delhi's contribution in India's E-waste = 9.5%

So, WCPB generated by Delhi annually = 9.5% of 205 = **19.475 million kg/year**

Proposed plant capacity = 500 kg/h = $500 \times 8000 = 40,00,000$ kg/year = **4 million kg/year**

Since the capacity of proposed plant falls within the production limit.

Thesis output



Thesis output

Journal publications

1. **B. Boro** and P. Tiwari, "Effect of metals and brominated flame retardants on thermal degradation kinetics of waste printed circuit board", **Thermochimica Acta**, I.F. = 3.5, 736, 179747, 2024.
2. **B. Boro** and P. Tiwari, "Pyrolysis of waste printed circuit board fragments: Response surface methodology optimization and effect of temperature on product characteristics", **Energy**, I.F. = 9.4, 319, 134892, 2025.
3. **B. Boro** and P. Tiwari, "Effects of pre-treatment on product characteristics and bromine behavior during pyrolysis of waste printed circuit boards for resource recovery", **Journal of Analytical and Applied Pyrolysis**, I.F. = 6.2, 193, 107375, 2026.
4. **B. Boro** and P. Tiwari, "Effect of pyrolysis and comminution on copper extraction and techno-economic assessment for resource recovery from waste printed circuit board", **Journal of Environmental Management**, I.F. = 6.4, 397, 128365, 2026.

Conference Proceeding

1. **B. Boro** and P. Tiwari, "Material recovery from Waste printed circuit board using pyrolysis and metal extraction", 11, Sustainable Environment, Springer, 978-981-19-8463-1, 2023.



Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Effect of metals and brominated flame retardants on thermal degradation kinetics of waste printed circuit board

Bibari Boro, Pankaj Tiwari*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, India

ARTICLE INFO

Keywords:
Brominated flame retardants
Isoconventional principle
Kinetic triplets
Reconstruction
Waste printed circuit board

ABSTRACT

Waste printed circuit board (WPCB) is an indispensable component in any waste electrical and electronic equipment (WEEE). A promising method for recycling WPCB is pyrolysis. To understand the effect of metals and brominated flame retardants (BFR) on WPCB pyrolysis, four samples were prepared, namely (a) raw WPCB (RW), (b) non-metallic WPCB (NM), (c) bromine extracted WPCB (RW_{BFR,ext}) and (d) bromine and metal extracted WPCB (NM_{BFR,ext}). The degradation kinetics study using the isoconventional methods: Friedman, Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), and Starink showed that the extraction of metals exhibited an increase in final degradation temperature and activation energy (E_a), and altered the reaction mechanism ($f(a)$) whereas, the reduction of BFR reduced initial degradation temperature. The identified kinetic triplets were verified using the reconstruction profiles. The parameters can be used in designing applications and developing an energy-efficient pyrolysis process.

1. Introduction

The demand for electrical and electronic equipment (EEE) is increasing due to population growth and lifestyle changes. However, due to the lack of recycling facilities and poor management, the discarded EEE ends up in landfills or being moved to developing countries that have less stringent laws [1]. In 2019, only 17.4 % of the total electronic waste (E-Waste) generated worldwide was documented and recycled. E-Waste is increasing at an alarming rate of 2 Mt per annum, and the amount is predicted to reach up to 74.7 Mt by 2030 [2]. E-Waste consists of a variety of waste electrical and electronic equipment (WEEE), which diverges from equipment as small as an electric toothbrush to as large as a washing machine. Thus, the waste stream can be inferred as a complex mixture of various components/parts of WEEE. Among all the components, the printed circuit board is commonly found in any WEEE, as it is a crucial part of any EEE. It is also the most valuable fraction in the E-Waste stream as it contains metals, including precious metals such as silver, platinum, and gold. However, depending on the time of manufacture and application, the design of a printed circuit board varies, and hence its composition [3]. Nevertheless, the material composition comprises approximately 40 % metals, 30 % organic materials, and 30 % ceramics [4]. The printed circuit board also contains toxic materials, such as heavy metals and brominated flame retardants

(BFRs) [4]. Heavy metals like lead are found majorly in the solder parts. BFRs are added to the polymer matrix of printed circuit boards to reduce fire hazards; however, it is well known that they are toxic and bio-accumulative [5]. The BFRs are added in the range of 5–20 % in the polymer matrix of a printed circuit board [6]. The presence of valuable materials (metals such as copper, tin, gold, etc.) in waste printed circuit boards (WPCB) has lured informal recyclers to perform extraction activities without proper safety and protection norms, such as open burning near residential areas and using toxic chemicals [6–8]. Barontini and Cozzani [9] have reported the release of Polybrominated dibenzo-p-dioxin (PBDD) and Polybrominated dibenzofurans (PBDF) for metal-free printed circuit board on thermal degradation in an oxygen environment. Hence, the fate of BFRs during the recycling process of WPCB is to be taken care of [10].

Various recycling methods, such as mechanical, chemical, and thermochemical, are being studied to recover targeted WPCB material [11]. The traditional methods for dealing with the WPCBs include landfilling and incineration. Since WPCB consists of heavy metals and toxic chemicals such as BFR, landfilling of WPCB raises several environmental issues. Even though incineration reduces the volume of the waste, the release of harmful gas and metals is often ignored [12,13]. The recycling methods can be grouped into mechanical, chemical and thermochemical processes. The mechanical treatment includes

* Corresponding author.

E-mail address: pankaj.tiwari@iitg.ac.in (P. Tiwari).<https://doi.org/10.1016/j.tca.2024.179747>

Received 13 December 2023; Received in revised form 12 April 2024; Accepted 13 April 2024

Available online 14 April 2024

0040-6031/© 2024 Elsevier B.V. All rights reserved.



Pyrolysis of waste printed circuit board fragments: Response surface methodology optimization and effect of temperature on product characteristics

Bibari Boro, Pankaj Tiwari *

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, 781039, India

ARTICLE INFO

Keywords:

Waste printed circuit board
Pyrolysis
Central composite design
Response surface methodology
Temperature
Resource recovery

ABSTRACT

The direct pyrolysis of waste printed circuit board (WPCB) produces metal-enriched char, while its polymer fraction converts to valuable gas and liquid fractions. However, the low amount of organic fraction produces less liquid yield. Thus, the current study is focused on optimizing the pyrolysis parameters (temperature, heating rate, and hold time) towards maximum liquid and minimum solid (char) yields using response surface methodology (RSM). The purpose of the objective functions is to completely remove the organic material and convert most of it to liquid fraction while producing metal-enriched char. The RSM study was employed using a face-centered central composite design (CCD). The responses were analyzed using the analysis of variance (ANOVA), and the quadratic model was found to be the best-fit model. The 'temperature' was found to be the most significant parameter. Hence, further experiments were conducted by varying the temperature, keeping the heating rate and hold time constant, and the obtained products were subjected to detailed characterization. The obtained liquid samples were rich in aromatics with high calorific value (~ 35 MJ/kg) and produced gases like H_2 and CH_4 . This study provides a comprehensive approach, integrating both qualitative and quantitative analyses, to optimize WPCB pyrolysis for enhanced resource recovery.

1. Introduction

The rapid evolution of technological advancement has made the world witness a substantial rise in electronic devices ranging from mobile phones and laptops to household appliances, resulting in a rise in E-Waste generation. According to the Global E-Waste Monitor 2024, 62 billion kg of E-Waste was generated in 2022, while only 22.3% of it was recycled [1]. India is the third largest producer after China and the United States, with 4100 million kg of E-Waste (2022). The lack of proper E-Waste management systems has led to the release of harmful substances into the environment, including toxic chemicals such as brominated flame retardants (BFRs) [2–4]. A key component of the E-Waste stream is the printed circuit board (4–7 wt%) commonly found in any electrical and electronic equipment [5]. Waste printed circuit board (WPCB) is a complex mixture of materials consisting of polymers (~ 30 wt%), metals (~ 30 wt%) and ceramics (~ 40 wt%) and the compositions vary by its type and application [6–8]. The presence of valuable metals makes WPCB a suitable candidate for urban mining. According to Gao et al. [9], the polymer fraction is reinforced with the

non-metallic fraction which makes it challenging to separate these fractions. Recycling techniques such as magnetic and electrostatic separations, pyrometallurgical and hydrometallurgical approaches target the recovery of metals. These technologies neglect to account for the inclusion of polymers and potentially dangerous compounds [10–12]. After the metal extraction, the remaining non-metallic fraction is often ignored because of its lower market value [13]. Pyrolysis has demonstrated potential in recovering metals while transforming the organic part into valuable liquid and gas fractions [5,9,14,15]. The quantity of metals can be concentrated in char by performing direct pyrolysis of WPCB, i.e. without prior removal of the metals. The direct pyrolysis of WPCB produces a valuable liquid fraction; nonetheless, the high proportion of inorganic fraction (70%) consisting of metal and ceramic fractions result in a lower liquid yield. Establishing the controlling parameters to provide the highest possible liquid yield is, therefore, essential.

