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CO-PYROLYSIS OF PCB AND COTTON STALK: TOWARDS ENHANCED PHENOL PRODUCTION AND DEBROMINATION OF PYROLYSIS OIL

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With advancing technology, printed circuit board (PCB), one of the most important components of e-waste, has become a source of pollution due to an ineffective waste management system. This problem can be solved by converting PCB waste into a valuable product which will emerge to maximize the renewable energy supplies. In this aspect, co-pyrolysis is advantageous in both simple and successful in producing high-quality pyrolysis oil. In this paper, cotton stalk (CS) as biomass was used and pyrolysis of PCB, CS, and a mixture of both in 1:1 have been carried out. CS has a good combustibility at 500 °C which was chosen for the pyrolysis reaction in a fixed bed reactor for slow pyrolysis. The pyrolytic oil was analysed by GC–MS and FTIR. The results indicate that there is an increase in oil yield from 19.6% to 27.5% by weight and phenol and phenolic compounds in oil of co-pyrolysis from 60.94% to 76.82% compared to literature available. There is an increase in bromine solidification in char by 25% with a mixture of CS and PCB compared to CS and PCB individually which is much higher than literature data. To the best of the authors' knowledge, co-pyrolysis of PCB:CS has been attempted first time and debromination of oil was found excellent in the present work.

Keywords: co-pyrolysis, debromination, PCB, cotton stalk

1. INTRODUCTION

E-waste is simply landfilled or burnt due to a lack of awareness and suitable recycling technologies, damaging our land, air, and soil. As per (Chatterjee, 2012) if e-waste in india grows at a 10% annual rate, it will reach 1851337 mt in 2025, so it is necessary to apply cost effective and environmentally friendly techniques to minimize this waste. Many studies have been undertaken to date in order to recover and utilise the precious elements found in e-waste, with the majority of them focusing on the recycling of metallic fractions (Shen, 2018). However, the recycle of non-metallic fraction of pcbs (printed circuit

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boards) is a difficult process as it contains flame retardants such as brominated and chlorinated organic compounds (Das et al., 2021; Xiao et al., 2017), which help to keep fire damage to a minimum, while other compounds, such as phosphorous or nitrogen-based fire retardants, are being developed, brominated fire retardants are the most extensively utilised (Hense et al., 2015). Additionally, it contains several poisonous metals Cr, Hg, Pb, Cd and Se (Das et al., 2021). When incinerated, highly toxic polycyclic aromatic hydrocarbons (pah), polyhalogenated aromatic hydrocarbons (phah) as well as pbdd/f (poly–bromo dibenzodioxines/furans) and pcdd/f (poly–chlorodibenzodioxines/furans) are produced in the presence of oxygen, which is catalytically amplified by the presence of heavy metals, especially copper and its oxides (Raje at al., 2020). As a solution, pyrolysis of pcb has been demonstrated to be a promising alternative for generating energy and minimising waste in a number of investigations (Ma and Kamo, 2019). Pyrolysis, one of the thermal decomposition techniques, is carried out in the absence of oxygen. The technique is well known to produce fuel oil from biomass. Additionally, the char and gas produced as a by-product can be used in a variety of ways (Rieger et al., 2021). Furthermore, other wastes can also be pyrolysed such as e-waste plastic which is present at the level of 50–60% in printed circuit boards (PCB). However, due to presence of a significant proportion of ash, it has a lower heating value and low thermolysis efficiency. In this context, adding biomass with PCB could be an alternative strategy that improves these two criteria. Several studies have demonstrated that co-pyrolysis improved the properties of oil generated, as well as increased oil yield. Secondly, biomass has a higher H/C molar ratio than PCBs, thus this high hydrogen content can act as a hydrogen donor to PCBs during co-pyrolysis (Panchasara and Ashwath, 2021). Most importantly, the use of biomass as an additive is the approach for dehalogenation and prevention of highly toxic PBDD/F (Poly–Bromodibenzodioxins/furans) and PCDD/F (Poly–Chlorodibenzodioxins/furans), due to a high amount of hydrogen (Abnisa et al., 2014). After consideration of these factors of biomass, cotton stalk was chosen as biomass which was added in PCB during pyrolysis due to its better combustibility at the slow pyrolysis temperature (500 °C) than other biomasses. Additionally, it contains a large amount of volatile matter and lower O/C (Madhu et al., 2018) which demonstrates higher expectation of high bio-oil yield with improved quality (Liu et al., 2013). Therefore, there were two wastes which were combined to produce energy in the form of fuel oil and gas.

The prime objective of this study was to perform pyrolysis of PCB, cotton stalk (as biomass), and co-pyrolysis of PCB:CS (1:1) to generate low bromine oil and to apply qualitative and quantitative analysis. The liquid phase obtained from the co-pyrolysis is highly dependent on the reactor conditions like temperature, heating rate, pressure, and composition (Abnisa et al., 2014). Moreover, fuel oil generated was analysed in GC–MS to know the composition of oil and any reduction in brominated compounds. The co-pyrolysis of PCB:CS has been done as per authors' knowledge for the first time to know the effect of CS with PCB on bromine reduction in pyrolytic oil. In general, individual PCB and other biomasses are present in literature.

2. MATERIALS AND METHODS

2.1. Sample preparation

The cotton stalk waste samples used in this work were collected from the local farm Chandisana district, Gandhinagar, Gujarat located in India. The cotton stalk waste samples were crushed and air-dried to a residue. The PCB waste samples, on the other hand, were obtained from Shiwalik solid waste management in Punjab, where metals from PCB were removed by physical separation after crushing in a hammer mill. Both samples were ground and sieved to obtain an average particle size of 100–200 µm to assure homogeneity of the sample.

2.2. TGA analysis

Mettler Toledo equipment was used to perform Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG). To avoid combustion, the system was purged with nitrogen gas with 50 ml/min of volumetric flow rate. The degradation of all three samples was performed at three different heating rates: 5, 10, and 15 °C/min with approximately 10 mg. The sample was kept in a ceramic crucible inside the furnace and heated from ambient temperature to 700 °C with the mentioned heating rates.