RSM is a trusted tool for identifying the significant and optimum parameters of a system [16]. A limited number of RSM studies on different aspects of thermal degradation behavior of circuit board have

* Corresponding author.

E-mail address: pankaj.tiwari@iitg.ac.in (P. Tiwari).

<https://doi.org/10.1016/j.energy.2025.134892>

Received 21 August 2024; Received in revised form 11 December 2024; Accepted 5 February 2025

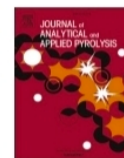
Available online 11 February 2025

0360-5442/© 2025 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.



Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Effects of pre-treatment on product characteristics and bromine behavior during pyrolysis of waste printed circuit boards for resource recovery

Bibari Boro, Pankaj Tiwari^{*}

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, India

ARTICLE INFO

Keywords:

Brominated flame retardant

Pyrolysis

Metals

Waste printed circuit board

Acid leaching

Soxhlet extraction

ABSTRACT

Pyrolysis presents a viable route for resource recovery from waste printed circuit boards (WPCBs); however, the presence of brominated flame retardants (BFRs) pose challenges due to their toxicity and potential to contaminate recovered products. This study investigates the influence of pre-treatment methods—acid leaching and Soxhlet extraction on the pyrolysis behavior of WPCBs. Four feedstocks were evaluated: raw WPCB (RW), nonmetallic fraction post-acid leaching (NM), and their Soxhlet-treated counterparts (RW-sox, NM-sox). Pyrolysis was conducted at 500 °C, with a 30 °C/min heating rate and a 156 min hold time. FTIR and ¹H NMR analyses confirmed the aromatic nature of pyrolytic oil, while GC-SimDist indicated a predominance of light hydrocarbons (C₇-C₁₁) across all feedstocks. GC-MS analysis revealed that metallic constituents in RW and RW-sox suppressed phenol formation and elevated p-cumenol concentration. However, Soxhlet extraction had minimal effect on oil composition. Gas chromatography (GC-TCD/FID) showed major gaseous products to be H₂, CO, CO₂, and minor light hydrocarbons (C₁-C₅), with higher H₂ and CO yields associated with metal-containing feedstocks. Bomb calorimeter-ion chromatography analysis indicated that acid leaching promoted bromine volatilization, increasing Br transfer to the liquid and gas phases while reducing its retention in char. These findings highlight the potential of pre-treatment strategies to optimize pyrolysis for higher resource recovery while mitigating environmental impact from brominated compounds.

1. Introduction

The digital transformation and frequent upgradation of electronic items, combined with limited recycling infrastructure, have contributed to the rise in generation of E-waste globally (62 billion kg in 2022). Although the recycling rate has increased in recent years (since 2010), but the generation rate continues to outpace it by a factor of five [1]. E-waste comprises a diverse array of components, such as mobile phones, laptops, refrigerators, and other electronic items, each varying in size, material composition, and associated toxic constituents. Among these, waste printed circuit boards (WPCBs) are regarded as one of the most critical and valuable components of E-waste. Typically, WPCBs consist of 70 % nonmetallic fraction (polymers and ceramics) and 30 % metals. Considering the higher market value of metals, these are often targeted for recovery, but are embedded within the polymer matrix; thus, specific pre-treatment methods (chemical or thermal) are often employed to enable efficient recovery [2,3]. For instance, Panda et al. [2] used dimethylformamide (DMF) to dissolve brominated epoxy resin, followed by roasting for copper recovery. Similarly, Kumari et al. [4]

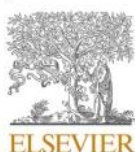
demonstrated the use of supercritical methanol for organic matrix degradation, achieving up to 98 % Cu recovery using glycine. Thermal degradation techniques, including roasting, have been explored to enhance metal liberation and its recovery from WPCBs [5]. However, direct pyrolysis of WPCB offers dual advantage: it not only delaminates and converts the polymer fraction into value-added liquid and gaseous products, but also facilitates recovery of metals and glass fibers from the char [6]. Hence, pyrolysis has emerged as a promising and sustainable technology for material recovery from WPCBs [7]. A major challenge in WPCB pyrolysis is the formation of brominated compounds in the volatile (oil and gas) phase due to the brominated flame retardants (BFRs), primarily present in the epoxy resin. Moreover, the presence of organo-brominated compounds in the oil makes it unsuitable for the application. Understanding the distribution of Br during the pyrolysis is crucial as it enables optimization of experimental conditions to obtain the desired product. The current study is focused on producing an oil fraction with minimal Br quantity. The Br content can be reduced in the feed material (before pyrolysis) or deviate (during pyrolysis) its distribution into other phases by use of additives/catalyst. Pre-treatment

^{*} Corresponding author.E-mail address: pankaj.tiwari@iitg.ac.in (P. Tiwari).<https://doi.org/10.1016/j.jaap.2025.107375>

Received 23 May 2025; Received in revised form 3 August 2025; Accepted 6 September 2025

Available online 8 September 2025

0165-2370/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.



Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Effect of pyrolysis and comminution on copper extraction and techno-economic assessment for resource recovery from waste printed circuit board

Bibari Boro, Pankaj Tiwari^{*}

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, 781039, India

ARTICLE INFO

Keywords:

Waste printed circuit board
Resource recovery
Pyrolysis
Metal extraction
Aspen Plus®
Techno-economic

ABSTRACT

Waste printed circuit boards (WPCBs) are resourceful waste materials that comprises of a combination of organic and inorganic materials. Material recovery from WPCB is necessary for both environmental and economic reasons. The current study investigated the effect of comminution and/or pyrolysis on the leaching efficiency of copper using WPCB of two sizes: S1 ($1 \times 1 \text{ cm}^2$) and S2 ($<100 \mu\text{m}$), and their pyrolyzed versions, S3 and S4. The grinding and pyrolysis of WPCB before leaching increased the efficiency. The S3 sample exhibited the highest recovery efficiency, and copper was subsequently recovered in solid phase through zinc cementation, achieving a purity of 97.4 %. Based on the performance of sample S3, an Aspen Plus® simulation was conducted for a plant integrating comminution, pyrolysis, and metal extraction, designed for a feed capacity of 500 kg/h and an operational lifetime of 20 years. Economic evaluation parameters were determined using discounted cash flow analysis, and the minimum selling price (MSP) of oil was calculated for four different scenarios. A net present value of \$2.87 M, payback period of 5.4 years, internal rate of return of 29 % and profitability index of 2.25 was obtained. Overall, this study demonstrates an integrated approach for WPCB valorization through pyrolysis and copper recovery.

1. Introduction

The rise in consumption of electrical and electronic equipment (EEE), along with frequent model upgrades and a preference for replacement over repair, has contributed to the increase in E-waste. In 2022, 62 billion kg of E-waste was generated globally, which is equivalent to an average of 7.8 kg per capita (Baldé et al., 2024). Out of this, 31 billion kg is contributed by metals and its worth is about \$91 billion. Various types of metal can be found in E-waste, such as base metals, heavy metals and precious metals. Among these, copper (Cu) holds the highest wealth contribution of \$19 billion (Fig. 1). The sources of copper in E-waste are mainly electrical wires and waste printed circuit boards (WPCBs). WPCB is an important component of any EEE, consisting of a wide range of metals along with the non-metallic constituents. The copper concentration can be as high as 30 % depending on its type (He et al., 2022; Udayakumar et al., 2022). Moreover, WPCBs contain approximately 13–26 times more copper and 100 times more gold (Au) compared to the primary mining resources (Tanisali et al., 2021; Rao and Singh, 2024). Therefore, WPCB is a secondary source of metals and a

suitable candidate for urban mining. Toxic components such as brominated flame retardants (BFRs) and heavy metals are also found in WPCBs. Thus, discarding WPCBs in landfills will lead to material loss and raise environmental concerns.

A multi-layer WPCB comprises a substrate of glass fiber reinforced with epoxy resin that provides mechanical support, copper layers that enable electrical conductivity of electronic components (ECs), and a solder mask present on both sides, which serves as protection against environmental damage (Fig. S1). Copper, or other metals in the WPCBs, can be recovered via pyrometallurgical, hydrometallurgical and bio-metallurgical approaches. Due to the release of toxic gases, the pyrometallurgical method is not an environmentally friendly process, and the infrastructure cost is also high; the bio-metallurgical approach is environmentally friendly, but time-consuming and has less potential for commercialization (Rao and Singh, 2024; Smith and Behdad, 2025). The hydrometallurgical approach provides higher selectivity of metals and has a lesser economic burden (Sudarsan et al., 2025). The leaching of copper depends on various parameters such as the type and concentration of the leaching agent, time, temperature, mixing rate, and so on,

^{*} Corresponding author.