2.3. Pyrolysis experiments

The pyrolysis experiments were performed in a fixed-bed reactor under nitrogen as an inert gas, mainly including a pyrolysis furnace, an electrical controller, a cooling system, a liquid collector, and a gas collection system. The cylindrical reactor is made of SS 316 (I.D 100 mm, height 320 mm, and 7 mm thickness) and heated by three parallel electrical heaters each of 2 kW, and was well insulated with glass wool. The top of the reactor is openable from where feed was entered and sealed during experiment. After the experiment the same top was opened to remove char. The bottom of the reactor was fitted with a silica frit through which nitrogen was passed and acted as a support to the reactor. The reactor was initially charged with 200 gm of the material and purged for 20 min with nitrogen removing any oxygen. After that the temperature of the reactor was raised as per the heating rate required up to 500 °C. As the temperature rose, the vapours of the feed evolved and were collected in a glass condenser attached with a chiller which maintained running water at 2 ± 1 °C. Non-condensable gases were collected in a PTFE balloon for further composition analysis through GC. The temperature of the reactor was then raised from ambient to 500 °C at a rate of 10 °C/min for 30 minutes. Reactor temperature was set at 500 °C temperature because according to TGA/DTG analysis, the majority of the mass loss occurred up to this temperature only, after which no more pyrolysis products were produced. As the temperature increased, the feed vapours evolved and passed through a glass condenser connected to a chiller which was maintained at 2–3 °C temperature and generated liquid and non-condensable gases were collected. After the experiment was done, the top of the reactor was opened to remove the char. In each experiment, solid and liquid pyrolysis yields were calculated by weighing the amount of each obtained and calculating the corresponding percentage, whilst gas yields were calculated by difference.

2.4. Sample analysis

The produced liquid was collected and analysed using Thermo Scientific TSQ 8000 Gas Chromatograph – Mass Spectrometer. The MS element of the system consists of a Triple Quadrupole paired with a TRACE 1300 GC and an auto-sampler for automated sample processing. Helium was used as the carrier gas at a constant flow rate of 1.5 ml/min through a 15 m long, 0.25 mm i.d., and 0.25 mm thick film (SQC). Peaks were scanned in the m/z range from 40 to 650 with an ionizing voltage of 70 eV and an emission current of 350 A of electron ionization (EI). Furthermore, probable functional groups of the co-pyrolyzed oil were determined by FTIR (Fourier Transform Infrared Spectroscopy) analysis on Perkin Elmer – Spectrum RX-IFTIR with a resolution set at 1 cm^{-1} and the spectral region at 600–4000 cm^{-1}. Additionally, gas samples were analysed in gas chromatography on model Shimadzu GC–2014.

3. RESULTS AND DISCUSSION

3.1. TGA results

Figure 1 shows the Thermogravimetric (TGA) and Derivative Thermogravimetric (DTG) curves for all three samples at three different heating rates of 5, 10, and 15 °C/min. A very slow and initial weight loss of up to 180 °C temperatures in PCB was observed because of the release of CO_2, H_2O, CH_4, HBr (Lin and Chiang, 2014) and in the CS sample it was a result of moisture loss associated with depolymerization and vitrification transition (Leroy et al., 2010). The main pyrolysis process begins at around 180–200 °C temperature range and nearly at 577 °C temperature the devolatilization ceases to act for all three samples, which indicates the char generation and carbonization stage (Chen et al., 2018). As can be seen in Table 1, CS has higher volatile material and lower ash content that favours the production of a large amount of pyrolysis oil upon condensation as it has an advantage of high reactivity which results in lesser yields of char and more condensable gases as oil. Moreover, CS tends to have higher moisture content than PCB, the mixture will contribute to the reduction of water content in the pyrolysis oil, which consecutively helps to increase HHV.

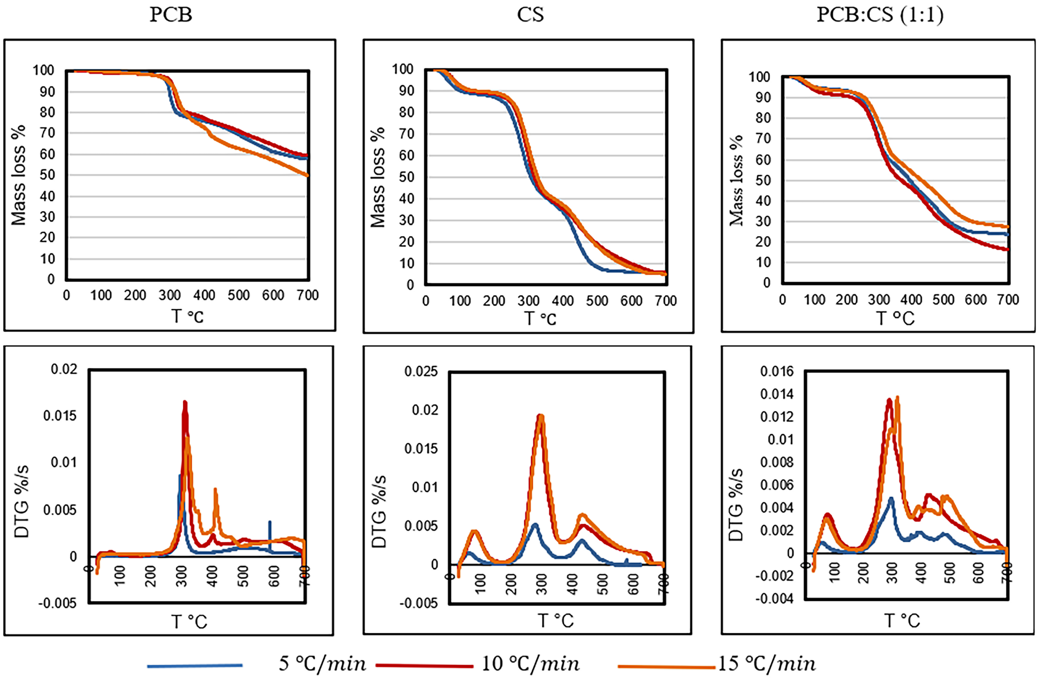


Fig. 1. DTG as a function of temperature plots for the sample PCB, CS and PCB:CS (1:1) at heating rates of 5, 10 and 15 °C/min