E-mail address: pankaj.tiwari@iitg.ac.in (P. Tiwari).

<https://doi.org/10.1016/j.jenvman.2025.128365>

Received 18 September 2025; Received in revised form 6 December 2025; Accepted 15 December 2025

Available online 23 December 2025

0301-4797/© 2025 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

Conferences

1. **B. Boro** and P. Tiwari, "Investigation on pyrolysis of waste printed circuit board: kinetic analysis, product characterization and economic analysis", **JTACC**, Budapest, Hungary, 24th– 27th June 2025.
2. **B. Boro** and P. Tiwari, "Effect of copper on kinetic parameters and pyrolysis product characterization of waste printed circuit board", **PYROASIA**, IIT Guwahati, 28th– 29th November 2024.
3. **B. Boro** and P. Tiwari, "Pyrolysis of waste printed circuit board: kinetic analysis and detail product characterization", **ICTAC**, IIT Madras, 2nd– 7th September 2024.
4. **B. Boro** and P. Tiwari, "Effect of pyrolysis on copper extraction from waste printed circuit board fragments", **RIC**, IIT Guwahati, 9th– 11th August 2024.
5. **B. Boro** and P. Tiwari, "Removal of brominated flame retardants from Waste Printed circuit board using organic solvent prior to pyrolysis", **ChemEEE**, IIPE Visakhapatnam, Andhra Pradesh, India, 19th– 21st February 2024.
6. **B. Boro** and P. Tiwari, "Parameter optimization and product characterization for the pyrolysis of waste printed circuit board", **PYROASIA**, Kuala Lumpur, Malaysia, 26th – 28th June 2023.
7. **B. Boro** and P. Tiwari, "Effect of Metals and Brominated Flame Retardants on Thermal degradation Kinetics of Waste Printed Circuit Board", **RIC**, IIT Guwahati, 14th -16th May 2023.
8. **B. Boro** and P. Tiwari, "Thermal degradation kinetic studies of waste computer printed circuit board", **CHEMCON**, HBTU, Kanpur, India, 27th– 30th December 2022.
9. **B. Boro** and P. Tiwari, "Material recovery from waste printed circuit board using pyrolysis and metal extraction", **NERC**, IIT Guwahati, India, 20th– 22nd May 2022.

-
10. **B. Boro** and P. Tiwari, "Understanding E-Waste: challenges and opportunities", **RIC**, IIT Guwahati, India, 20th – 23rd January 2022.

Awards and Grants

1. Received **International Travel Support** (ITS), from ANRF, Govt. of India, ITS/2025/001444 to attend the 4th JTAC conference, Budapest, Hungary, 2025.
2. Awarded the **Best Oral Presentation** in PYROASIA, held on November 28th – 29th, 2024 at IIT Guwahati.
3. G. Dubey, B. Boro, P. Tiwari, and P. Vairakannu “Development of lab-scale clean coal conversion technology to convert Indian non-coking coal directly to liquid fuel”, grant amount of Rs 2.5 lakhs, **NewGen IEDC**, 2022.
4. B. Baruah, B. Boro, and P. Tiwari “Development of a lab-scale catalytic pyrolysis unit for in-situ upgradation and selectivity of pyrolytic oil”, grant amount of INR 2.5 lakhs, **NewGen IEDC**, 2020.

References



References

- [1] Liu, K., Tan, Q., Yu, J., Wang, M., 2023. A global perspective on e-waste recycling, Circular Economy, 2, 100028.
- [2] Sudarsan, S., Anandkumar, M., Trofimov, E. A., 2025. Survey of diverse hydrometallurgy techniques for recovering and extracting valuable metals from PCB waste: an overview, International Journal of Environmental Science and Technology, 22, 1263-1282.
- [3] Step Initiative, One Global Definition of E-waste, 2014. Solving the E-Waste Problem (Step) White Paper. Link: https://www.step-initiative.org/files/_documents/whitepapers/StEP_WP_One%20Global%20Definition%20of%20E-waste_20140603_amended.pdf (Accessed 9/10/2025).
- [4] Forti, V., Baldé, C. P., Kuehr, R., Bel, G., 2020. The Global E-waste Monitor 2020: Quantities, flows and the circular economy potential, United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Rotterdam.
- [5] Ministry of Environment, Forest and Climate Change, E-Waste (Management) Amendment Rules, 2023, Link: <https://cpcb.nic.in/uploads/Projects/E-Waste/E-waste-Second-Amendment-Rules-2023.pdf> (Accessed 25/10/2025).
- [6] Ministry of Environment, Forest and Climate Change, E-Waste (Management) Rules, 2022, Link: <https://www.mppcb.mp.gov.in/proc/E-Waste-Management-Rules-2022-English.pdf> (Accessed 23/12/2025).
- [7] Official Journal of the European Union, DIRECTIVE 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 4 July 2012 on waste electrical and electronic equipment (WEEE) (recast), 2012. Link: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32012L0019> (Accessed 29/10/2025).
- [8] Baldé, C. P., Kuehr, R., Yamamoto, T., McDonald, R., D'Angelo, E., Althaf, S., Bel, G., Deubzer, O., Fernandez-Cubillo, E., Forti, V., Gray, V., Herat, S., Honda, S., Iattoni, G., Khetriwal, D. S., Cortemiglia, V. L. d., Lobuntsova, Y., Nnorom, I., Pralat, N., Wagner, M., 2024. The Global E-Waste Monitor 2024, International Telecommunication Union (ITU) and United Nations Institute for Training and Research (UNITAR), Geneva/Bonn.
-

-
- [9] DIRECTIVE 2011/65/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, 2011. Link: <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:174:0088:0110:en:PDF> (Accessed 23/12/2025).
- [10] Baldé, C. P., Forti V., Gray, V., Kuehr, R., Stegmann, P., 2017. The Global E-waste Monitor 2017: Quantities, Flows, and Resources, United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna.
- [11] Mor, R. S., Sangwan, K. S., Singh, S., Singh, A., Kharub, M., 2021. E-waste Management for Environmental Sustainability: an Exploratory Study, *Procedia CIRP*, 98, 193-198.
- [12] Patil, R. A., Ramakrishna, S., 2020. A comprehensive analysis of e-waste legislation worldwide, *Environmental Science and Pollution Research*, 27, 14412-14431.
- [13] Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, Link: <https://www.basel.int/theconvention/overview/tabid/1271/default.aspx> (Accessed 28/10/2025).
- [14] Rautela, R., Arya, S., Vishwakarma, S., Lee, J., Kim, K.-H., Kumar, S., 2021. E-waste management and its effects on the environment and human health, *Science of The Total Environment*, 773, 145623.
- [15] Guo, J., Luo, X., Tan, S., Ogunseitan, O. A., Xu, Z., 2020. Thermal degradation and pollutant emission from waste printed circuit boards mounted with electronic components, *Journal of Hazardous Materials*, 382, 121038.
- [16] Gangwar, C., Choudhari, R., Chauhan, A., Kumar, A., Singh, A., Tripathi, A., 2019. Assessment of air pollution caused by illegal e-waste burning to evaluate the human health risk, *Environment International*, 125, 191-199.
- [17] Wong, C. S. C., Wu, S. C., Duzgoren-Aydin, N. S., Aydin, A., Wong, M. H., 2007. Trace metal contamination of sediments in an e-waste processing village in China, *Environmental Pollution*, 145, 434-442.
-

-
- [18] E-waste generation in India, 2025. Link: <https://www.meity.gov.in/static/uploads/2024/02/7ab.pdf#page=4.41> (Accessed 25/10/2025).
- [19] Ministry of Environment, Forest and Climate Change, Annual report 2023-2024, 2025. Link: <https://moef.gov.in/uploads/2023/05/Annual-Report-English-2023-24.pdf#page=59.47> (Accessed 25/10/2025).
- [20] Central Pollution Control Board, Annual report 2022-23, 2025. Link: <https://cpcb.nic.in/openpdffile.php?id=UmVwb3J0RmlsZXMTY2OV8xNzI3NDE0NTc1X21lZGhlhcGhvdG8yOTAYNy5wZGY=> (Accessed 25/10/2025).
- [21] Sengupta, D., Ilankoon, I. M. S. K., Kang, K. D., Chong, M. N., 2023. Circular economy and household e-waste management in India. Part II: A case study on informal e-waste collectors (Kabadiwalas) in India, *Minerals Engineering*, 200, 108154.
- [22] Dutta, D., Goel, S., 2021. Understanding the gap between formal and informal e-waste recycling facilities in India, *Waste Management*, 125, 163-171.
- [23] Zeng, X., Huo, X., Xu, X., Liu, D., Wu, W., 2020. E-waste lead exposure and children's health in China, *Science of The Total Environment*, 734, 139286.
- [24] Jain, M., Kumar, D., Chaudhary, J., Kumar, S., Sharma, S., Singh Verma, A., 2023. Review on E-waste management and its impact on the environment and society, *Waste Management Bulletin*, 1, 34-44.
- [25] Uchida, N., Matsukami, H., Someya, M., Tue, N. M., Tuyen, L. H., Viet, P. H., Takahashi, S., Tanabe, S., Suzuki, G., 2018. Hazardous metals emissions from e-waste-processing sites in a village in northern Vietnam, *Emerging Contaminants*, 4, 11-21.
- [26] Zhu, Y., Li, B., Wei, Y., Zhou, S., Wang, H., 2023. Recycling potential of waste printed circuit boards using pyrolysis: Status quo and perspectives, *Process Safety and Environmental Protection*, 173, 437-451.
- [27] 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.
-

- [28] Feng, F., Wang, W., Peng, Y., Liu, H., Zhang, J., Zhang, M., Wang, W., Ma, J., 2025. Innovative development of green nitrogen-phosphorus-based flame retardant for enhancing fire safety of cotton fabrics, *Polymer Degradation and Stability*, 231, 111089.
- [29] Özer, M. S., Gaan, S., 2022. Recent developments in phosphorus based flame retardant coatings for textiles: Synthesis, applications and performance, *Progress in Organic Coatings*, 171, 107027.
- [30] Kaya, M., 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes, *Waste Management*, 57, 64-90.
- [31] Okeke, E. S., Emmanuel, S. S., Ezeorba, T. P. C., Enochoghene, A. E., Okeke, V. C., Eze, C. T., Feng, W., Mao, G., Chen, Y., Wu, X., 2026. Tetrabromobisphenol A (TBBPA) in e-waste and e-waste recycling/dismantling sites: Endocrine disruption, ecotoxicological and human health risks, remediation strategies, and policy recommendations, *Journal of Environmental Chemical Engineering*, 14, 120797.
- [32] Petrlik, J., Bell, L., DiGangi, J., Lucero, A., Kuepouo, G., Ochieng Ochola, G., Jelinek, N., Jopkova, M., Pulkrabova, J., Gramblicka, T., Skalsky, M., Ismawati, Y., Akortia, E., Adu-Kumi, S., Saetang, P., Boontongmai, T., Carcamo, M., Beeler, B., Behnisch, P., Herold, C., Walaska, H., Weber, R., 2025. Review of brominated flame retardants and polybrominated dibenzo-p-dioxins and dibenzofurans in eggs and contamination sources, *Emerging Contaminants*, 11, 100567.
- [33] Tsydenova, O., Bengtsson, M., 2011. Chemical hazards associated with treatment of waste electrical and electronic equipment, *Waste Management*, 31, 45-58.
- [34] Boro, B., Tiwari, P., 2026. Effect of pyrolysis and comminution on copper extraction and techno-economic assessment for resource recovery from waste printed circuit board, *Journal of Environmental Management*, 397, 128365.
- [35] Wang, H., Zhang, S., Li, B., Pan, D. a., Wu, Y., Zuo, T., 2017. Recovery of waste printed circuit boards through pyrometallurgical processing: A review, *Resources, Conservation and Recycling*, 126, 209-218.

-
- [36] Park, S., Kim, S., Han, Y., Park, J., 2015. Apparatus for electronic component disassembly from printed circuit board assembly in e-wastes, *International Journal of Mineral Processing*, 144, 11-15.
- [37] Tanısalı, E., Özer, M., Burat, F., 2021. Precious Metals Recovery from Waste Printed Circuit Boards by Gravity Separation and Leaching, *Mineral Processing and Extractive Metallurgy Review*, 42, 24-37.
- [38] Hsu, E., Barmak, K., West, A. C., Park, A.-H. A., 2019. Advancements in the treatment and processing of electronic waste with sustainability: a review of metal extraction and recovery technologies, *Green Chemistry*, 21, 919-936.
- [39] Rao, M. D., Singh, K. K., Morrison, C. A., Love, J. B., 2020. Challenges and opportunities in the recovery of gold from electronic waste, *RSC Advances*, 10, 4300-4309.
- [40] Wang, Z., Zhang, Y., Feng, P., Meng, L., Wang, J., Guo, Z., Gong, Z., 2024. Selective separation of metals from waste printed circuit boards using supergravity-assisted liquation technology, *Journal of Environmental Chemical Engineering*, 12, 111801.
- [41] Abbadi, A., Rácz, Á., Bokányi, L., 2024. Exploring the comminution process of waste printed circuit boards in recycling: a review, *Journal of Material Cycles and Waste Management*, 26, 1326-1348.
- [42] Chen, T.-L., Chen, Y.-S., Chiang, P.-C., Chen, Y.-H., Hsu, C.-H., 2024. NO_x removal and copper recovery from the leaching process for waste printed circuit boards: performance evaluation and potential environmental impact assessment, *Environmental Science and Pollution Research*, 31, 9935-9947.
- [43] Dhanunjaya Rao, M., Shahin, C., Jha, R., 2021. Optimization of leaching of copper to enhance the recovery of gold from liberated metallic layers of WPCBs, *Materials Today: Proceedings*, 46, 1515-1518.
- [44] Birloaga, I., Coman, V., Kopacek, B., Vegliò, F., 2014. An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals, *Waste Management*, 34, 2581-2586.
-

-
- [45] Priyan, M. V., Annadurai, R., Onyelowe, K. C., Alaneme, G. U., Giri, N. C., 2023. Recycling and sustainable applications of waste printed circuit board in concrete application and validation using response surface methodology, *Scientific Reports*, 13, 16509.
- [46] Oke, E. A., Potgieter, J. H., 2025. Sustainable leaching of metals from waste printed circuit boards using efficient carboxylic acid-based deep eutectic solvents, *Separation and Purification Technology*, 374, 133712.
- [47] Jadhao, P. R., Pandey, A., Pant, K. K., Nigam, K. D. P., 2021. Efficient recovery of Cu and Ni from WPCB via alkali leaching approach, *Journal of Environmental Management*, 296, 113154.
- [48] Nan, T., Yang, J., Aromaa-Stubb, R., Zhu, Q., Lundström, M., 2024. Process simulation and life cycle assessment of hydrometallurgical recycling routes of waste printed circuit boards, *Journal of Cleaner Production*, 435, 140458.
- [49] Verbrugge, B., Lanzano, C., Libassi, M., 2021. The cyanide revolution: Efficiency gains and exclusion in artisanal- and small-scale gold mining, *Geoforum*, 126, 267-276.
- [50] Breuer, P. L., Dai, X., Jeffrey, M. I., 2005. Leaching of gold and copper minerals in cyanide deficient copper solutions, *Hydrometallurgy*, 78, 156-165.
- [51] Li, H., Oraby, E., Eksteen, J., 2021. Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards, *Waste Management*, 125, 87-97.
- [52] Ding, Y., Zhang, S., Liu, B., Zheng, H., Chang, C.-c., Ekberg, C., 2019. Recovery of precious metals from electronic waste and spent catalysts: A review, *Resources, Conservation and Recycling*, 141, 284-298.
- [53] Islam, A., Ahmed, T., Awual, M. R., Rahman, A., Sultana, M., Aziz, A. A., Monir, M. U., Teo, S. H., Hasan, M., 2020. Advances in sustainable approaches to recover metals from e-waste-A review, *Journal of Cleaner Production*, 244, 118815.
- [54] Sahin, M., Akcil, A., Erust, C., Altynbek, S., Gahan, C. S., Tuncuk, A., 2015. A Potential Alternative for Precious Metal Recovery from E-waste: Iodine Leaching, *Separation Science and Technology*, 50, 2587-2595.
-

- [55] Jing-ying, L., Xiu-li, X., Wen-quan, L., 2012. Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones, *Waste Management*, 32, 1209-1212.
- [56] Gamiño-Arroyo, Z., Pareau, D., Buch, A., Gomez-Castro, F. I., Sánchez-Cadena, L. E., Stambouli, M., Bekri, J. E., Avila-Rodriguez, M., 2021. Design of Multistage Extraction System for Simultaneous Separation of Silver and Gold from Thiourea Solutions, *Chemical Engineering and Processing - Process Intensification*, 164, 108391.
- [57] Nie, C.-c., Li, X.-g., Sun, Q.-y., Gao, Q., Zhu, X.-n., Lyu, X.-j., Li, L., You, X.-f., 2024. Clean and efficient process for the recycling of all components from waste printed circuit boards: Pre-treatment, bio-metallurgy, and deep utilization, *Journal of Cleaner Production*, 466, 142810.
- [58] Abbruzzese, C., Fornari, P., Massidda, R., Vegliò, F., Ubaldini, S., 1995. Thiosulphate leaching for gold hydrometallurgy, *Hydrometallurgy*, 39, 265-276.
- [59] Ha, V. H., Lee, J.-c., Huynh, T. H., Jeong, J., Pandey, B. D., 2014. Optimizing the thiosulfate leaching of gold from printed circuit boards of discarded mobile phone, *Hydrometallurgy*, 149, 118-126.
- [60] Merrill-Crowe process, Link: https://taylorandfrancis.com/knowledge/Engineering_and_technology/Chemical_engineering/Merrill-Crowe_process/#:~:text=Since%20the%201890s%2C%20Merrill%2DCrowe,the%20further%20reaction%20%5B11%5D (Accessed 23/12/2025).
- [61] Konaté, F. O., Vitry, V., Yonli, A. H., 2024. Leaching of base metals in PCBs and copper cementation by iron powder, *Journal of Hazardous Materials Advances*, 15, 100449.
- [62] Nie, Y., Wang, S., Wang, Q., Chen, J., Jiang, Y., 2023. Applying an external reduction potential to reduce the consumption of zinc powder during gold cementation, *Minerals Engineering*, 191, 107981.
- [63] Park, Y. J., Fray, D. J., 2009. Recovery of high purity precious metals from printed circuit boards, *Journal of Hazardous Materials*, 164, 1152-1158.