Table 1. Proximate and ultimate analysis of samples

Sample	HCV cal/gm	LOD (%)	Proximate analysis			Ultimate analysis			
			Ash (%)	Volatile material (%)	Fixed C (%)	C (%)	H (%)	N (%)	S (%)
PCB	1415	14.05	43.95	41.87	0.13	26.73	2.39	1.93	0.19
CS	2319	23.93	5.49	70.51	0.07	32.52	4.12	2.15	0.16
PCB:CS (1:1)	2279	12	23.73	64.2	0.07	29.76	5.45	2.86	0.148

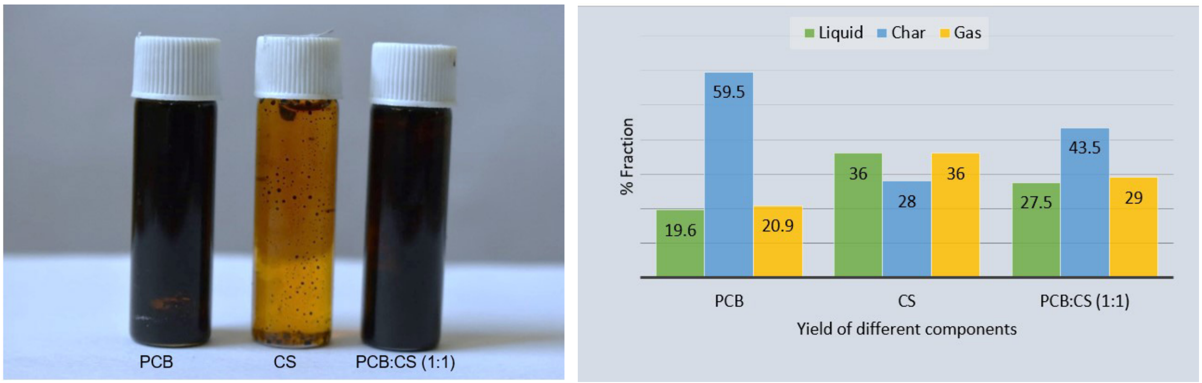
It is also worth noting that the residue of PCB which is collected as char at the end of the process is relatively very high (50–60%) while using PCB:CS (1:1) composition char was decreased to 16–27%. Moreover, when compared to the degradation patterns of PCB and CS; the degradation profiles of mixed samples initiated at a lower temperature.

The appearance of the shoulder in the DTG curve may be due to the degradation of the hemicellulose and lignin in the CS sample and attributed to the decomposition of tetra–bromo–bisphenol–A in the PCB sample (Chen et al., 2018). Whereas, a continuous slow degradation in CS and mixture may correspond to the slow decomposition of lignin (Mailto et al., 2018; Dhaundiyal et al., 2018). For the PCB sample, this slow degradation is due to the rupture of ether bonds in brominated resin into bisphenol A, propyl alcohol, tetra–bromo–bisphenol–A, and small phenolic molecules (Islam et al., 2018). The total weight loss at the end of 700 °C was 42–50, 94–95, 73–84 (wt%) for PCB, CS and PCB:CS (1:1), respectively. The total weight loss in CS was higher due to higher volatile matter and lower ash content, as shown in Table 1. From the same table, one can also observe that there is a higher H/C ratio for PCB:CS (0.183) in comparison to PCB (0.089) and CS (0.126). This could be the reason for the higher calorific value.

3.2. Pyrolysis experimental results

As per TGA analysis, the optimum temperature for producing maximum oil was in the range of 300–500 °C. Above 500 °C the operation reduces liquid and char production and provides an increased amount of gas, several studies have explored the same effect (Mankhand et al., 2012). This reduced liquid and char at higher temperatures could be the reason of the secondary reaction for the liquid fraction of the volatiles and further decomposition of the char particles. However, lowering the temperature below 300 °C may cause incomplete decomposition of the biomass (Quan et al., 2012).

As the pyrolysis reaction progressed while increasing temperature, vapours generated were cooled with chilled water in a condenser and collected as oil. Non-condensable gases were collected as gas product and the residue remaining after the completion of pyrolysis reactions was received as char. The yield of these three products was calculated based on feed by weight. The density of oil from three different samples was found to be 1.2, 0.98 and 1.02 gm/ml for PCB, CS and PCB:CS (1:1), respectively. The yield of different components with reference to the % fraction of generated oil, gas, and char is shown in Fig. 2b. As demonstrated, the amount of oil was increased significantly with co-pyrolysis of PCB:CS (1:1) to 27.5 wt% while 19.6 wt% was obtained for PCB. This rise in oil quantity is owing to the fact that presence of cellulose and hemicelluloses in CS contributes significantly to the production of volatile matter. Cellulose is more volatile than hemicellulose and has the ability to generate a large amount of volatile materials, resulting in an overall increase in oil yield. Further, water is one of the most significant components in biomass, and it can function as a reactive agent, stimulating further cracking of PCB tar and raising pyrolysis oil yields.



(a) (b)

Fig. 2. (a) Appearance of generated oil with different feedstock; (b) different feedstock with generated amount of liquid oil, solid char and gas in percentage

PCB generated oil was dark brown in colour compared to CS alone. As shown in Fig. 2a, light colour of CS could be the reason of higher water content, which leads to low energy density, corrosivity, and chemical instability, also high oxygen content makes it difficult to blend with fossil fuels. Whereas, blending it with PCB helps lower water content. A number of studies evidenced that a sufficient amount of water can have a positive effect to use it as fuel, like reduced viscosity, reduced pollutant emissions, which contributes to a micro explosion of droplets in combustion and increased oxidation (Lu et al., 2009). Furthermore, solid particles in CS oil make phase separation difficult due to the presence of lignin which makes solids being adsorbed with it and generates gummy tars whereas, during the co-pyrolysis event, radical interaction can enhance the development of a stable pyrolysis oil that avoids phase separation (Brebu and Spiridon, 2012).