-
- [64] Jha, M. K., Gupta, D., Lee, J.-c., Kumar, V., Jeong, J., 2014. Solvent extraction of platinum using amine based extractants in different solutions: A review, *Hydrometallurgy*, 142, 60-69.
- [65] Liu, Z., Guo, X., Xu, Z., Tian, Q., 2024. Recent advancements in aqueous electrowinning for metal recovery: A comprehensive review, *Minerals Engineering*, 216, 108897.
- [66] Zhao, Q., Ma, S., Ho, W., Wang, Y., Ho, J. Y. T., Shih, K., 2023. Simple and environmentally friendly metal recovery from waste printed circuit boards by using deep eutectic solvents, *Journal of Cleaner Production*, 421, 138508.
- [67] Qi, Y., Yi, X., Zhang, Y., Meng, F., Shu, J., Xiu, F., Sun, Z., Sun, S., Chen, M., 2019. Effect of ionic liquid [MIm]HSO₄ on WPCB metal-enriched scraps refined by slurry electrolysis, *Environmental Science and Pollution Research*, 26, 33260-33268.
- [68] Fazari, J., Hossain, M. Z., Charpentier, P., 2024. A review on metal extraction from waste printed circuit boards (wPCBs), *Journal of Materials Science*, 59, 12257-12284.
- [69] Rahimi, V., Inzulza-Moraga, E. A., Gómez-Díaz, D., Freire, M. S., González-Álvarez, J., 2024. Screening of variables affecting the selective leaching of valuable metals from waste motherboards' PCBs, *Environmental Science and Pollution Research*, .
- [70] Birloaga, I., De Michelis, I., Ferella, F., Buzatu, M., Vegliò, F., 2013. Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery, *Waste Management*, 33, 935-941.
- [71] Pietrantonio, M., Pucciarmati, S., Forte, F., De Angelis, D., Fontana, D., 2025. Recovery of metallic gold, silver and copper from end-of-life mobile phones by hydrometallurgy, *Journal of Material Cycles and Waste Management*, 27, 2395-2403.
- [72] He, J., Zhang, M., Chen, H., Guo, S., Zhu, L., Xu, J., Zhou, K., 2022. Enhancement of leaching copper by organic agents from waste printed circuit boards in a sulfuric acid solution, *Chemosphere*, 307, 135924.
- [73] Cui, H., Anderson, C. G., 2016. Literature Review of Hydrometallurgical Recycling of Printed Circuit Boards (PCBs), *Journal of Advance Chemical Engineering*, 6.
-

-
- [74] Wang, Y., Xu, J., Liu, G., 2023. Characteristics and health risk assessment of heavy metals in dust of a waste printed circuit board recycling workshop, China, *RSC Advances*, 13, 22216-22225.
- [75] Jadhav, U., Su, C., Hocheng, H., 2016. Leaching of metals from large pieces of printed circuit boards using citric acid and hydrogen peroxide, *Environmental Science and Pollution Research*, 23, 24384-24392.
- [76] Kurniawan, K., Lee, J.-c., Bae, M., Lee, H., Kim, H., Kim, S., 2024. Highly efficient and eco-friendly process for selective recovery of copper from waste printed circuit boards via pyrolysis and ammoniacal solvleaching, *Journal of Cleaner Production*, 470, 143229.
- [77] Lv, X., Wu, Q., Huang, X., Wu, L. l., Hu, L., Fei, P., Liu, T. m., Yu, Q., 2023. Effect of Microwave Pretreatment on the Leaching and Enrichment Effect of Copper in Waste Printed Circuit Boards, *ACS Omega*, 8, 2575-2585.
- [78] Huang, Y.-F., Pan, M.-W., Lo, S.-L., 2020. Hydrometallurgical metal recovery from waste printed circuit boards pretreated by microwave pyrolysis, *Resources, Conservation and Recycling*, 163, 105090.
- [79] Rao, M. D., Singh, K. K., 2024. Sequential recovery of copper, nickel, gold, silver and zinc from WPCBs of obsolete mobile phones through hydrometallurgical recycling, *Materials Today: Proceedings*, 112, 83-90.
- [80] Jadhav, U., Hocheng, H., 2015. Hydrometallurgical Recovery of Metals from Large Printed Circuit Board Pieces, *Scientific Reports*, 5, 14574.
- [81] Esyra Hani Ku Ishak, K., Ismail, S., Irfan Bin Abd Razak, M., 2022. Recovery of copper and valuable metals from E-waste via hydrometallurgical method, *Materials Today: Proceedings*, 66, 3077-3081.
- [82] Moosakazemi, F., Ghassa, S., Mohammadi, M. R. T., 2019. Environmentally friendly hydrometallurgical recovery of tin and lead from waste printed circuit boards: Thermodynamic and kinetics studies, *Journal of Cleaner Production*, 228, 185-196.
- [83] Sohrab Hossain, M., Naim Ahmad Yahaya, A., Suhaila Yacob, L., Zulkhairi Abdul Rahim, M., Nadiyah Mohamad Yusof, N., Thomas Bachmann, R., 2018. Selective recovery of Copper
-

from waste mobile phone printed circuit boards using Sulphuric acid leaching, *Materials Today: Proceedings*, 5, 21698-21702.

[84] 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.

[85] Dino da Silva, A. K., de Souza, A. F., Rodríguez, D. M., da Silva Ferreira, I. N., Oliveira Protetor, C. J., Mendes Moraes, C. A., de Campos-Takaki, G. M., da Silva Andrade, R. F., 2025. Bioleaching of copper from waste printed circuit boards by *Aspergillus tubingensis* UCP 1208: a sustainable alternative, *Environmental Technology*, 1-12.

[86] Tan, G., Xie, Z., Zhang, S., 2025. Insight into the mechanism for bioleaching copper from waste printed circuit boards with pyrite as the microbial substrate, *Journal of Environmental Chemical Engineering*, 13, 120129.

[87] Deng, S., Wang, Y., Yang, W., Long, T., Yang, C., Ju, J., Bian, Q., Yan, C., 2026. Improved bioleaching of copper from waste printed circuit boards by magnetite addition, *Separation and Purification Technology*, 382, 135716.

[88] Jaiswal, M., Srivastava, S., 2024. A review on sustainable approach of bioleaching of precious metals from electronic wastes, *Journal of Hazardous Materials Advances*, 14, 100435.

[89] Al-Rumaihi, A., Shahbaz, M., McKay, G., Mackey, H., Al-Ansari, T., 2022. A review of pyrolysis technologies and feedstock: A blending approach for plastic and biomass towards optimum biochar yield, *Renewable and Sustainable Energy Reviews*, 167, 112715.

[90] Mong, G. R., Chong, C. T., Chong, W. W. F., Ng, J.-H., Ong, H. C., Ashokkumar, V., Tran, M.-V., Karmakar, S., Goh, B. H. H., Mohd Yasin, M. F., 2022. Progress and challenges in sustainable pyrolysis technology: Reactors, feedstocks and products, *Fuel*, 324, 124777.

[91] Zhu, Y., Li, B., Wei, Y., Zhou, S., Wang, H., 2023. Pyrolysis of waste printed circuit boards: Parametric effects on product distribution, characterization and gas emissions, *Process Safety and Environmental Protection*, 178, 1083-1093.

-
- [92] Jadhao, P. R., Panda, R., Pant, K. K., Nigam, K. D. P., 2023. Integrated Approach for Metallic Fraction Recovery and Generation of Valuable Products from Electronic Waste, *Industrial & Engineering Chemistry Research*, 62, 19372-19380.
- [93] Diaz, F., Flerus, B., Nagraj, S., Bokelmann, K., Stauber, R., Friedrich, B., 2018. Comparative Analysis About Degradation Mechanisms of Printed Circuit Boards (PCBs) in Slow and Fast Pyrolysis: The Influence of Heating Speed, *Journal of Sustainable Metallurgy*, 4, 205-221.
- [94] Cao, R., Zhou, R., Liu, Y., Ma, D., Wang, J., Guan, Y., Yao, Q., Sun, M., 2022. Research on the pyrolysis characteristics and mechanisms of waste printed circuit boards at fast and slow heating rates, *Waste Management*, 149, 134-145.
- [95] Wang, J., Xi, Z., Gao, R., Niu, B., Xu, Z., 2025. Catalysis pyrolysis debromination from waste printed circuit boards: Catalysts selection, parameter effects, products, and mechanisms, *Waste Management*, 191, 191-202.
- [96] Quintana, M. A., Garcia-Garcia, G., Blazquez, G., Martín-Lara, M. A., Calero, M., Muñoz-Batista, M. J., 2026. Pyrolysis as the gateway thermochemical route for plastic-to-hydrogen-rich gas valorization, *Journal of Analytical and Applied Pyrolysis*, 193, 107480.
- [97] Janga, K., begum, S., Anupoju, G. R., 2025. Effect of residence time and temperature on pyrolysis of Water Hyacinth Leaf Biomass (WHLB): Experiments and modelling through ML and validation by Leave One Out Cross Validation (LOOCV), *Bioresource Technology Reports*, 32, 102369.
- [98] Newalkar, G., Iisa, K., D'Amico, A. D., Sievers, C., Agrawal, P., 2014. Effect of Temperature, Pressure, and Residence Time on Pyrolysis of Pine in an Entrained Flow Reactor, *Energy & Fuels*, 28, 5144-5157.
- [99] Zhu, Y., Li, B., Wei, Y., Zhou, S., Wang, H., 2025. Research on high-temperature fast pyrolysis of waste printed circuit boards for gas release and carbon structure evolution, *Waste Management*, 193, 84-94.
- [100] Boro, B., Tiwari, P., 2024. Effect of metals and brominated flame retardants on thermal degradation kinetics of waste printed circuit board, *Thermochimica Acta*, 736, 179747.
-

- [101] Liu, W., Xu, J., Han, J., Jiao, F., Qin, W., Li, Z., 2019. Kinetic and Mechanism Studies on Pyrolysis of Printed Circuit Boards in the Absence and Presence of Copper, *ACS Sustainable Chemistry & Engineering*, 7, 1879-1889.
- [102] Gao, R., Liu, B., Zhan, L., Guo, J., Zhang, J., Xu, Z., 2021. Catalytic effect and mechanism of coexisting copper on conversion of organics during pyrolysis of waste printed circuit boards, *Journal of Hazardous Materials*, 403, 123465.
- [103] Liu, J., Jiang, Q., Wang, H., Li, J., Zhang, W., 2021. Catalytic effect and mechanism of in-situ metals on pyrolysis of FR4 printed circuit boards: Insights from kinetics and products, *Chemosphere*, 280, 130804.
- [104] Krishna, J. V. J., Prashanth, P. F., Vinu, R., 2022. Distributed Activation Energy Modeling and Py-GC/MS Studies on Pyrolysis of Different Printed Circuit Boards for Resource Recovery, *ACS Omega*, 7, 31713-31725.
- [105] Wu, D., Ding, G., Chi, W., Jiang, L., 2022. Research on the pyrolysis kinetics of resin powder on waste printed circuit board with different particle sizes at different heating rates: inspiration for the pyrolysis mechanism, *Journal of Thermal Analysis and Calorimetry*, 147, 8047-8059.
- [106] Krishna, J. V. J., Damir, S. S., Vinu, R., 2021. Pyrolysis of electronic waste and their mixtures: Kinetic and pyrolysate composition studies, *Journal of Environmental Chemical Engineering*, 9, 105382.
- [107] Jayapradha, A., AbbasMohaideen, J., Senthil Kumar, P., Kavitha, V., Narendrakumar, G., 2019. Management of printed circuit boards by newly designed thermal pyrolytic process: Process optimization by RSM approach, *Environmental Progress & Sustainable Energy*, 38, 489-499.
- [108] Liu, Y., Li, K., Guo, J., Xu, Z., 2018. Impact of the operating conditions on the derived products and the reaction mechanism in vacuum pyrolysis treatment of the organic material in waste integrated circuits, *Journal of Cleaner Production*, 197, 1488-1497.
- [109] Kurniawan, K., Kim, S., Lee, J.-c., 2023, Pyrolysis of Waste Printed Circuit Boards: Optimization Using Response Surface Methodology and Characterization of Solid Product, *TMS Annual Meeting & Exhibition*, 227-238, Springer.

- [110] Yu, M., Zhang, C., Li, X., Liu, Y., Siyal, A. A., Qu, J., Dai, J., Yuan, Y., Jin, Y., Liu, C., 2023. Products and bromine migration characteristics of non-metallic components of waste printed circuit boards pyrolysis in a fluidized bed pyrolyzer, *Fuel Processing Technology*, 250, 107898.
- [111] Zhang, J., Peng, Z., Wang, J., Yang, H., Chen, H., Zhuo, L., Liu, Q., Luo, N., Zhou, Y., Yan, Y., Yang, C., 2025. Selective separation and value-added utilization of non-metallic components from waste mobile phone circuit boards for reinforcing epoxy composites, *Chemical Engineering Journal*, 504, 159123.
- [112] Das, P., Zeng, Q., Leybros, A., Gabriel, J.-C. P., Yong Tay, C., Lee, J.-M., 2023. Enhanced extraction of brominated flame retardants from e-waste plastics, *Chemical Engineering Journal*, 469, 144126.
- [113] Gripon, L., Belyamani, I., Legros, B., Seaudeau-Pirouley, K., Lafranche, E., Cauret, L., 2021. Brominated flame retardants extraction from waste electrical and electronic equipment-derived ABS using supercritical carbon dioxide, *Waste Management*, 131, 313-322.
- [114] Auvinen, P., Nissinen, V. H., Karjalainen, E., Korpijärvi, K., Olkkonen, E., Grönlund, K., Rytöluoto, I., Kuutti, L., Suvanto, M., Jänis, J., Saarinen, J. J., 2025. Selective solvothermal extraction of tetrabromobisphenol A to promote plastic recycling, *Chemical Engineering Journal Advances*, 21, 100688.
- [115] Ali, L., A.Mousa, H., Al-Harabsheh, M., Al-Zuhair, S., Abu-Jdayil, B., Al-Marzouqi, M., Altarawneh, M., 2022. Removal of Bromine from the non-metallic fraction in printed circuit board via its Co-pyrolysis with alumina, *Waste Management*, 137, 283-293.
- [116] Zhu, Y., Li, B., Wei, Y., Zhou, S., Wang, H., 2024. Catalytic pyrolysis of waste printed circuit board with copper slag for the production of H₂-rich gas, *Fuel*, 357, 129704.
- [117] Chen, Y., Ke, Y., Liang, S., Hu, J., Hou, H., Yang, J., 2023. Enhanced bromine fixation and tar lightweighting in co-pyrolysis of non-metallic fractions of waste printed circuit boards with Bayer red mud, *Waste Management*, 162, 72-82.
- [118] Ye, Z., Yang, F., Lin, W., Li, S., Sun, S., 2018. Improvement of pyrolysis oil obtained from co-pyrolysis of WPCBs and compound additive during two stage pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 135, 415-421.

-
- [119] Chen, W., Shu, Y., Li, Y., Chen, Y., Wei, J., 2021. Co-pyrolysis of waste printed circuit boards with iron compounds for Br-fixing and material recovery, *Environmental Science and Pollution Research*, 28, 64642-64651.
- [120] Pyo, S., Kumar, A., Ali Khan, M., Jeon, B.-H., Choi, S. Q., Kim, Y.-M., Park, Y.-K., 2023. The production of debrominated aromatics via the catalytic pyrolysis of flexible printed circuit boards, *Chemical Engineering Journal*, 472, 144783.
- [121] Zhang, T., Mao, X., Qu, J., Liu, Y., Siyal, A. A., Ao, W., Fu, J., Dai, J., Jiang, Z., Deng, Z., Song, Y., Wang, D., Polina, C., 2021. Microwave-assisted catalytic pyrolysis of waste printed circuit boards, and migration and distribution of bromine, *Journal of Hazardous Materials*, 402, 123749.
- [122] Shen, Y., Yuan, R., Chen, X., Ge, X., Chen, M., 2018. Co-pyrolysis of E-Waste Nonmetallic Residues with Biowastes, *ACS Sustainable Chemistry & Engineering*, 6, 9086-9093.
- [123] Jadhao, P. R., Vuppaladadiyam, A. K., Prakash, A., Pant, K. K., 2022. Co-pyrolysis characteristics and kinetics of electronic waste and macroalgae: A synergy study based on thermogravimetric analysis, *Algal Research*, 61, 102601.
- [124] Prajapati, S. B., Gautam, A., Gautam, S., Yao, Z., Tesfaye, F., Lü, X., 2023. Co-Pyrolysis Behavior, Kinetic and Mechanism of Waste-Printed Circuit Board with Biomass, .
- [125] Yao, Z., Cai, D., Chen, X., Sun, Y., Jin, M., Qi, W., Ding, J., 2024. Thermal behavior and kinetic study on the co-pyrolysis of biomass with polymer waste, *Biomass Conversion and Biorefinery*, 14, 1651-1662.
- [126] Zhu, C., Xia, Y., Long, Y., Li, L., Xie, Y., Deng, T., Yang, K., Tsang, C.-W., Ouyang, S., 2024. Synergistic effect during co-pyrolysis of tea seed shell and waste printed circuit board: Thermogravimetric characteristics and operation parameter optimization, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 46, 15773-15790.
- [127] Shen, Y., Wu, Y., 2025. Pyrolysis valorization of waste epoxy thermosets, *Journal of Analytical and Applied Pyrolysis*, 186, 106908.
-