3.3. Liquid analysis

Various hydrocarbons present in the oil of three samples are shown on peaks of the spectrum. In the first 20 minutes of GC/MS spectra acquisition, more than 25 distinct aromatic compounds were discovered in each sample. The components were identified with an increase in retention time. The compounds that had an area % of more than 0.1 are discussed here. The area % of the peak for a compound was correlated with the concentration of that compound in the oil. The liquid analysis performed in a GC–MS showed that the main products of the pyrolysis of PCB were fragments of polycarbonate epoxy resin. Table 2 shows all the detected compounds in PCB, CS, and PCB:CS (1:1) listed from higher to the lower area %.

Table 2. Compounds detected by GC–MS for PCB, CS and PCB:CS (1:1) samples

PCB		CS		PCB: CS (1:1)	
Area %	Compounds	Area %	Compounds	Area %	Compounds
38.47	Phenol	27.72	Guanidine, N,N–dimethyl	54.83	Phenol
7.95	Styrene	21.85	Phenol	6.17	phenol, 3–(1–methylethyl)
5.66	4–methyl, Phenol	12.82	N–cyano–2–methylpyrrolidine	5.04	2–methyl, phenol
5.07	2–methyl, phenol	8.71	2–cyclopenten–1–one, 3,5,5–trimethyl	4.46	1,6:2,3–Dianhydro–4–O–acetyl–beta–d–gulopyranose
4.6	1h–pyrrolo[2,3–b] pyridine,1–methyl–	5.44	2–pentanone, 4–hydroxy–4–methyl	3.77	4–methyl, Phenol
4.31	phenol, 3–(1–methylethyl)	3.73	2–methyl, phenol	2.47	Thiourea, ethyl
4.01	Naphthalene	2.25	2–acetyl–2–methyl–succinonitrile	2.36	phenol, 2,3–dimethyl
3.83	P–Xylene	2.19	2–cyclopenten–1–one, 3–methyl	1.89	Naphthalene
2.94	P–isopropenylphenol	1.62	1–Methoxy–1,3–cyclohexadiene	1.88	Cyclohexanol, 3,3–dimethyl–
0.16	ethanone,1(3–bromo–4–hydroxyphenyl)	1.54	Acetic formic anhydride	1.62	phenol, 3,4–dimethyl–
2.54	phenol, 3,4–dimethyl–	1.32	Pyridine, 2,3–dimethyl–	1.31	P–isopropenylphenol
1.59	1,2–Benzenedicarbonitrile	1.32	9–Undecenal, 2,10–dimethyl–	0.98	5′,6′,7′,8′–Tetrahydro–2′–acetonaphthone

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Table 2 [cont.]

PCB		CS		PCB: CS (1:1)	
Area %	Compounds	Area %	Compounds	Area %	Compounds
1.4	phenol, 3–ethyl	1.27	3,4–Dihydro–1–methylpyrrolo[1,2–a] pyrazine	0.89	5–Methyloxazolidine
1.32	Benzene,1–ethynyl–4–methyl	1.16	7–Hydroxy–6–methyloct–3–enoic acid	0.88	Phenol, m–tert–butyl–
1.06	Naphthalene, 2–methyl–	1.14	Cyclohexanol, 3–(acetyloxymethyl)–2,2,4–trimethyl–	0.81	1–Heptanol, 6–methyl–
1	Anthracene	1.07	Pentadecanoic acid, 14–methyl–, methyl ester	0.54	Phenol, 3,4,5–trimethyl–
0.99	3–Hydroxybiphenyl	1.02	2–Octanol, 2–methyl–6–methylene–	0.51	Heptanoic acid, 6–oxo–
0.86	1–Naphthalenol, 5,8–dihydro–	0.71	8–Methyl–6–nonenamide	0.42	Benzofuran, 2–isopropenyl–3–methyl–
0.86	naphthalene, 2–ethenyl	0.43	Bis(tridecyl)phthalate	0.42	9,10–Ethanoanthracene, 9,10–dihydro–11,12–diacetyl–
0.83	Dibenzofuran	0.41	Eicosane, 9–cyclohexyl–	0.4	Fluorene
0.8	N–(1–Cyanovinyl) benzamide	0.36	phenol, 3,4–dimethyl–	0.36	Dibenzofuran
0.63	2–Propenal, 2–methyl–3–phenyl–	0.32	2–Azidomethyl–1,3,3–trimethyl–cyclohexene	0.32	1,4–Bis (1′–hydroxycyclopentyl)–1,3–butadiyne
0.56	5′, 6′, 7′, 8′–Tetrahydro–2′–acetonaphthone	0.3	5,8–Decadien–2–one, 5,9–dimethyl–, (E)–	0.31	naphthalene, 2–ethenyl
0.45	Cyclotetrasiloxane, octamethyl–	0.28	Pyrazine, 2,5–dimethyl–3–(1–propenyl)–, (E)–	0.3	Phenol, 2–ethyl
0.42	Acenaphthylene	0.27	Z–8–methyl–9–tetradecenoic acid	0.28	Carbonic acid, heptyl phenyl ester
0.42	Fluorene	0.22	1,4–Dioxanyl hydroperoxide	0.28	10,12–Octadecadiynoic acid
0.39	Benzofuran, 2–isopropenyl–3–methyl–			0.28	Pentadecanoic acid, 14–methyl–, methyl ester
0.29	Naphthalene, 2,3–dimethyl–			0.25	4,5–di–epi–aristolochene

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Table 2 [cont.]