-
- [128] Debnath, B., Pati, S., Kayal, S., De, S., Chowdhury, R., 2024. Pyrolytic urban mining of waste printed circuit boards: an enviro-economic analysis, *Environmental Science and Pollution Research*, 31, 42931-42947.
- [129] Romano, P., Melchiorre, E., Vegliò, F., 2023. ASPEN PLUS Predictive Simulation of Printed Circuit Boards Pyrolysis and Steam Gasification for Organic Fraction Valorization, .
- [130] Ti, S., Deng, S., Yang, J., Liu, X., Zhu, Y., Yang, Z., Gao, K., Wang, H., 2025. Feasibility analysis of resource recovery from electronic waste and biomass through pyrolysis technology, *Journal of Environmental Management*, 391, 126507.
- [131] ASTM D 5142, Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures.
- [132] Boro, B., Tiwari, P., 2025. Pyrolysis of waste printed circuit board fragments: Response surface methodology optimization and effect of temperature on product characteristics, *Energy*, 319, 134892.
- [133] Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., Sbirrazzuoli, N., 2011. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Thermochimica Acta*, 520, 1-19.
- [134] Wright, M. M., Daugaard, D. E., Satrio, J. A., Brown, R. C., 2010. Techno-economic analysis of biomass fast pyrolysis to transportation fuels, *Fuel*, 89, S2-S10.
- [135] Rosha, P., Kumar, S., Ibrahim, H., 2022. Sensitivity analysis of biomass pyrolysis for renewable fuel production using Aspen Plus, *Energy*, 247, 123545.
- [136] Mari Selvam, S., Balasubramanian, P., Chintala, M., Gujjala, L. K. S., 2025. Techno-economic analysis of microwave pyrolysis of sugarcane bagasse biochar production, *Biomass Conversion and Biorefinery*, 15, 14229-14239.
- [137] Ismail, H. Y., Abbas, A., Azizi, F., Zeaiter, J., 2017. Pyrolysis of waste tires: A modeling and parameter estimation study using Aspen Plus®, *Waste Management*, 60, 482-493.
- [138] Mwanat, M. H.-M., Kasongo, K. B., Muliangala, M. F., Kayembe, M. M., Kapiamba, K. F., Ngenda, B. R., 2022. Simulation of Simultaneous Leaching of Copper and Cobalt Minerals
-

in Acid-Reductive Media: Sensitivity Analysis and Optimization, *Journal of Sustainable Metallurgy*, 8, 837-850.

[139] Yang, H., Liu, J., Yang, J., 2011. Leaching copper from shredded particles of waste printed circuit boards, *Journal of Hazardous Materials*, 187, 393-400.

[140] Tran, D. T., Tran, N. T. T., Pham, T. P. T., Yun, Y.-S., 2025. Process development and techno-economic feasibility of thiosulfate-based hydrometallurgical recycling for waste printed circuit boards, *Journal of Cleaner Production*, 520, 146094.

[141] The Times of India, How Delhi's First Eco Park Plans To Scrap Its Old Ways, Link: <https://timesofindia.indiatimes.com/city/delhi/how-delhis-first-eco-park-plans-to-scrap-its-old-ways/articleshow/123222851.cms> (Accessed 27/8/2025).

[142] Umenweke, G. C., Pace, R. B., Santillan-Jimenez, E., Okolie, J. A., 2023. Techno-economic and life-cycle analyses of sustainable aviation fuel production via integrated catalytic deoxygenation and hydrothermal gasification, *Chemical Engineering Journal*, 452, 139215.

[143] Hasan, M. M., Rasul, M. G., Jahirul, M. I., Sattar, M. A., 2024. An Aspen plus process simulation model for exploring the feasibility and profitability of pyrolysis process for plastic waste management, *Journal of Environmental Management*, 355, 120557.

[144] Natelson, R. H., Wang, W.-C., Roberts, W. L., Zering, K. D., 2015. Technoeconomic analysis of jet fuel production from hydrolysis, decarboxylation, and reforming of camelina oil, *Biomass and Bioenergy*, 75, 23-34.

[145] Chemical Engineering magazine, 2023 CEPCI annual average value decreases from previous year, Link: <https://www.chemengonline.com/2023-cepci-annual-average-value-decreases-from-previous-year/> (Accessed 12/09/2025).

[146] Alcazar-Ruiz, A., Silva, L. S., Dorado, F., 2024. Economic viability assessment of bioenergy production from agroindustrial wastes through fast pyrolysis, *Energy*, 311, 133441.

[147] Saha, S., Sau, D., Hazra, T., 2023. Economic viability analysis of recycling waste plastic as aggregates in green sustainable concrete, *Waste Management*, 169, 289-300.

- [148] Industrial electricity tariff, Industrial Power Tariff 2025 – Revised Rates & Slab Rules, Link: <https://www.swastikpowersupply.co.in/industrial-power-tariff-2025-rates/> (Accessed 25/08/2025).
- [149] Indiamart, Hydrogen Peroxide 30 Percent, Link: https://www.indiamart.com/proddetail/hydrogen-peroxide-30-percent-23067277812.html?srltid=AfmBOorVS_1wVYE84AKMm1eMnUYRv5UCcGOT3OjqDTWV9xDkcRYc1NyD (Accessed 11/08/2025).
- [150] Indiamart, Zinc powder, Link: <https://www.indiamart.com/proddetail/zinc-powder-20130236791.html> (Accessed 11/08/2025).
- [151] Ferry Chem Industries, Sulphuric Acid - Application: Industrial, Link: <https://www.tradeindia.com/products/sulphuric-acid-c5973896.html> (Accessed 12/09/2025).
- [152] Deng, S., Xiao, Z., Zhang, W., Noble, A., Das, S., Yih, Y., Sutherland, J. W., 2023. Economic analysis of precious metal recovery from electronic waste through gas-assisted microflow extraction, Resources, Conservation and Recycling, 190, 106810.
- [153] ExportersIndia.com, Alaxender E Glass Fiber, For Industrial, Grade : Recycled, Link: <https://www.exportersindia.com/product-detail/industrial-e-glass-fiber-5747187872.htm> (Accessed 12/09/2025).
- [154] ExportersIndia.com, Cooper Copper Powder, Purity : 90%, Link: <https://www.exportersindia.com/product-detail/brown-copper-powder-2693878.htm> (Accessed 16/09/2025).
- [155] Fivga, A., Dimitriou, I., 2018. Pyrolysis of plastic waste for production of heavy fuel substitute: A techno-economic assessment, Energy, 149, 865-874.
- [156] Shahbaz, M., AlNouss, A., Parthasarathy, P., Abdelaal, A. H., Mackey, H., McKay, G., Al-Ansari, T., 2022. Investigation of biomass components on the slow pyrolysis products yield using Aspen Plus for techno-economic analysis, Biomass Conversion and Biorefinery, 12, 669-681.
- [157] Yang, Y., Wang, J., Chong, K., Bridgwater, A. V., 2018. A techno-economic analysis of energy recovery from organic fraction of municipal solid waste (MSW) by an integrated

intermediate pyrolysis and combined heat and power (CHP) plant, *Energy Conversion and Management*, 174, 406-416.

[158] Evangelopoulos, P., Arato, S., Persson, H., Kantarelis, E., Yang, W., 2019. Reduction of brominated flame retardants (BFRs) in plastics from waste electrical and electronic equipment (WEEE) by solvent extraction and the influence on their thermal decomposition, *Waste Management*, 94, 165-171.

[159] Khawam, A., Flanagan, D. R., 2006. Solid-State Kinetic Models: Basics and Mathematical Fundamentals, *The Journal of Physical Chemistry B*, 110, 17315-17328.

[160] Cheng, S., Chang, F., Zhang, F., Huang, T., Yoshikawa, K., Zhang, H., 2018. Progress in thermal analysis studies on the pyrolysis process of oil sludge, *Thermochimica Acta*, 663, 125-136.

[161] Das, P., Tiwari, P., 2017. Thermal degradation kinetics of plastics and model selection, *Thermochimica Acta*, 654, 191-202.

[162] Yao, Z., Reinmöller, M., Ortuño, N., Zhou, H., Jin, M., Liu, J., Luque, R., 2023. Thermochemical conversion of waste printed circuit boards: Thermal behavior, reaction kinetics, pollutant evolution and corresponding controlling strategies, *Progress in Energy and Combustion Science*, 97, 101086.

[163] Xiu, F.-R., Li, Y., Qi, Y., Yu, X., He, J., Lu, Y., Gao, X., Deng, Y., Song, Z., 2019. A novel treatment of waste printed circuit boards by low-temperature near-critical aqueous ammonia: Debromination and preparation of nitrogen-containing fine chemicals, *Waste Management*, 84, 355-363.

[164] Singh, S., Chakraborty, J. P., Mondal, M. K., 2020. Pyrolysis of torrefied biomass: Optimization of process parameters using response surface methodology, characterization, and comparison of properties of pyrolysis oil from raw biomass, *Journal of Cleaner Production*, 272, 122517.

[165] Westerhof, R. J. M., Kuipers, N. J. M., Kersten, S. R. A., van Swaaij, W. P. M., 2007. Controlling the Water Content of Biomass Fast Pyrolysis Oil, *Industrial & Engineering Chemistry Research*, 46, 9238-9247.

- [166] Chen, W., Chen, Y., Shu, Y., He, Y., Wei, J., 2021. Characterization of solid, liquid and gaseous products from waste printed circuit board pyrolysis, *Journal of Cleaner Production*, 313, 127881.
- [167] Gao, R., Zhan, L., Guo, J., Xu, Z., 2020. Research of the thermal decomposition mechanism and pyrolysis pathways from macromonomer to small molecule of waste printed circuit board, *Journal of Hazardous Materials*, 383, 121234.
- [168] Evangelopoulos, P., Kantarelis, E., Yang, W., 2015. Investigation of the thermal decomposition of printed circuit boards (PCBs) via thermogravimetric analysis (TGA) and analytical pyrolysis (Py-GC/MS), *Journal of Analytical and Applied Pyrolysis*, 115, 337-343.
- [169] Mohammed, I. Y., Abakr, Y. A., Yusup, S., Kazi, F. K., 2017. Valorization of Napier grass via intermediate pyrolysis: Optimization using response surface methodology and pyrolysis products characterization, *Journal of Cleaner Production*, 142, 1848-1866.
- [170] Baruah, B., Tiwari, P., Thakur, P., Kataki, R., 2018. TGA-FTIR analysis of Upper Assam oil shale, optimization of lab-scale pyrolysis process parameters using RSM, *Journal of Analytical and Applied Pyrolysis*, 135, 397-405.
- [171] Baruah, B., Tiwari, P., 2022. Investigation of co-pyrolysis mechanism of oil shale and rubber seed shell, product yield and optimization of pyrolysis parameter using response surface methodology, *Fuel*, 317, 123441.
- [172] Das, S., Goud, V. V., 2021. RSM-optimised slow pyrolysis of rice husk for bio-oil production and its upgradation, *Energy*, 225, 120161.
- [173] Jadhao, P. R., Ahmad, E., Pant, K. K., Nigam, K. D. P., 2020. Environmentally friendly approach for the recovery of metallic fraction from waste printed circuit boards using pyrolysis and ultrasonication, *Waste Management*, 118, 150-160.
- [174] Nie, C.-c., Wang, Y.-y., Zhang, H., Zhang, Y.-k., Zhang, Y.-q., Yan, Z.-q., Li, B., Lyu, X.-j., Tao, Y.-j., Qiu, J., Li, L., Zhang, G.-w., Zhu, X.-n., 2020. Cleaner utilization of non-metallic components in separation tailings of waste printed circuit board: Pyrolysis oil, calorific value and building aggregate, *Journal of Cleaner Production*, 258, 120976.

- [175] Sun, J., Wang, W., Liu, Z., Ma, C., 2011. Recycling of Waste Printed Circuit Boards by Microwave-Induced Pyrolysis and Featured Mechanical Processing, *Industrial & Engineering Chemistry Research*, 50, 11763-11769.
- [176] Evangelopoulos, P., Kantarelis, E., Yang, W., 2017. Experimental investigation of the influence of reaction atmosphere on the pyrolysis of printed circuit boards, *Applied Energy*, 204, 1065-1073.
- [177] Chiang, H.-L., Lin, K.-H., 2014. Exhaust constituent emission factors of printed circuit board pyrolysis processes and its exhaust control, *Journal of Hazardous Materials*, 264, 545-551.
- [178] Yuan, X., Leng, L., Huang, H., Chen, X., Wang, H., Xiao, Z., Zhai, Y., Chen, H., Zeng, G., 2015. Speciation and environmental risk assessment of heavy metal in bio-oil from liquefaction/pyrolysis of sewage sludge, *Chemosphere*, 120, 645-652.
- [179] Pulles, T., Denier van der Gon, H., Appelman, W., Verheul, M., 2012. Emission factors for heavy metals from diesel and petrol used in European vehicles, *Atmospheric Environment*, 61, 641-651.
- [180] Liang, Q., Wang, J., Chen, S., Chen, S., Hu, L., Qin, J., Han, Y., Zeng, X., Li, X., Guo, Q., Chen, M., Shu, J., 2023. Electrolyte circulation: Metal recovery from waste printed circuit boards of mobile phones by alkaline slurry electrolysis, *Journal of Cleaner Production*, 409, 137223.
- [181] Abbas, H. F., Wan Daud, W. M. A., 2010. Hydrogen production by methane decomposition: A review, *International Journal of Hydrogen Energy*, 35, 1160-1190.
- [182] Ma, C., Kamo, T., 2018. Two-stage catalytic pyrolysis and debromination of printed circuit boards: Effect of zero-valent Fe and Ni metals, *Journal of Analytical and Applied Pyrolysis*, 134, 614-620.
- [183] Senophiyah-Mary, J., Loganath, R., 2020. A novel method of utilizing waste Printed Circuit Board for the preparation of Fibre Reinforced Polymer, *Journal of Cleaner Production*, 246, 119063.

-
- [184] Bidini, G., Fantozzi, F., Bartocci, P., D'Alessandro, B., D'Amico, M., Laranci, P., Scozza, E., Zagaroli, M., 2015. Recovery of precious metals from scrap printed circuit boards through pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 111, 140-147.
- [185] Das, P., Tiwari, P., 2018. Valorization of packaging plastic waste by slow pyrolysis, *Resources, Conservation and Recycling*, 128, 69-77.
- [186] Chien, Y.-C., Paul Wang, H., Lin, K.-S., Huang, Y. J., Yang, Y. W., 2000. Fate of bromine in pyrolysis of printed circuit board wastes, *Chemosphere*, 40, 383-387.
- [187] Shen, Y., Chen, X., Ge, X., Chen, M., 2018. Chemical pyrolysis of E-waste plastics: Char characterization, *Journal of Environmental Management*, 214, 94-103.
- [188] Liu, J., Zhang, H.-j., Xia, Y.-g., Hu, B., Yuan, X.-h., Zhang, Z.-x., Jiang, X.-y., Zhao, L., Lu, Q., 2025. The fate of bromine during pyrolysis of tetrabromobisphenol A-bis(2,3-dibromopropyl ether): A combined experimental and computational study, *Journal of Analytical and Applied Pyrolysis*, 189, 107104.
- [189] Barontini, F., Cozzani, V., 2006. Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards, *Journal of Analytical and Applied Pyrolysis*, 77, 41-55.
- [190] Boro, B., Tiwari, P., 2026. Effects of pre-treatment on product characteristics and bromine behavior during pyrolysis of waste printed circuit boards for resource recovery, *Journal of Analytical and Applied Pyrolysis*, 193, 107375.
- [191] Evangelopoulos, P., Persson, H., Kantarelis, E., Yang, W., 2020. Performance analysis and fate of bromine in a single screw reactor for pyrolysis of waste electrical and electronic equipment (WEEE), *Process Safety and Environmental Protection*, 143, 313-321.
- [192] Nagarajan, N., Panchatcharam, P., 2023. Cost-effective and eco-friendly copper recovery from waste printed circuit boards using organic chemical leaching, *Heliyon*, 9, e13806.
- [193] Zhang, D.-j., Dong, L., Li, Y.-t., Wu, Y., Ma, Y.-x., Yang, B., 2018. Copper leaching from waste printed circuit boards using typical acidic ionic liquids recovery of e-wastes' surplus value, *Waste Management*, 78, 191-197.
-