PCB		CS		PCB: CS (1:1)	
Area %	Compounds	Area %	Compounds	Area %	Compounds
0.29	4H–Cyclopenta [def]phenanthrene			0.23	Anthracene
0.28	Phenol, 2–ethyl			0.23	Pentadecanenitrile
0.28	9H–Xanthene			0.22	Ethanone, 1–(2,3–dihydro–1H–inden–5–yl)–
0.27	Methanone, (2–methylphenyl) phenyl–			0.2	6–Hydroxyhexan–2–one
0.27	4–Cyclohepta–2,4,6–trienyl–phenol			0.2	Triphenyl phosphate
0.25	Cyclopentasiloxane, decamethyl			0.18	Cyclotetrasiloxane, octamethyl–
0.24	Fluoranthene			0.17	Carbamic acid, phenyl ester
0.23	Benzoic acid, 2(cyanomethyl), methyl ester			0.16	Methanone, (2–methylphenyl) phenyl–
0.23	Naphthalene, 2–phenyl–			0.13	Fluoranthene
0.22	2(5H)–furanone, 3–hydroxy–4,5–dimethyl–			0.12	Acenaphthylene
0.21	9H–Fluoren–9–ol			0.1	cyclopentasiloxane, decamethyl
0.19	1H–Indene, 1–(phenylmethylene)–			0.08	Ethanone, 2–(benzoyloxy)–1–[–1,1′–biphenyl]–4–yl–
0.19	Triphenyl phosphate				
0.18	Phenanthrene, 4–methyl–				
0.17	Pyrene				

A large difference in product distribution can be observed for PCB, CS and PCB:CS (1:1) samples for phenol and phenolic compounds like phenol, 2–methyl,phenol, 4–methyl,phenol, phenol,3,4–dimethyl–, phenol,3–(1–methylethyl), Phenol, 2–ethyl, Phenol, 3,4,5–trimethyl–, Phenol, m–tert–butyl–, phenol, 3–ethyl and P–isopropenylphenol.

Phenol present in PCB by area % was 38.47 which is comparable with a number of studies which have examined PCB oil components where phenol varied from 10–40% due to compositional and pyrolysis parameter difference, whereas (Quan et al., 2010) has pyrolysed PCB up to 600 °C and found phenol as the most dominant compound (58.58%).

Figure 3 reveals that there is an increase in phenol from 38.47% to 54.83% when co-pyrolysis was done with PCB. The collected oil was analysed in GC–MS and the chromatograms for all three samples are presented in Fig. 4. Other phenolic compounds were present in PCB, CS and PCB: CS (1:1) as 22.47, 4.09 and 21.99% area, respectively, so total of 60.94, 25.94, 76.82% area Phenol and phenolic compounds are present in PCB, CS and PCB:CS (1:1) which also shows highest in co-pyrolysis mixture. This result is true in accordance that the addition of polycarbonate in the pyrolysis of biomass can increase the phenol compounds in the oil where bisphenol. A present in PCB is a poly carbonate which has enhanced the amount of phenol during co-pyrolysis with CS (Brebu and Spiridon, 2012). It is also worth noting that the high amount of phenolic compounds in CS, may be originated from the decomposition of lignin, and can help to enhance phenolic concentration in PCB:CS (1:1).

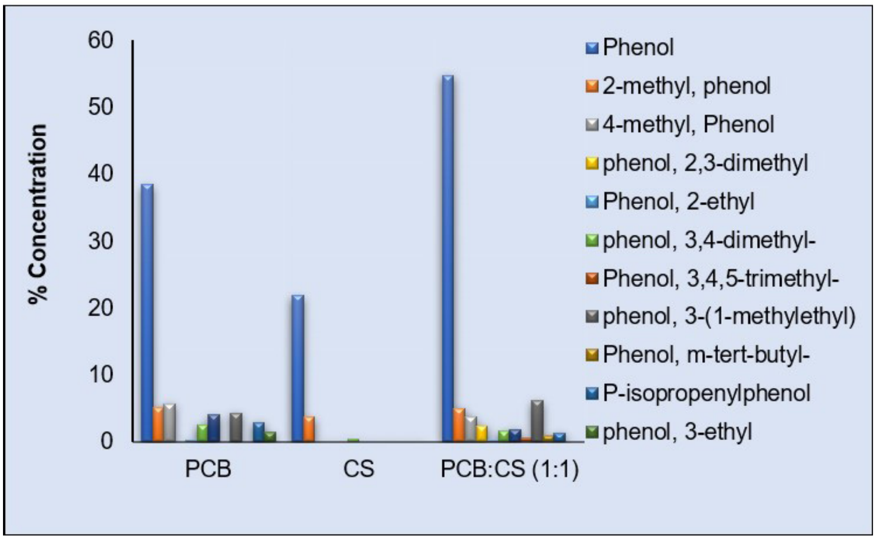
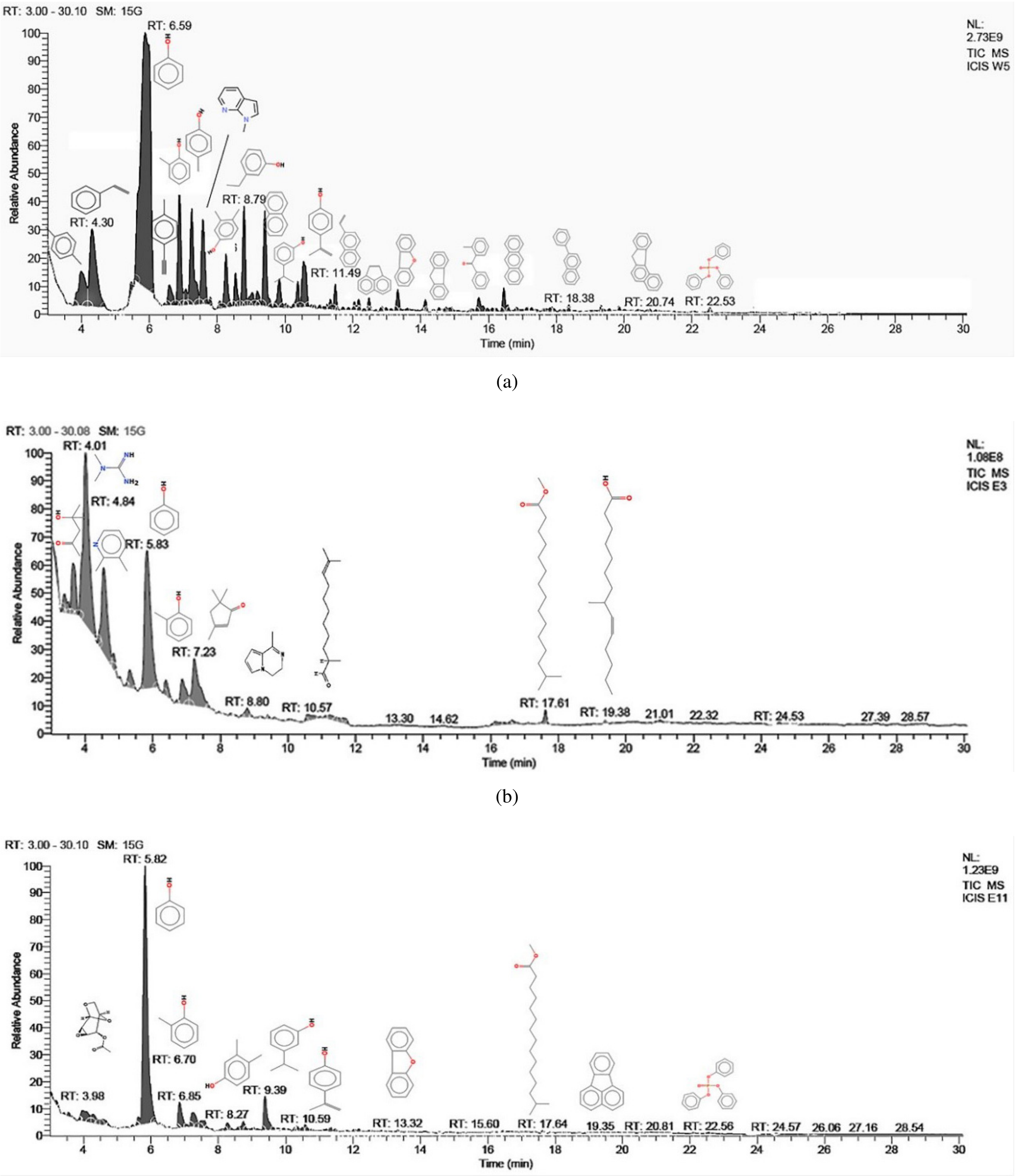


Fig. 3. Area % comparison of the major phenolic components present in the PCB and PCB:CS (1:1) oils

Furthermore, Naphthalene and other polycyclic aromatic hydrocarbons (PAHs) has the highest concentration in PCB, like naphthalene,2–methyl, anthracene, naphthalene,2–ethenyl, acenaphthylene, fluorene, fluoranthene, Pyrene, 4H–Cyclopenta[def]phenanthrene, having a total of 13.92% area covered, with carbon ranges from C10–C18. In contrast, CS sample contains aliphatic hydrocarbons only, ranging from C3–C8. Whereas, co-pyrolysis includes Naphthalene as well as naphthalene,2–ethenyl, acenaphthylene, fluorene, anthracene and fluoranthene as major PAHs having 3.64% area in total. As overall PCB compounds include hydrocarbons ranging from C6 to C12, whereas CS and the mixture includes components with C6–C18. Heat deterioration is the consequence of a number of competing breakdown events which shows complex behaviour of the reaction mechanism. Due to debromination of BFRs in PCB, HBr, bromophenol, di-bromophenol and other derivatives were found in liquid products (Ma and Kamo, 2019). However, in the present GC/MS result, only ethanone,1(3–bromo–4–hydroxyphenyl) was found in PCB oil with a very small amount (0.16% area) and it is completely removed or below detection limit in a co-pyrolysis oil.

This can be explained as bromophenol is an aromatic compound and higher temperature can provide enough energy to partially break chemical bond and decompose it to compounds with lower molecular weight (Islam et al., 2018; Xing and Zhang, 2013). Meanwhile, CS acts as a hydrogen donor in the debromination reaction, and the increased supply of hydrogen in the phenol resin aids in the conversion of most organic bromine to inorganic HBr and its fixation in char (Uzoejinwa et al., 2018). The bromine compounds were also solidified in the char, it can also be explained with the XRF of char produced by all three samples.



(a)

(b)

(c)

Fig. 4. GC–MS chromatograms of oils collected during pyrolysis for the samples:
(a) PCB, (b) CS and (c) PCB:CS (1:1)

It was found that the char produced from PCB, CS and CS:PCB (1:1) consists of bromine content of 32.3%, 31.9% and 55.85%, respectively. It shows that co-pyrolysis has facilitated the removal of bromine content from pyrolytic oil.

Additionally, Tetrabromobisphenol-A (TBBA) is the most widely used fire retardant in PCB, and degradation of this compound in presence of oxygen releases brominated dibenzodioxines and furans, but as evidenced by the GC/MS results listed in Table 2, pyrolysis of PCB products do not contain PBDD/Fs because the de-hydrogen or de-hydroxyl radicals is difficult to happen in this reductive environment (Liu et al., 2013) also, at higher temperatures, brominated materials undergo debromination and additional deterioration, inhibiting the production of PBDD/Fs.

Furthermore, at the retention time of 22.53, triphenyl phosphate was observed which is a phosphorous based fire retardant. The phosphate based flame retardants are mostly found in thermoplastics, hence their presence in PCB pyrolysis oil is most likely attributable to the pyrolysis of plastic components attached to the printed circuit boards (Hall and Williams, 2007). Some authors presented TBBA degradation mechanism and release of brominated compounds in their research (Grause et al., 2008). Moreover, furans are highly toxic components and they are present in PCB oil in the form of benzofuran, 2–isopropenyl–3–methyl–, dibenzofuran, and 2(5H)–furanone, 3–hydroxy–4,5–dimethyl– (total of 1.44% area) but with co-pyrolysis only dibenzofuran and benzofuran, 2–isopropenyl–3–methyl–, were detected, with total of 0.78%. This is also evidenced by some researchers (Liu et al., 2013) that for lower temperatures of pyrolysis, say up to 500 °C, the amount of furans decreases. Co-pyrolysis has no apparent influence on the amount of furans in the oil produced. Overall, 98.25% area of the PCB pyrolysis oil, 99.47% area of the CS pyrolysis oil, and 96.17% area of the PCB:CS (1:1) pyrolysis oil in total were identified.

4. IMPLICATIONS OF THE PRODUCTS OBTAINED THROUGH PYROLYSIS

The uses of bio-oils are well known and can be found in the literature (Hasan et al., 2017) and contribute to a high-quality fuel oil production or can be used to extract high value chemical compounds. As discussed with composition of oil by GC–MS a major concentration of PCB and CS sample oil was of phenol and phenolic compounds, and the concentration increased with co-pyrolysis. Therefore, it may be a good source for phenol and phenolic compounds. Phenol can also be used as a raw material to produce binder through crosslinking reactions.

Furthermore, to use this oil as a fuel in industrial burners, furnaces, and boilers, its fuel characteristics, like thermal stability, calorific value, viscosity, and acidity need to be monitored. Hydrodeoxygenation (HDO) reaction can also be used to increase the fuel property by removing oxygen (Panchasara and Ashwath, 2021). Although, some attempts have been made to address this issue, it is still very expensive since external hydrogen is needed in the engine and a metal oxide catalyst is added in the process. Moreover, pyrolysed oils should be checked for water content, viscosity, and coking tendency, as this property makes them difficult to atomize, resulting in incomplete combustion and higher emissions (Sánchez-Borrego et al., 2021). Several new strategies are proposed like the addition of methanol or ethanol as polar solvents to improve some of the oil's problematic features, such as calorific value and volatility which reduces viscosity and acidity of the resulting fuel (Raje, 2020). However, in this work, fuel characteristics and improvement methods are not discussed as the main purpose was to find the product distribution of all three samples.

Despite the fact that the process is designed to maximise oil production with improved quality and reduced brominated components, it generates valuable gases such as CH_4, CO_2, CO and a variety of other small hydrocarbons C1–C4 (Abnisa et al., 2014). Also, the solid char left behind can have a variety of applications based on their quality, including adsorbents, carbon fuel cells, supercapacitors, soil amendment, gasification and co-combustion (Al Afif et al., 2020), formation of activated carbons, and graphene production. However, its specific applications are dependent on its physicochemical characteristics, which might vary depending on the feed stalk and processing method used to obtain it. Also, it requires a number of upgrading techniques like demineralization (Bernardo et al., 2012) and activation pre-treatment (Li et al., 2010) as it may contain toxic halogens, metals and glass fibre components which must be removed before any suggested applications.

5. CONCLUSIONS

It can be concluded from the results that the TGA degradation profiles of PCB:CS samples were initiated at a lower temperature when compared with PCB and CS degradation profiles. The synergistic effect of mass loss can be seen in a mixture of PCB:CS (1:1).

By experiments on lab-scale pyrolysis equipment, it was observed that PCB individually produced less amount of oil compared with more bromine and less phenol and phenolic compounds than CS and the mixture of PCB:CS. Whereas, the addition of CS had improved the yield of oil and reduced brominated components which was the main objective of the work. It is confirmed by GC/MS of oil that there were more oxygenated compounds like phenols and other aromatics in the oil produced for PCB:CS mixture compared to PCB and CS alone. It is due to a high amount of phenolic compounds originated from decomposition of lignin in CS facilitated increasing phenolic compounds in the mixture.

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REFERENCES

Abnisa F., Mohd W., Wan A., 2014. A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. *Energy Convers. Manage.*, 87, 71–85. DOI: 10.1016/j.enconman.2014.07.007.

Al Afif R., Anayah S.S., Pfeifer C., 2020. Batch pyrolysis of cotton stalks for evaluation of biochar energy potential. *Renewable Energy*, 147, 2250–2258. DOI: 10.1016/j.renene.2019.09.146.

Bernardo M., Lapa N., Gonçalves M., Mendes B., Pinto F., Fonseca I., Lopes H., 2012. Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. *J. Hazard. Mater.*, 219–220, 196–202. DOI: 10.1016/j.jhazmat.2012.03.077.

Brebu M., Spiridon I., 2012. Co-pyrolysis of LignoBoost®lignin with synthetic polymers. *Polym. Degrad. Stab.*, 97, 2104–2109. DOI: 10.1016/j.polymdegradstab.2012.08.024.

Chatterjee S.D., 2012. Electronic waste and India. *Department of Information Technology, Electronics Niketan*. Available at: http://meity.gov.in/writereaddata/files/EWaste_Sep11_892011.pdf.

Chen D., Shuang E., Liu L., 2018. Analysis of pyrolysis characteristics and kinetics of sweet sorghum bagasse and cotton stalk. *J. Therm. Anal. Calorim.*, 131, 1899–1909. DOI: 10.1007/s10973-017-6585-9.

Das P., Gabriel J.C.P., Tay C.Y., Lee J.M., 2021. Value-added products from thermochemical treatments of contaminated e-waste plastics. *Chemosphere*, 269, 129409. DOI: 10.1016/j.chemosphere.2020.129409.

Dhaundiyal A., Singh S.B., Hanon M.M., Rawat R., 2018. Determination of kinetic parameters for the thermal decomposition of parthenium hysterophorus. *Environ. Clim. Technol.*, 22, 5–21. DOI: 10.1515/rtuect-2018-0001.

Grause G., Furusawa M., Okuwaki A., Yoshioka T., 2008. Pyrolysis of tetrabromobisphenol-A containing paper laminated printed circuit boards. *Chemosphere*, 71, 872–878. DOI: 10.1016/j.chemosphere.2007.11.033.

Hall W.J., Williams P.T., 2007. Processing waste printed circuit boards for material recovery. *Circuit World*, 33, 43–50. DOI: 10.1108/03056120710836936.

Hasan N.U., Rahman M.M., Rahat R.I., 2017. Characteristics comparison of pyrolysed oils obtained from waste of plastic, tyres and biomass solid. *4th International Conference on Advances in Electrical Engineering ICAEE 2017*, 450–454. DOI: 10.1109/ICAEE.2017.8255398.

Hense P., Reh K., Franke M., Aigner J., Hornung A., Contin A., 2015. Pyrolysis of waste electrical and electronic equipment (WEEE) for recovering metals and energy: Previous achievements and current approaches. *Environ. Eng. Manage. J.*, 14, 1637–1647. DOI: 10.30638/eemj.2015.175.

Islam M.N., Ali M.H., Haziq M., 2018. Fixed bed pyrolysis of biomass solid waste for bio-oil. *AIP Conference Proceedings*, 1875, 020015. DOI: 10.1063/1.4998369.

Leroy V., Cancellieri D., Leoni E., Rossi J.L., 2010. Kinetic study of forest fuels by TGA: Model-free kinetic approach for the prediction of phenomena. *Thermochim. Acta*, 497, 1–6. DOI: 10.1016/j.tca.2009.08.001.

Li X., Guo X., Wang S., Wang K., Luo Z., Wang Q., 2010. Characterization and analysis of char produced by biomass fast pyrolysis. *2010 Asia-Pacific Power and Energy Engineering Conference, APPEEC*, 10–13. DOI: 10.1109/APPEEC.2010.5448524.

Lin K.H., Chiang H.L., 2014. Liquid oil and residual characteristics of printed circuit board recycle by pyrolysis. *J. Hazard. Mater.*, 271, 258–265. DOI: 10.1016/j.jhazmat.2014.02.031.

Liu W.J., Tian K., Jiang H., Zhang X., Yang, G., 2013. Preparation of liquid chemical feedstocks by co-pyrolysis of electronic waste and biomass without formation of polybrominated dibenzo-p-dioxins. *Bioresour. Technol.*, 128, 1–7. DOI: 10.1016/j.biortech.2012.10.160.

Lu Q., Li W.Z., Zhu, X.F., 2009. Overview of fuel properties of biomass fast pyrolysis oils. *Energy Convers. Manage.*, 50, 1376–1383. DOI: 10.1016/j.enconman.2009.01.001.

Ma C., Kamo T., 2019. Effect of steam-iron reaction on product characteristics and debromination during pyrolysis of epoxy-printed circuit boards. *J. Hazard. Mater.*, 379, 120803. DOI: 10.1016/j.jhazmat.2019.120803.

Madhu P., Kanagasabapathy H., Manickam I.N., 2018. Conversion of cotton residues to bio-oil and chemicals through flash pyrolysis in a fluidised bed reactor. *Int. J. Energy Technol. Policy*, 14, 20–33. DOI: 10.1504/IJETP.2018.088275.

Mailto G., Mahar R.B., Unar I.N., Brohi K.M., 2018. Kinetic study of cotton stalk and rice husk samples under an inert and oxy combustion atmospheres. *Mehran Univ. Res. J. Eng. Technol.*, 37, 327–336. DOI: 10.22581/muet1982.1802.09.

Mankhand T.R., Singh K.K., Gupta S.K., Das S., 2012. Pyrolysis of printed circuit boards. *Int. J. Metall. Eng.*, 1, 102–107. DOI: 10.5923/j.ijmee.20120106.01.

Panchasara H., Ashwath N., 2021. Effects of pyrolysis bio-oils on fuel atomisation – A review. *Energies*, 14, 794. DOI: 10.3390/en14040794.

Quan C., Li A., Gao N., 2010. Synthesis of carbon nanotubes and porous carbons from printed circuit board waste pyrolysis oil. *J. Hazard. Mater.*, 179, 911–917. DOI: 10.1016/j.jhazmat.2010.03.092.

Quan C., Li A., Gao N., 2012. Research on pyrolysis of PCB waste with TG-FTIR and Py-GC/MS. *J. Therm. Anal. Calorim.*, 110, 1463–1470. DOI: 10.1007/s10973-011-2048-x.

Raje N., Jain A., Kumar A., Pente A.S., Tiwari A.P., Badodkar D.N., 2020. E-Waste: Characterization and disposal through solid state route. *Int. J. Environ. Sci. Nat. Res.*, 23, 556106. DOI: 10.19080/ijesnr.2020.23.556106.

Rieger T., Oey J.C., Palchyk V., Hofmann A., Franke M., Hornung A., 2021. Chemical recycling of WEEE plastics – Production of high purity monocyclic aromatic chemicals. *Processes*, 9, 530. DOI: 10.3390/pr9030530.

Sánchez-Borrego F.J., Álvarez-Mateos P., García-Martín J.F., 2021. Biodiesel and other value-added products from bio-oil obtained from agrifood waste. *Processes*, 9, 797. DOI: 10.3390/pr9050797.

Shen Y., 2018. Effect of chemical pretreatment on pyrolysis of non-metallic fraction recycled from waste printed circuit boards. *Waste Manage.*, 76, 537–543. DOI: 10.1016/j.wasman.2018.02.036.

Uzoejinwa B.B., He X., Wang S., El-Fatah Abomohra A., Hu Y., Wang Q., 2018. Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide. *Energy Convers. Manage.*, 163, 468–492. DOI: 10.1016/j.enconman.2018.02.004.

Xiao H., Zhou Z., Zhou H., Liu Q., Ren W., Lin H., Zhu H., He C., Tian K., 2017. Conversion of HBr to Br_2 in the flue gas from the combustion of waste printed circuit boards in post-combustion area. *J. Cleaner Prod.*, 161, 239–244. DOI: 10.1016/j.jclepro.2017.05.117.

Xing M., Zhang F.S., 2013. Degradation of brominated epoxy resin and metal recovery from waste printed circuit boards through batch sub/supercritical water treatments. *Chem. Eng. J.*, 219, 131–136. DOI: 10.1016/j.cej.2012.12.066.

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